

MONITORING FOR INDICATORS OF ANTIFOULING PAINT POLLUTION IN CALIFORNIA MARINAS

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ABSTRACT

In the summer and fall of 2006, the Department of Pesticide Regulation (DPR) sampled water and sediment from 23 marinas to assess the geographical scope and severity of pollution stemming from the use of antifouling paint (AFP) pesticides in California. Copper, zinc, Irgarol, M1 (the primary breakdown product of Irgarol), and aquatic toxicity were selected as potential indicators of AFP pollution.

The highest dissolved copper concentrations were observed in larger salt water marinas along California's Central and South Coast, the lowest were seen in freshwater lake marinas. Copper and zinc concentrations were almost always higher in the marinas than in the adjacent local reference sites, indicating that significant sources of metals existed in the marinas. Concentrations of zinc never exceeded California's water quality standards. In contrast, concentrations of dissolved copper in salt and brackish water marinas were frequently above California water quality standards established for the protection of aquatic life.

Developmental toxicity tests on the copper-sensitive embryo of the mussel *Mytilus galloprovincialis* were conducted on 47 marina water samples. Eight of these samples showed a statistically significant toxic response and copper was the likely cause of the toxicity. Several copper toxicity models that account for copper bioavailability to aquatic organisms were used to predict toxicity for the 517 samples for which site-specific water quality data were available. These models were the freshwater Biotic Ligand Model (BLM), the saltwater BLM, and the Dissolved Organic Carbon Model. Model output indicated that copper sensitive aquatic organisms, particularly *M. galloprovincialis* in saltwater marinas, were occasionally exposed to toxic levels of copper.

Forty-five marina water samples were collected and analyzed for Irgarol and M1. Irgarol and M1 were detected in all of these samples. Irgarol concentrations were often higher than sub-lethal toxicity thresholds for marine algae. In some saltwater marinas, Irgarol concentrations exceeded benchmark values used to determine if risk to aquatic plants exists.

Source evaluation suggests that during dry periods, boat AFPs are a major source of copper, Irgarol, and M1 to salt and brackish water marinas. The contribution of zinc AFPs to the total marina zinc load is likely to be less than the contribution of copper AFPs to the total marina copper load due to the input of zinc from the corrosion of sacrificial zinc anodes in salt water marinas and due to the much lower use of zinc AFPs compared to copper AFPs.

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LIST OF FREQUENTLY-USED ABBREVIATIONS AND ACRONYMS

AFP – antifouling paint
ANOVA – analysis of variance
ANR – Agriculture and Natural Resources
BLM – Biotic Ligand Model
CAHMPC – California Association of Harbor Masters and Port Captains
CCC – Criterion Continuous Concentration
CDEC – California Data Exchange Center
CI – confidence interval
CMC – Criterion Maximum Concentration
CTR – California Toxics Rule
CuPt₂ – copper pyrithione
CWA – Clean Water Act
DCu – dissolved copper
DO – dissolved oxygen
DOC – dissolved organic carbon
DPR – Department of Pesticide Regulation
DZn – dissolved zinc
EC – electrical conductivity
EC₅₀ – effective concentration (50% observed effect)
ERA – ecological risk assessment
ERL – Environmental Risk Limit (Irgarol toxicity threshold)
ERL – Effects Range Low (sediment quality guideline)
ERM – Effects Range Medium
FAC – Final Acute Concentration
FAV – Final Acute Value
FCC – Final Chronic Concentration
GPS – global positioning system
HML – Hollings Marine Laboratory
LC₅₀ – lethal concentration (50% mortality)
LNB – Lower Newport Bay
LOD – limit of detection
LOEC – lowest observed effect concentration
LRS – local reference site
M1 – primary degrade of Irgarol
MBYH – Marina Bay Yacht Harbor (Richmond Marina)
MDL – method detection limit
MdR – Marina del Rey
MRA – Marina Recreation Association
NOAA – National Oceanic and Atmospheric Administration
NPS – non point source
ppb – parts per billion (equivalent to µg/L)
ppm – parts per million (equivalent to mg/L or mg/kg)
ppt – parts per trillion (equivalent to ng/L)
QA/QC – quality assurance/quality control
QAPP – Quality Assurance Project Plan
RWQCB – Regional Water Quality Control Board
SCCWRP – Southern California Coastal Water Research Project
SWRCB – State Water Resources Control Board
TCu – total copper concentrations
TDS – total dissolved solids
TIE – Toxicity Identification Evaluation
TMDL – Total Maximum Daily Load
TSS – total suspended solids
TZn – total zinc
U.S. EPA – United States Environmental Protection Agency
ZnPt₂ – zinc pyrithione

I. Introduction

In California, the Department of Pesticide Regulation (DPR) registers antifouling paint (AFP) products since they are pesticides. Like other pesticides, AFP products are formulated by combining pesticide active ingredients with other compounds (e.g., solvents, adjuvants, inert ingredients) to produce useable and effective products. In AFP products, active ingredients are often referred to as biocides. Copper oxide, copper hydroxide, copper thiocyanate, zinc pyrithione (ZnPt_2), and Irgarol are the biocides that are most frequently formulated into AFP products currently registered in California (DPR, 2008a). A single AFP product may actually contain multiple biocides. Copper oxide is the most popular of these biocides, appearing in more than 90 percent of California AFP products.

The leaching of copper from AFPs used on recreational boats has been determined to be the major source of copper pollution in a large boat basin known as the Shelter Island Yacht Basin (SIYB) in San Diego Bay (SDRWQCB, 2005). Water column levels of dissolved copper (DCu) at SIYB are high enough to impair beneficial uses and exceed California Toxics Rule (CTR) standards for copper (chronic value of $3.1 \mu\text{g/L}$ and acute value of $4.8 \mu\text{g/L}$). More recently, 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, 2005; U.S. EPA, 2002).

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). Recently, an increase in the development of copper-related Total Maximum Daily Loads (TMDLs) and the placement of additional copper-impaired water bodies on the Clean Water Act section 303(d) list challenges the presumption that this issue is only limited to San Diego Bay.

Irgarol has been detected with increasing frequency at ecologically sensitive levels in coastal water worldwide. In the U.S., Irgarol (and its major metabolite M1) has been detected in the waters of Chesapeake Bay and Florida (Hall and Gardinali, 2004). The United States Environmental Protection Agency (U.S. EPA) has expressed concern over the potential phytotoxic effects of Irgarol on aquatic plants and algae (U.S. EPA, 2003a). In 2005, the National Oceanic and Atmospheric Administration (NOAA) conducted an investigation of the occurrence and magnitude of Irgarol and M1 in a number of marinas in San Diego Bay (Sapozhnikova et al., 2007). However, this was the only investigation that has been completed on these constituents in California thus far.

Zinc from the use of AFP products is another potential contaminant in marinas. With the use of ZnPt_2 AFPs growing in recent years and the possibility that more zinc-based products could enter the AFP market, zinc levels in California marinas need to be evaluated. There is currently little documentation of zinc concentrations in marinas.

For this study, DPR collected water and sediment samples from a number of California marinas and analyzed them for indicators of AFP pollution. The biocides of particular interest are copper oxide, copper hydroxide, copper thiocyanate, ZnPt_2 , and Irgarol. This monitoring study focused specifically on marinas because these areas harbor densely packed recreational and commercial vessels, most of which have hulls that are painted with AFPs. Moreover, marinas are purposefully constructed to shelter boats from currents and waves thus resulting in poor flushing in the marina. Thus, AFP pollution at these locations should represent some of the worst water quality conditions resulting from the use of AFPs on boats.

Findings from this monitoring study will help DPR, State Water Resources Control Board (SWRCB), Regional Water Quality Control Boards (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 DPR determine if mitigation actions (regulatory and/or voluntary) are needed on a local or a statewide scale.

The primary objective of this study is to:

- Determine the occurrences and concentrations of copper, zinc, and Irgarol and M1 in the water and sediment of selected California marinas and determine whether these levels exceed water quality standards (e.g., CTR copper and zinc standards, site-specific objectives), criteria (e.g., U.S. EPA's

updated aquatic life criteria for copper), guidelines (e.g., NOAA's sediment quality guidelines), and other ecologically relevant values (e.g., LC₅₀, EC₅₀).

Secondary objectives are to:

- Determine if copper and zinc concentrations in marinas are significantly higher than concentrations in the adjacent local reference sites (LRS).
- Determine whether AFP analyte concentrations differ between salt water, brackish water, and fresh water marinas.
- Apply U.S. EPA's Biotic Ligand Model (BLM) or other scientifically-relevant models to estimate bioavailability and toxicity of copper.
- Measure the toxicity of marina waters using metal-sensitive test species and endpoints, compare measured toxicity with copper and zinc concentrations and BLM-predicted toxicity, and identify the likely cause of observed toxicity using Toxicity Identification Evaluation (TIE) procedures.

II. Materials and Methods

Sampling Approach

Copper, zinc, Irgarol, and M1 are the principal AFP-related constituents of interest. Water and sediment samples were taken from inside and outside of marinas and evaluated for AFP analytes as well as a number of other water quality parameters. If marina levels of these analytes are consistently and statistically higher than ambient levels outside the marina, this would provide strong evidence that marinas are a significant source of AFP pollutants. Moreover, if AFP sources of AFP analytes can be shown to be large compared to other in-marina non-AFP sources, particularly during dry periods, then it is likely that AFPs are the primary cause of elevated concentrations of these analytes in marinas. This approach does not apply to Irgarol since AFPs are the most significant use of this biocide in surface waters. Hence, samples collected for Irgarol and M1 analysis were all taken inside the marinas.

The sampling period was confined to California's summer months (July through October) to avoid confounding hydrologic factors that could be introduced by storm events. Processes such as flushing, dilution, mixing, and sediment resuspension affect the water and sediment concentrations of AFP indicators and other analytes. Moreover, during storm periods, other non-marina inputs of AFP analytes into the marina could exceed AFP sources within the marina. Because DPR is interested in evaluating pollution from AFP use, sampling for this study was conducted in the dry summer months.

Due to the popularity of copper-based AFPs and exceedances of copper water quality standards, this study focuses on copper as an AFP analyte. Particular attention is given to the dissolved fraction of copper (i.e., DCu) as the aforementioned standards are defined in this manner. DCu concentrations at any given time are heavily influenced by the level of suspended solids in the water column. Copper that becomes bound to solids will be accounted for in the total copper (TCu) measurement. To improve the understanding and interpretation of DCu results, concentrations of TCu and total suspended solids (TSS) were also assessed.

To provide input into U.S. EPA's copper BLM, a number of water quality parameters and constituents were measured for each water sample taken. These include alkalinity, calcium, salinity (as chloride), dissolved organic carbon, magnesium, pH (*in situ*), potassium, sodium, sulfate, and temperature (*in situ*). Although only the fresh water BLM was available at the onset of this study, DPR measured its input parameters for all of the study's ambient water samples in anticipation of the availability of the salt water BLM. Developers of the salt water BLM disclosed that similar parameters would be also be required for the salt water version of the model (R. Arnold., personal communication, 2006).

A subset of salt and brackish marina water samples were assessed for toxicity using U.S. EPA's method for short-term chronic toxicity test on mussel (*Mytilus galloprovincialis*) embryo development. Since this test is sensitive to copper, the results will help establish whether levels of DCu correspond to sample toxicity. The determination of actual toxicity will also be useful toward the validation of the salt water BLM.

TIEs were used to better link chemistry results with adverse biological effects. TIE procedures were conducted on a subset of toxic samples to confirm the cause of the observed toxicity. TIE treatments are designed to selectively remove or neutralize classes of compounds and their associated toxicity to identify the most likely cause of the toxicity. Results from toxicity/TIE samples were compared to DCu and predicted toxicity.

This study was conducted in accordance with the Quality Assurance Project Plan (QAPP) document, which was prepared and approved prior to the onset of sampling activities (DPR, 2006).

Assumptions & Limitations

Certain assumptions were made in the development of the study design:

- AFP-painted boats are sources of copper, zinc, Irgarol, and M1 to marina waters and sediments.
- The pathways that introduce AFP pollutants to marina waters and sediments are passive leaching and underwater hull-cleaning of AFP-painted boats.
- AFP-painted boats in the marina represent the most significant source of Irgarol and M1 detected in the marina.

Certain limitations were recognized in the development of the study design:

- There are also non-AFP sources of copper and zinc inside of marinas
- DCu and dissolved zinc (DZn) concentrations at any given site could vary over time due to a number of factors including tidal influence, site-specific hydrology, and fluctuations in total suspended solid levels. The design of this study attempts to address these limitations; however, these factors may still have some effects on study results.

Site Selection Criteria

Hundreds of California marinas were evaluated using information produced by the Marina Mapping Sub-Workgroup of the Non-Point Source Interagency Coordinating Committee's Marina and Recreational Boating Workgroup. The pool of candidate marinas were then reduced from the large initial list with the use of maps and application of the following considerations (in descending order of importance):

- 1) Marina contains a relatively high number of slips for its water body type.
- 2) Marina is located in an area that receives poor flushing (the likelihood of finding elevated levels of marina-borne pollutants over an extended period is high.)
- 3) Marinas are distributed over various regions of the state.

Forty candidate marinas remained after this initial reduction. Aerial photos and more-detailed maps were used to further evaluate individual marina layouts and relevant local and regional anthropogenic, geologic, and hydrologic features. DPR staff then visited many of the candidate marinas to gauge collaborative interest from individual marina managers and to discuss logistical and site-specific criteria with them. These criteria include:

- 1) The marina owner/operator is cooperative.
- 2) The marina has a boat on-site that can be used for sampling.
- 3) The marina contains slip areas that are sufficiently isolated from adjacent or surrounding sources (e.g., boatyards, industrial discharges, mining discharges).
- 4) Historical and current activities (e.g., dredging, construction) in the marina area will not significantly interfere with the interpretation of results.

Twenty-three marina areas were ultimately chosen (Table 1 and Figure 1). Many of the selected marinas are located in the San Francisco Bay Area (Figure 2).

Table 1. List of Marina Study Areas¹

	Water Body	County	City	Total Slips	Percent Occupancy Estimate²
FRESHWATER					
1) Folsom Lake Marina	Folsom Lake	El Dorado	Folsom	675	not available
2) Tahoe Keys Marina	Lake Tahoe	El Dorado	Lake Tahoe	250	100
3) Sacramento City Marina	Sacramento River	Sacramento	Sacramento	547	97
4) Village West Marina	Sacramento-San Joaquin	San Joaquin	Stockton	700	85
BRACKISH WATER					
1) Antioch Marina	San Joaquin River	Contra Costa	Antioch	310	82
2) Pittsburg Marina	Sacramento River	Contra Costa	Pittsburg	486	75
3) Benicia Marina	Carquinez Strait	Solano	Benicia	320	95
4) Vallejo Municipal Marina	Mare Island Strait	Solano	Vallejo	800	60
SALTWATER					
1) Clipper Yacht Harbor	Richardson Bay	Marin	Sausalito	735	90
2) San Francisco Marina	San Francisco Bay	San Francisco	San Francisco	700	95
3) South Beach Harbor	San Francisco Bay West	San Francisco	San Francisco	700	95
4) Berkeley Marina	San Francisco Bay East	Alameda	Berkeley	1,052	91
5) Marina Bay Yacht Harbor	San Francisco Bay East	Contra Costa	Richmond	850	85
6) Loch Lomond Marina	San Francisco Bay North	Marin	San Rafael	517	82
7) Ballena Isle Marina	San Francisco Bay East	Alameda	Alameda	504	75
8) Coyote Point Marina	San Francisco Bay West	San Mateo	San Mateo	565	85
9) Santa Cruz Harbor	Santa Cruz Harbor	Santa Cruz	Santa Cruz	1,000	100
10) Monterey Harbor	Monterey Bay	Monterey	Monterey	413	85 - 90
11) Santa Barbara Harbor	Santa Barbara Channel	Santa Barbara	Santa Barbara	1,133	95
12) Marina del Rey Basins D, E, F	Marina del Rey Harbor	Los Angeles	Marina del Rey	~ 3,000	not available
13) Marina del Rey Basins A, B, C, G, H	Marina del Rey Harbor	Los Angeles	Marina del Rey	~5,000	not available
14) Alamitos Bay Marina	Alamitos Bay	Los Angeles	Long Beach	1,191	95
15) Downtown Shoreline Marina	L. A. - Long Beach H.	Los Angeles	Long Beach	1,800	90

¹ Source: Marina and Recreational Boating Workgroup – Mapping Sub-Workgroup² Percent occupancy estimates were provided by individual marina managers via email surveys in 2007.

Figure 1. Statewide Map of Marina Sampling Areas

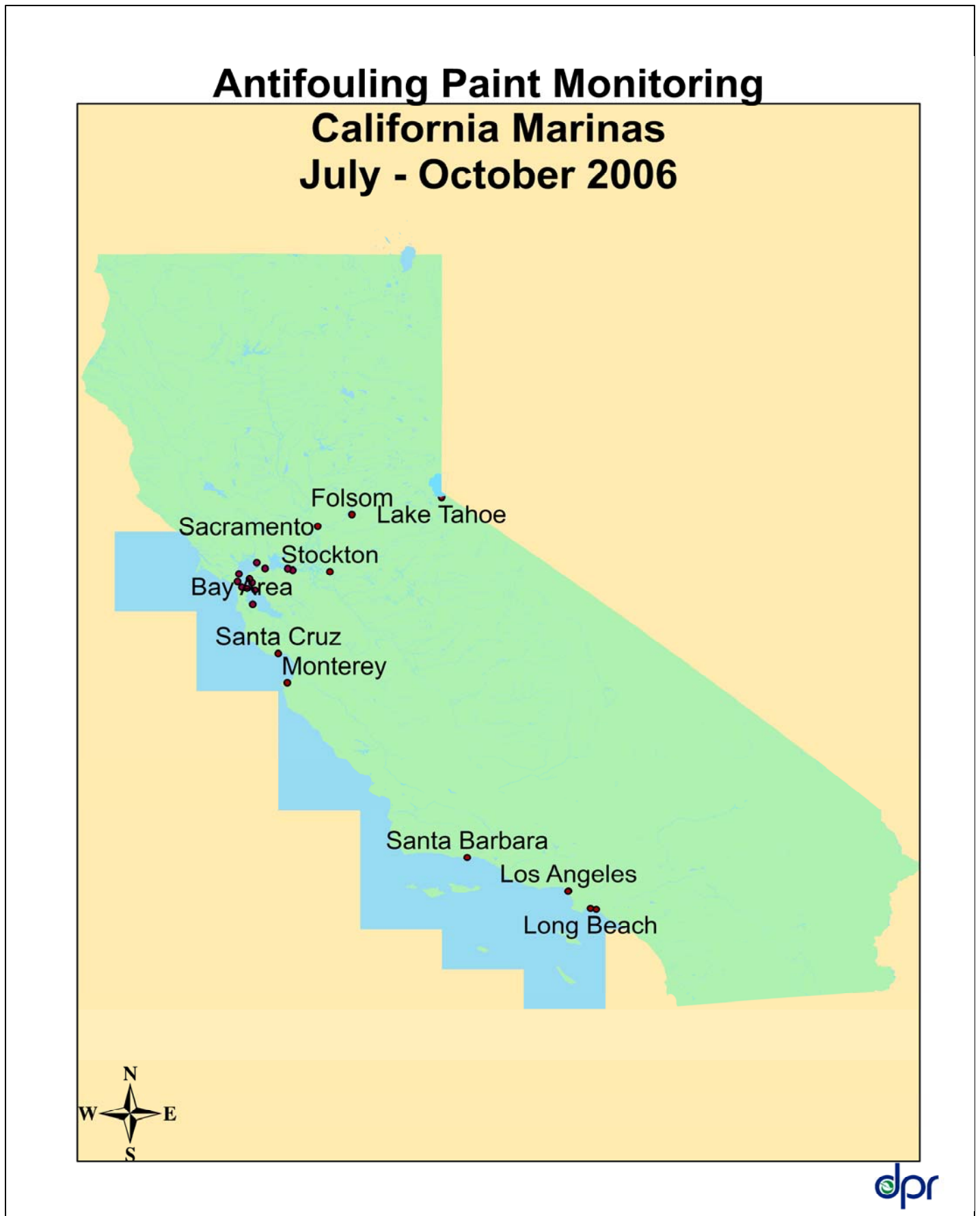


Figure 2. Close-Up Map of San Francisco Bay Area Marina Sampling Areas



Since copper levels in marinas have been documented to some extent in San Diego Bay, Mission Bay, Oceanside Harbor, and Dana Point Harbor, these regions were excluded (Singhasemanon, 2005; Schiff, 2007). Moreover, the Santa Ana RWQCB initiated a monitoring study of metals in Newport Bay Area marinas in the summer of 2006 (L. Candelaria, personal communication, 2006). Therefore, this study did not include sites in the Newport Bay Area; however, findings from these studies may be referred to later in this report.

DPR does not require use reporting for most AFPs. Thus, it is difficult to get a clear assessment of local and regional use of these pesticides. Anecdotal evidence suggest that copper-based AFPs are not as commonly applied to boats in fresh water areas because hard fouling organisms (e.g., barnacles, mollusks, and tubeworms), which predominantly occurs in salt water, are not a major pest concern. AFPs (e.g., non-copper and thin-film Teflon[®] paints) that are effective against soft fouling organisms (e.g., algae and aquatic weeds) are often adequate for use in fresh water. Furthermore, many of the smaller-sized boats that are used in fresh water areas spend a considerable amount of time out of the water in the off-season and may not have AFPs on their hulls at all. Field observations in Northern California and conversations with boating industry professionals suggest that copper-based AFPs are still used to a limited extent in fresh water areas.

AFP use for boats maintained in salt and brackish water areas tends to be higher than in fresh water areas. In California, fouling pressure is generally greatest on hulls of boats that moor or spend a considerable amount of time in more saline water. Since the largest marinas and the highest amount of AFP use occurs in saltwater areas, there was an emphasis on saltwater marinas. For the study, 15 saltwater marinas were chosen compared to four brackish water marinas and four freshwater marinas.

Measured electrical conductivity (EC) data were used to determine the water types in which each marina was located. USGS and DWR gauging station data were generally used to verify field-crew measured EC values. These measurements were compared to frequently-used ranges for EC of the three water types. The EC ranges were 0–1,500, 1,500–15,000, and > 15,000 micro Siemens/centimeter ($\mu\text{S}/\text{cm}$) for freshwater, brackish water, and saline water, respectively. Sea water has an EC reading of about 50,000 $\mu\text{S}/\text{cm}$.

The four marinas situated in the far north area of the San Francisco Bay Estuary (Vallejo, Benicia, Pittsburg, and Antioch marinas) were difficult to classify into water types. Measured EC data at Vallejo and Benicia during the study were almost always above the 15,000 $\mu\text{S}/\text{cm}$ EC threshold and could arguably be categorized as saltwater marinas; although, salinity values at these two marinas are much lower than those observed in San Francisco Bay Area and coastal marinas. Pittsburg Marina exhibited salinity that is mostly in the brackish range of 1,500–15,000 $\mu\text{S}/\text{cm}$; however, EC readings there occasionally dipped below the freshwater threshold of 1,500 $\mu\text{S}/\text{cm}$. Even Antioch Marina, which exhibited salinity that is considered to be in the high end of the freshwater range during the entire sampling period, is difficult to be neatly categorized. The annual salinity profile from a gauging station data (CDEC, 2008) near the Antioch marina shows that its salinity levels are in the brackish range about six months of the year.

For the purpose of analysis and discussion, we have classified brackish water marinas as those marinas that are exposed to salinity that is in the brackish EC range during some part of the year. Thus, Vallejo, Benicia, Pittsburg, and Antioch marinas are considered brackish in nature.

Local Reference Sites (LRSs) for each marina were identified to help determine whether concentrations of copper and zinc inside of the marina were attributable to local background concentrations, which were measured just outside of each marina. Marina owners, operators, managers, and dock masters and harbor masters (these individuals will be collectively referred to from here forth as marina managers) were consulted to determine the best locations for these LRS sites at their respective marina areas. LRSs were initially identified with the marina managers' help and then selected by DPR staff using the following criteria (in descending order of importance):

- 1) The site was located outside the influence of marina activities and potential sources of AFPs, but adjacent to the marina area and within the same body of water.
- 2) The site was sufficiently isolated from potentially confounding inputs (e.g., boatyards, industrial

- discharges, and various historical contamination).
- 3) Recent and current activities (e.g., dredging, construction) in the immediate area would not significantly interfere with the interpretation of results.
 - 4) The site contained underlying sediment that can be collected and analyzed.
 - 5) There was suitable and safe access to the site.

The exact locations of the LRSs were determined on the first day of sampling at each marina when the field crew were able to evaluate site-specific conditions. Once LRSs were determined in the first sampling round, they were resampled in the second and third round.

More detailed information on the study marinas, including the description, history, and Global Positioning System (GPS) locations can be found in Appendix A. Marina managers provided this marina-specific information via an email survey conducted in 2007. Survey responses greatly aided DPR in the interpretation of study data.

Sampling Vessels

Larger marinas tend to have at least one vessel for use by marina staff. During the site selection process, DPR staff established verbal agreements with each marina manager to verify his or her interest in participating in the study. DPR staff also confirmed the availability of a sampling vessel and an operator with the marina manager. In the case of the two Long Beach marinas, the City of Long Beach lifeguards provided the necessary vessels and operators to make sampling at these locations possible.

DPR staff established a sampling schedule to coordinate marina visits with each marina manager and his or her staff. DPR's sampling crew, who are based in Sacramento, CA, transported all necessary supplies and sampling equipment to each sampling site.

Sampling Method and Frequency

Table 2 provides an overview of the sampling scheme and sampling frequencies. When deviations from the original monitoring plan occurred, the planned number of samples are shown in parentheses. These deviations are noted and discussed throughout this Materials and Methods Section.

Table 2. Sampling Scheme and Number of Samples Taken

			Round 1		Round 2		Round 3			
			Water		Water		Water		Sediment	
Sampling Location	Water Type ¹	Abbreviated Site ID	Metals/BLM ²	Irgarol/M1	Metals/BLM ²	Toxicity/TIE	Metals/BLM ²	Irgarol/M1	Metals, TOC ³ , Grain Size ⁴	Irgarol/M1
Folsom Lake Marina	F	FL1 to FL8	8		8		8		7(8) ⁵	
Tahoe Keys Marina	F	TK1 to TK8	8		8		0(8)		0(8)	
Sacramento City Marina	F	SA1 to SA8	8		8		8		8	
Village West Marina	F	VW1 to VW8	7 (8)		8		8		8	
Antioch Marina	B	AM1 to AM8	8		8		8		0(8)	
Pittsburg Marina	B	PM1 to PM8	8	2	8	4	8	2	0(8)	0(2)
Benicia Marina	B	BM1 to BM8	8	2	8	4	8	2	0(8)	0(2)
Vallejo Municipal Marina	B	VM1 to VM8	8	2	8	4	8	2	0(8)	0(2)
Clipper Yacht Harbor	S	CY1 to CY8	8		8		8		0(8)	
San Francisco Marina	S	SF1 to SF8	8	2	8	4	8	2	0(8)	0(2)
South Beach Harbor	S	SH1 to SH8	8	2	8	4	8	2	0(8)	0(2)
Berkeley Marina	S	CB1 to CB8	8	2	8	4	8	2	0(8)	0(2)
Marina Bay Yacht Harbor	S	MB1 to MB8	6(8)	2	6(8)	4	6(8)	2	0(8)	0(2)
Loch Lomond Marina	S	LL1 to LL8	8	2	8	4	8	2	0(8)	0(2)
Ballena Isle Marina	S	BI1 to BI8	8	2	8	4	8	1(2)	0(8)	0(2)
Coyote Point Marina	S	CP1 to CP8	8		8		0(8)		0(8)	
Santa Cruz Harbor	S	SC1 to SC8	8		8		8		0(8)	
Monterey Harbor	S	MH1 to MH8	8		8		8		0(8)	
Santa Barbara Harbor	S	SB1 to SB8	8		8		8		0(8)	
MdR Basins D, E, F (Back Basins)	S	BB1 to BB4	4	4(2)	4	4	4	2(2)	0(4)	0(2)
MdR Basins A, B, C, G, H (Front Basins)	S	FB1 to FB8	8		8		8		0(8)	
Alamitos Bay Marina	S	AB1 to AB8	8	2	8	4	8	2	0(8)	0(2)
Downtown Shoreline Marina	S	DS1 to DS8	8	0(2)	8	4	8	0(2)	0(8)	0(2)
Total			177(180)	24(24)	178(180)	48	162(180)	21(24)	23(180)	0(24)

¹ Sampling sites located in F: Freshwater; B: Brackish water; S: Saltwater

² Metals and BLM parameters include: DCu, TCu, DZn, TSS, Dissolved Organic Carbon (DOC), Salinity (Cl), Sulfate, Alkalinity, Mg, Ca, Na, and K.

³ TOC = Total Organic Carbon

⁴ For sediment samples, metals parameters include TCu and TZn

⁵ Numbers in parentheses indicate the number of samples planned in the original sampling plan.

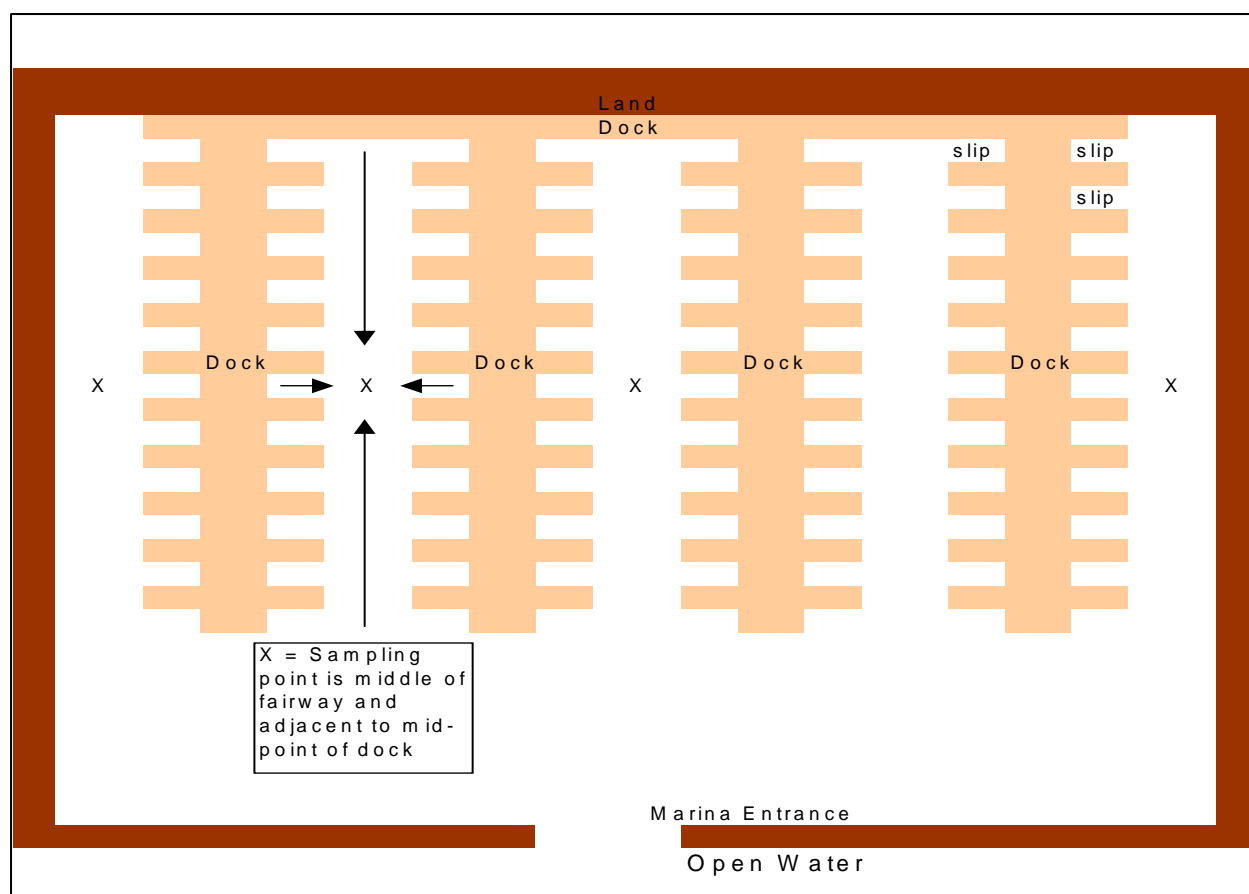
Marina Sites - Copper, Zinc, TSS, and BLM-Associated Parameters

Water and sediment samples were taken by boat from four points within each of the 23 marinas for DCu, DZn, TCu, TSS, and BLM-associated parameters. Water samples were collected about once a month at each site over a three-month period.

Sediment samples were only collected in the third sampling round. Sediment samples were collected after water samples at each sampling point to help minimize contamination of the water samples. Note that sediment samples were only collected from three freshwater marina sites (Folsom Lake Marina, Sacramento Marina, and Village West Marina). Consideration of safety and logistical concerns resulted in the decision to not collect sediment samples for the remaining 20 marinas as was planned in the original monitoring plan and QAPP.

Past monitoring studies of copper in marinas suggested that copper levels in both water and sediment tend to be highest near the area of moored vessels and lowest toward the entrance of the marina (SDRWQCB, 2005; Pap, 2004). Marina sampling sites were therefore located in areas where vessels were moored. To maintain site-to-site consistency and to ensure that samples taken were not too close to boat hulls, DPR staff chose sampling sites that were located near the center of the fairway (common term for the channels between the docks) and adjacent to the midway point of the dock/pier structure (see Figure 1, below).

Figure 3. Diagram of Sampling Locations in a Marina



Although each marina has a unique layout of docks and slips, DPR staff identified the candidate fairways at each marina using marina layout diagrams and assigned numbers to the fairways. Four fairways were randomly chosen in each marina as sampling sites. Fairways that were adjacent to docks with less than 50% of their slips filled during the first sampling round were not selected and another fairway was chosen using the same selection criteria.

To precisely relocate sampling sites during subsequent rounds, each sampling location was initially identified using a GPS unit to mark the exact latitudinal and longitudinal coordinates. Field crew also recorded the identification numbers of adjacent docks. If a marina or sampling site was inaccessible during a revisit, the sampling event was rescheduled within the shortest possible time of the original scheduled date.

Marina Sites - Irgarol/M1

Water samples were collected for Irgarol analysis from 12 of the 23 study marinas. Holding time constraints and shipping schedules limited which marinas the DPR field crew could sample for Irgarol. The 12 chosen marinas are identified in Table 2.

The DPR field crew collected two samples from each marina in the first and third sampling rounds. The first two sites within the marina that were identified for the sampling of copper, zinc, TSS, and BLM-associated parameters were chosen as Irgarol sampling sites.

In the study monitoring plan, sediment samples were originally to be collected from each of the 12 marinas during the third sampling round. Due to the inability of field crew to collect sediment samples at these locations, no sediment samples were taken for Irgarol/M1 analysis.

Marina Sites - Toxicity and TIEs

Water samples were collected for toxicity testing from a subset of marinas. Four samples were taken from the same 12 marinas selected for Irgarol sampling (again due to shipping constraints) in the second sampling round. A toxicity sample was taken from each of the four sampling sites within the marinas that were identified for the sampling of copper, zinc, TSS, and BLM-associated parameters.

TIE procedures were conducted on selected toxic marina water samples.

Local Reference Sites - Copper, Zinc, TSS, and BLM-Associated Parameters

Water and sediment samples were taken by boat at the four LRSs outside of the selected marinas. Water samples were collected about once a month at each site over a three-month period.

A limited number of sediment samples were collected in the third sampling round. Recall that the DPR field crew were only able to collect sediment samples from three freshwater marina sites (Folsom Lake Marina, Sacramento Marina, and Village West Marina). Safety and logistical concerns prevented sediment sampling at all 23 marinas as originally outlined in the monitoring plan. When sediment sampling was done, it took place after the collection of water samples at each sampling site to minimize contamination of the water samples.

The field crew determined specific LRSs during the first sampling visit to each marina. The criteria listed under the Site Selection Criteria sub-section were used to determine the sites.

Local Reference Sites - Irgarol, Toxicity, and TIEs

No samples were taken at LRSs for Irgarol, toxicity, and TIE analysis.

Sample Collection - Water

Water samples were collected from approximately one meter below the water surface. Schiff et al. (2007) documented a depth-related gradient for copper in marinas with the highest concentrations near the surface. Furthermore, to avoid AFP contamination from the sampling vessel itself, samples were taken approximately two meters from the side of the boat.

The water sampling apparatus consisted of a battery-operated peristaltic pump that draws water through polyethylene tubing and deposits it directly into a collection container. On the inlet end, the tubing is attached to a long plastic extendable pole, which allows for greater freedom of movement and reach.

For metal samples, U.S. EPA-certified, pre-cleaned 250-ml polyethylene plastic bottles were used. For Irgarol/M1 samples, U.S. EPA-certified, pre-cleaned 1-L amber glass bottles were used. For TSS and BLM-associated parameter samples, 250-ml polyethylene bottles were used. For toxicity samples, 1-L polyethylene containers were used.

Samples for DCu, DZn, magnesium, calcium, sodium, and potassium, and dissolved organic carbon (DOC) analyses were filtered with an in-line 0.45- μ m filter and then acidified with Optima® ultra-pure nitric acid to a pH level of < 2.0. Samples for sulfate, chloride, and alkalinity analyses were simply filtered (no subsequent acidification). Samples for TCu analysis were simply acidified (no filtration prior to acidification). Samples for TSS, Irgarol/M1, and toxicity/TIE analyses were not filtered nor acidified.

Sample Collection - Sediment

Sediment was collected using a Van Veen® grab sampler. The jaws and doors are coated with Teflon® to prevent contamination from the sampler. Each grab satisfied the following criteria to be considered valid:

- Complete closure of the sampler
- No evidence of significant sediment washout through the doors
- Minimum disturbance of the sediment surface

The overlying water in the sampler was first drained by slightly opening the sampler such that there was minimal disturbance of the fine-grained top layer of sediment. The top 2 cm of sediment were then collected with a clean Teflon® coated scoop and placed into a 4 oz., U.S. EPA-certified, pre-cleaned polyethylene container. This collection procedure was repeated until sufficient sediment had been collected to fill the sample container.

Field Quality Assurance/Quality Control

Field blanks and equipment rinse blanks (from here on referred to as rinse blanks) were taken to assess potential contamination of water samples in the field. Field blanks were collected by filling sample containers with de-ionized or distilled water at the site of collection. Rinse blanks were collected by running de-ionized or distilled water through the identical sampling apparatus that was used to collect environmental samples. Rinse blanks were taken after the sampling apparatus had been cleaned at least once through the sampling event.

Sample Handling and Custody

Since low (parts per billion) concentrations of metals in the water samples are expected in this study, sample collection and handling followed U.S. EPA Method 1669–Sampling of Ambient Water for Trace Metals at U.S. EPA Water Quality Criteria Levels (U.S. EPA, 1996a).

All samples were transported in coolers with ice. Glass containers were placed in pre-formed styrofoam packs to minimize chance of breakage. After transport, samples were refrigerated and stored at 4°C until extraction or chemical analysis. Irgarol and toxicity samples were immediately shipped to their respective analytical laboratories due to short holding time requirements. These samples were carefully packed and shipped (through the United Parcel Service) in styrofoam packs and well-insulated coolers with blue ice. Some toxicity samples were picked up directly by toxicity-laboratory personnel. Each sample had an accompanying DPR chain-of-custody form, which contains sample collection and identification information as well as sampling tracking information. All individuals who come into contact with the sample bottles were required to sign and date the form to acknowledge their handling of the samples.

Sample Analysis

Due to the variety of analyses needed for this study, DPR utilized several laboratories for the analytical work. A summary of analytical methods and their citations are provided in the subsequent sub-sections.

Water Samples - Copper, Zinc, TSS, and BLM-Associated Parameters

The University of California, Davis, Agriculture and Natural Resources (ANR) Analytical Laboratory analyzed water samples for DCu, TCu, DZn, TSS, magnesium, calcium, sodium, potassium, salinity (as chloride), sulfate, and alkalinity. Note that magnesium, calcium, sodium, potassium, chloride, sulfate, and alkalinity are also measured as dissolved concentrations.

The ANR Laboratory used the following methods (See Appendix B for complete methods):

- ANR Method 837 with quantification by Graphite Furnace Atomic Absorption Spectrometry (GFAAS) for DCu.
- ANR Method 891 with quantification by GFAAS for TCu.
- ANR Method 870, employing gravimetric analysis following oven drying for TSS.
- ANR Method 835 for DZn, calcium, magnesium, potassium, sodium with quantification by flame Atomic Absorption, Emission Spectrometry (AAS, AES), or Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) depending on the analyte.
- ANR Method 880, an ion chromatography conductivity method for chloride and sulfate

DPR analyzed water samples for DOC using EPA Method 415.3 (U.S. EPA, 2005). A summary of this method can also be found in Appendix B.

Water Samples - Irgarol/M1

NOAA's Hollings Marine Laboratory (HML) in Charleston, South Carolina, analyzed water samples for Irgarol (also known as Irgarol 1051 or 2-methylthio-4-*tert*-butylamino-6-cyclopropyl-amino-*s*-triazine) and M1 (also known as GS26575 or 2-methylthio-4-*tert*-butylamino-6-amino-*s*-triazine) using a high performance liquid chromatography electro spray ionization tandem mass spectrometry method as published in Thomas (2002). A summary of this method is presented in Appendix B.

Water Samples - Toxicity and TIEs

The Southern California Coastal Water Research Project's (SCCWRP's) laboratory in Westminster, California, tested salt and brackish water samples for sub-chronic developmental toxicity on the mussel *Mydulis galloprovincialis* based on methods in EPA/600/R-95/136 (U.S. EPA, 1995). SCCWRP's complete toxicity method is presented in Appendix C. This test measures the reduction in the mussel's ability to develop fertilized eggs after a 48-hour exposure to water samples. Samples with salinity concentrations of less than 30 g/kg were adjusted using hypersaline brine. The tests were conducted in glass shell vials containing 10 mL of solution at a temperature of 15°C. Four replicates were tested for each sample. A seawater blank was included as negative control. A copper reference toxicant test was included as positive control.

After a 48-hour exposure period, the embryos were preserved and examined with a microscope to assess normal development. The data are presented as percent normal-alive, which was calculated as the number of normal embryos after exposure relative to the number of fertilized eggs added at the beginning of the exposure. Samples were considered toxic if the difference between mean percent normal development of the sample and the control was statistically significant and if the sample's mean percent normal development was less than 80% when compared to the control.

SCCWRP also performed follow up TIEs on a subset of toxic samples based on methods from EPA/600/R-96/054 (U.S. EPA, 1996b). SCCWRP's Phase I TIE method is also presented in Appendix C. The toxicity threshold that triggered a TIE was 50% abnormal embryo development relative to control.

Sediment Samples - Copper and Zinc

UCD ANR analytical laboratory analyzed sediment samples for total copper (TCu) and total zinc (TZn) using ANR method

390, which relies on analysis by atomic absorption spectrometry. In the study monitoring plan, DPR was to analyze sediment samples for grain size and total organic carbon (TOC) using DPR method SOPMETH 004.00 (Dietrich, 2005) and SOPMETH 005.00 (Gunasekara, 2006), respectively. However, DPR decided to not proceed with grain size and TOC analyses due to limited sediment samples that were collected.

Sediment Samples - Irgarol/M1

In the monitoring plan, NOAA's HML in South Carolina was to analyze a subset of samples for Irgarol and M1 using an accelerated solvent extraction liquid chromatography - tandem mass spectrometry method. However, DPR decided to not proceed with the analysis of Irgarol in sediment due to limited sediment samples that were collected. .

The analytical parameters measured, the methods used, and the method detection limits as reported by the analytical laboratories are listed in Table 3.

Table 3. Summary of Analytical Methods and Detection Limits (BLM-associated parameters presented in grey)

Analytes	Analytical Method	Method Detection Limit (MDL) or Limit of Detection (LOD)
Dissolved Copper	ANR 837	0.1 µg/L
Dissolved Zinc	ANR 835	1.0 µg/L
Irgarol	Thomas, 2002	1.0 ng/L
M1	Thomas, 2002	1.0 ng/L
Total Copper	ANR 891	0.1 µg/L
Total Suspended Solids	ANR 870	4 mg/L
Dissolved Organic Carbon	EPA 415.3	50 µg/L or 50 mg/L*
Chloride (Salinity)	ANR 880	0.5 mg/L
Sulfate	ANR 880	0.5 mg/L
Alkalinity	ANR 820	2 mg/L
Magnesium	ANR 835	0.5 mg/L
Calcium	ANR 835	0.5 mg/L
Sodium	ANR 835	0.5 mg/L
Potassium	ANR 835	0.5 mg/L
Total Copper (sediment)	ANR 390	1 mg/kg (dry weight)
Total Zinc (sediment)	ANR 390	1 mg/kg (dry weight)
Toxicity	EPA/600/R-95/136	N/A
Toxicant Identification Evaluation	EPA/600/R-96/054	N/A

* Two possible detection limits depending on the catalyst used.

The following *in-situ* field measurements (some of which are required for the BLM) were collected using a variety of meters and apparatus:

- Water Depth (various built-in depth finder of sampling boats)
- Dissolved Oxygen (DO) (YSI meter, model 85)
- Electrical Conductivity (EC) (YSI meter, model 85)
- pH (IQ Scientific Instrument)
- Temperature (YSI meter, model 85)
- Turbidity (LaMotte colorimeter, model Smart II)

During sampling events, information on site-specific activities and factors (e.g., active construction activities, possible under water hull-cleaning operations, weather conditions) was recorded.

Laboratory Quality Assurance/Quality Control

DPR requires that analytical laboratories must comply with a minimum standard of quality assurance/quality control (QA/QC) per DPR Standard Operating Procedure number QAQC.001.00 and study QAPP (DPR, 2006).

Early in the study preparation stage, laboratories validated methods using the appropriate environmental sample matrices (e.g., fresh water, salt water, sediment) or they alternately provided documentation that illustrated the accuracy and precision of the methods. See Appendix D for method validation results for ANR Laboratory methods.

For ongoing QA/QC, laboratories employed a variety of QA/QC samples as consistent with the study QAPP.

Statistical Analysis

DPR staff generated descriptive or summary statistics to help characterize the results. Various parametric and non-parametric tests were used to determine whether differences between or among groups existed. To explore relationships between data groups, correlation analysis was used. MINITAB (Version 15) statistical software for statistical analysis and related plots was used.

The Ryan-Joiner and Anderson-Darling tests were used to test the normality of concentration data. These tests indicated that the concentrations of copper, zinc, and the rest of the study analytes were log-normally distributed. Therefore, summary statistics were calculated using the log-transformed data. For example, the 95% confidence intervals (CIs) were calculated from log-transformed data and then back transformed to original units. Thus, the CIs are frequently asymmetric.

Similarly, the geometric mean (instead of an arithmetic mean) was the preferred estimate of the central tendency and used as the basis for conducting hypothesis testing to determine if differences exist among groups. For simplicity, the geometric mean is routinely referred to in this report as the median. Note, however, that many of the boxplots used in this report display median lines that denote the 50th percentile value of the untransformed data set. These lines are intended to help readers visualize the relative distribution of the untransformed data. The median values that these lines represent are based the middle value (or arithmetic mean of the middle two values for an even-numbered data set) of the sorted, untransformed data set. Hence, the median values generated from the two approaches may not be identical. In the end, all the calculations and statistical tests in this report are based on the geometric mean.

The four samples taken inside each marina and the four samples taken for each LRS area during each sampling event represented sub-samples for that particular marina and LRS area. In contrast, the three sampling events are considered to be replication over time. The latter assumption is supported by analyses of variance (ANOVA) results for DCu concentrations (and similarly for TCu, DZn, and TSS) over the three summer-month period that indicated no trends or major change in marina median concentrations.

Two ANOVA tests were conducted for DCu, TCu, DZn and TSS. A one-way ANOVA was used to test for the effect of water body type (i.e., salt, brackish, and freshwater) on analyte concentration data from the inside of marinas. These ANOVAs were conducted with median analyte concentrations from each sampling event within a marina because the determination of sub-samples versus true replicates, as discussed above. A second ANOVA was also conducted to test for the effect of the factors of individual marina, sampling location (inside versus outside the marinas), and sampling event on analyte concentrations. This fully-nested balanced ANOVA was conducted within each water type with marinas as the highest nesting factor, followed by inside versus outside (i.e., marina versus LRS), and then sampling event (1st, 2nd, and 3rd). A level of significance (α) of 0.05 was used for all hypothesis testing.

Note that results from Tahoe Keys Marina and Coyote Point Marina were omitted from the fully-nested balanced ANOVA since samples from only two out of the three events were collected at these two sites. Exclusion of these data allowed the ANOVA tests to remain balanced. On rare occasions, one or two sample results were missing for a particular event. When this occurred, the missing values were filled in using substitutions based on the averaging of the results of related sub-samples from the same event.

Only a small percentage of results were below detection, thus the method detection limit value was used as a substitute for non-detects when mean estimates were needed for graphical display. For hypothesis testing, the value that is ½ of the method detection limit was used as a substitute for non-detects.

Predictive Toxicity Models

Three computer models, which predict the toxicity of copper based on site-specific water quality data, were used for this study. These are the freshwater BLM, the DOC model, and the saltwater BLM. DPR's staff used the freshwater BLM to evaluate freshwater data and the saltwater BLM to evaluate saltwater data. Depending on the site-specific water quality characteristics of brackish water sites, their data were used in either the freshwater or saltwater BLM. The DOC model is useful for the evaluation of salt and brackish water data.

Biotic Ligand Model - Freshwater

In 2007, U.S. EPA issued revised national recommended freshwater aquatic life criteria for copper (U.S. EPA, 2007). The revised criteria updated U.S. EPA's previous hardness-based freshwater criteria, which have not been changed since they were established in 1984. The new criteria incorporated the use of the BLM as a developmental tool for site-specific water quality criteria. These criteria could potentially be used as future federal or state water quality standards (e.g., via an update of the CTR).

The copper BLM is a model originally developed by Hydroqual, Inc. that utilizes data on site-specific water constituents to predict the bioavailability of copper in natural waters and its toxicity to aquatic organisms. It establishes a simplified mechanistic framework that was originally based on the toxic effects of copper species on fish gills as the surface ligand. Although the BLM makes a number of simplifying assumptions (e.g., the system is in equilibrium, speciation of metals is constant over time, and cation effects are limited to competition at the gill site), its usefulness will ultimately be proven by its ability to successfully predict toxicity. Early validation of the freshwater model with real-world toxicity data thus far has proven the BLM to be a good predictor of toxic effects to fish (U.S. EPA, 2007). In any case, the accounting of the effects of various physicochemical characteristics of the water body on copper toxicity is an improvement over the previous more limited, hardness-based approach.

The following site-specific data were entered into the freshwater BLM: temperature, pH, DOC, calcium, magnesium, sodium, potassium, sulfate, chloride, and alkalinity. The BLM version that was released in the 2007 U.S. EPA criteria update (version 2.2.3) was operational only in the toxicity prediction mode. The metal speciation mode was not available. The freshwater BLM has a particular operating range for which it can generate an output (Table 4).

Table 4. Freshwater BLM Operating Parameters

Model Input	Lower Bound	Upper Bound
Temperature (°C)	10	25
pH	4.9	9.2
DOC (mg/L)	0.05	29.65
Humic Acid Content (%)	10	60
Calcium (mg/L)	0.204	120.24
Magnesium (mg/L)	0.024	51.9
Sodium (mg/L)	0.16	236.9
Potassium (mg/L)	0.039	156
Sulfate (mg/L)	0.096	278.4
Chloride (mg/L)	0.32	279.72
Alkalinity (mg/L)	1.99	360
DIC (mmol/L)	0.056	44.92
Sulfide (mg/L)	0	0

DOC Model - Salt and Brackish Water

The freshwater BLM was not developed to accurately account for the chemistry of copper in the saline environment. Thus, natural waters with higher salinity levels are beyond the acceptable operational range of the freshwater BLM. Furthermore, the responses of saltwater and estuarine species to copper must be taken into consideration to determine relevant toxic thresholds. Since the saltwater BLM was still in development during the early stage of this report's synthesis, we initially utilized a regression-based DOC model as an interim approach for estimating the potential toxicity of copper in marine and estuarine waters. The model has been field validated and is accurate at predicting toxicity (Arnold et al., 2005). (Note that an early version of the saltwater BLM has been recently released. Its use and output for this study will be discussed in the next sub-section.)

The DOC model represents a regression-based relationship (power function) of DOC concentrations to DCu EC₅₀ values for the mussel *Mytilus galloprovincialis* exposed to copper in sea water. Model outputs include: 1) an EC₅₀, 2) a final acute criterion (FAC), and 3) a final chronic criterion (FCC). Note that Arnold et al., 2005 specifically uses the acronyms: FCC and FAC when referring to the DOC model's calculated toxicity thresholds that were intended to be equivalent to the CTR CCC and CMC, respectively.

Biotic Ligand Model - Salt and Brackish Water

In 2008, Hydroqual, Inc. released a functional draft saltwater BLM. Although U.S. EPA did not include the saltwater BLM with the freshwater BLM in its 2007 revision of the national aquatic life criteria for copper, the saltwater version of the model will likely be incorporated into the next revision. U.S. EPA and Hydroqual, Inc. have been discussing the technical aspects of the model and the potential for its implementation (R. Arnold, personal communication, 2008). Until then, the output of this draft model should be used and interpreted accordingly until it has undergone more extensive review and gained formal acceptance from the scientific and regulatory communities.

At this time, the key output of this model includes predicted copper species and predicted EC₅₀ for both *M. galloprovincialis* and *Strongylocentrotus purpuratus* (purple sea urchin). Saltwater FAVs, CMC, and CCC are not yet generated by the version of the model used for this report. Therefore, the model results that are presented and discussed in the saltwater BLM results section will be the predicted site-specific EC₅₀ for *M. galloprovincialis*. The predicted EC₅₀ results for *S. purpuratus* are less relevant for discussion since they are about 2–4 times less sensitive when compared to the *Mytilus* species results.

The inputs needed to operate the saltwater BLM are identical to those for the freshwater BLM. The operating parameters are, however, different (Table 5). Hydroqual, Inc. conducted modeling runs of our data to predict toxicity.

Table 5. Saltwater BLM Operating Parameters

Model Input	Lower Bound	Upper Bound
Salinity (psu)	26	36
pH	7.5	8.3
DOC (mg/L)	0.4	12.0

III. Results

The analytical results of accuracy and precision measurements for the principal metal analytes (i.e., DCu, TCu, DZn) were excellent during method validation (Appendix D). Recoveries for these analytes were in the range of 90–107% and 92–105% for the low and high level spikes, respectively. Ongoing batch QA/QC results for all the analytes were almost always within accuracy and precision control limits with the exception of one recovery result for the TCu standard reference material.

Copper and zinc were occasionally detected in field and rinse blanks samples (Appendix E). Two of 21 rinse blank samples contained relatively high concentrations of DCu and TCu. After potential contaminant sources and pathways were considered, it appeared that these occurrences were likely isolated to these two incidents. Furthermore, the potential of a similar contamination to environmental samples would have been additionally reduced since the collection of non field-blank samples also involved a rigorous rinsing with native water prior to the collection of each sample. Overall, our analysis of laboratory and field QA/QC data suggested that the study's chemistry results (i.e., metals and all other analyses) are highly reliable and reflective of real world conditions.

While summary data are presented in this section, a complete tabulation of analytical data is in appendices F–N. Analyte concentrations were also compared to applicable water quality standards and toxicity thresholds. Finally, models that account for the effect of various factors on copper bioavailability were used to estimate copper toxicity.

Dissolved Copper

A total of 346, 96 and 88 water samples were collected from salt, brackish and freshwater sites, respectively. DCu concentrations were above the method detection limit (MDL = 0.1 µg/L) in 493 of 517 samples (95%) (Appendix F). The range of DCu concentrations for each marina and its associated LRS is shown in Table 6. The sample with the highest concentration of DCu (18.4 µg/L) came from one of MdR's back basins.

Median DCu concentrations for individual marinas ranged from 0.5 µg/L at Folsom Lake Marina to 13.6 µg/L at MdR's back basins (Table 7). The median concentrations for 21 of 23 marinas were below 7 µg/L.

The four freshwater marinas exhibited very low to moderate median DCu concentrations (Figure 4). Median concentrations for the riverine Sacramento and Village West marinas (3.0 and 3.4 µg/L, respectively) were considerably higher than the lake-bound Folsom Lake and Tahoe Keys marinas (0.5 and 0.6 µg/L, respectively). The boxplots for water types and regions illustrate the marina median (horizontal line inside each box) as well as the individual sample results (circles).

The four brackish water marinas exhibited low to moderate median DCu concentrations (Figure 5). Among the brackish water marinas, median concentrations were highest at Vallejo Marina (3.4 µg/L) and lowest at Pittsburg Marina (2.1 µg/L). There appears to be some variation in DCu concentrations among brackish water marinas although not as distinctive as in the freshwater case.

The eight San Francisco Bay Area saltwater marinas exhibited low to high median DCu concentrations (Figure 6). Among these marinas, the highest median concentration was observed at Loch Lomond Marina (5.8 µg/L) and the lowest median concentration was observed at San Francisco Marina (1.1 µg/L). The remaining six Bay Area marinas exhibited median DCu concentrations that ranged between 2 and 4 µg/L.

The seven Central and South Coast saltwater marinas exhibited low to very high median DCu concentrations (Figure 7). Among these marinas, DCu concentrations at MdR's front and back basins (12.4 and 13.6 µg/L) were much higher than other marinas in this region. In fact, the median concentrations at MdR were by far the highest in the entire study. Alamitos Bay Marina exhibited the lowest median concentration (1.2 µg/L) in this region. The remaining four Central and South Coast marinas exhibited median DCu concentrations that ranged between 4 and 7 µg/L.

The differences in DCu between marinas and their associated LRS were also noteworthy. At all 23 marinas, the median DCu concentrations were greater than median concentrations at their associated LRS. This difference is most pronounced among the saltwater marinas along the Central and South Coast where marina median concentrations were as high as 57

Table 6. Range of Metal (µg/L) and Total Suspended Solids (mg/L) Concentrations in Water (sorted by ascending order of marina median dissolved copper concentrations)

Marina ²	Range of Dissolved Copper Concentrations ¹		Range of Total Copper Concentrations ¹		Range of Dissolved Zinc Concentrations ¹		Range of Total Suspended Solids Concentrations ¹	
	Marina	LRS ³	Marina	LRS	Marina	LRS	Marina	LRS
Folsom Lake Marina	0.3 – 0.7	0.2 – 0.5	0.6 – 0.9	0.5 – 0.8	<1.0 – 8.6	<1.0 – 9.1	<4	<4
Tahoe Keys Marina	<0.1 – 0.9	<0.1 – 0.7	1.1 – 1.4	0.1 – 0.3	<1.0 – 4.4	<1.0 – 5.0	<4	<4
San Francisco Marina	0.3 – 3.9	<0.1 – 1.0	0.5 – 3.6	<0.1 – 0.7	1.1 – 9.0	<1.0 – 2.2	13 – 32	11 – 32
Alamitos Bay Marina	0.4 – 3.4	<0.1 – 1.2	<0.1 – 4.4	<0.1 – 1.2	2.9 – 22.3	1.6 – 20.3	<4 – 24	10 – 34
Coyote Point Marina	1.7 – 2.6 (n = 8)	1.1 – 1.5 (n = 8)	1.7 – 2.6 (n = 8)	0.7 – 1.2 (n = 8)	2.2 – 8.1 (n = 8)	<1.0 – 16.6 (n = 8)	10 – 24 (n = 8)	7 – 20 (n = 8)
Pittsburg Marina	1.7 – 3.6	1.4 – 1.6	2.4 – 4.9	2.5 – 3.3	1.2 – 7.1	<1.0 – 6.4	<4 – 10	13 – 28
Antioch Marina	1.7 – 2.9	1.4 – 1.7	2.5 – 3.9	2.2 – 2.9	<1.0 – 4.2	<1.0 – 3.1	4 – 10	9 – 22
South Beach Harbor	1.9 – 3.0	0.4 – 1.0	1.1 – 3.2	<0.1 – 1.5	3.3 – 6.2	<1.0 – 2.2	8 – 25	8 – 29
Clipper Yacht Harbor	1.3 – 6.6	0.3 – 1.2	0.8 – 9.0	0.6 – 2.3	2.4 – 12.7	<1.0 – 6.3	9 – 29	15 – 31
Marina Bay Yacht Harbor	1.7 – 3.6	1.5 – 2.5 (n = 6)	2.0 – 5.7	1.0 – 2.8 (n = 6)	2.9 – 5.3	1.8 – 4.0 (n = 6)	11 – 17	12 – 21 (n = 6)
Benicia Marina	1.8 – 3.7	1.5 – 2.2	3.3 – 5.4	2.6 – 9.7	1.1 – 11.7	<1.0 – 2.6	13 – 46	22 – 150
Ballena Isle Marina	1.2 – 4.9	0.8 – 3.7	1.0 – 9.3	0.6 – 4.3	<1.0 – 12.0	1.0 – 8.6	11 – 37	10 – 33
Sacramento Marina	2.2 – 3.7	0.5 – 2.3	2.5 – 5.8	2.0 – 3.0	<1.0 – 7.8	<1.0 – 5.4	<4 – 7	14 – 28
Berkeley Marina	1.8 – 6.8	0.2 – 2.0	2.4 – 7.0	0.4 – 3.2	2.9 – 8.8	<0.1 – 9.5	8 – 25	8 – 25
Village West Marina	2.9 – 4.0	1.5 – 2.2 (n = 11)	4.8 – 6.4	2.6 – 4.7 (n = 11)	2.6 – 16.7	1.4 – 6.4 (n = 11)	<4 – 23	12 – 27 (n = 11)
Vallejo Marina	2.3 – 4.7	1.3 – 1.7	3.1 – 5.6	3.0 – 7.9	3.3 – 9.9	<1.0 – 3.8	10 – 35 (n = 11)	28 – 112
Santa Cruz Harbor	3.0 – 5.8	<0.1 – 0.9	4.4 – 7.8	<0.1	8.8 – 22.3	<1.0 – 6.9	12 – 31	10 – 26
Monterey Harbor	3.1 – 7.8	0.1 – 0.5	2.6 – 9.2	<0.1 – 0.3	8.4 – 26.0	<0.1 – 12.0	<4 – 25	6 – 25
Santa Barbara Harbor	2.3 – 8.2	<0.1 – 0.5	3.6 – 8.6	<0.1	6.4 – 22.8	<1.0 – 4.8	10 – 31	11 – 25
Loch Lomond Marina	3.2 – 10.3	1.3 – 2.2	2.8 – 10.6	1.9 – 3.1	4.9 – 13.8	<1.0 – 3.7	10 – 30	17 – 43
Downtown Shoreline Marina	2.4 – 10.9	0.4 – 1.2	2.6 – 11.5	<0.1 – 1.2	9.9 – 40.1	2.1 – 7.6	11 – 26	6 – 22
Marina del Rey FB	8.9 – 16.2	0.3 – 4.7	9.2 – 17.0	<0.1 – 4.6	38.2 – 66.6	<1.0 – 22.1	9 – 24	10 – 29
Marina del Rey BB	8.1 – 18.4	0.3 – 4.7	9.0 – 20.2	<0.1 – 4.6	33.3 – 59.5	<1.0 – 22.1	10 – 29	10 – 29

¹ The number of replicates (n) is 12 unless otherwise indicated.

² Marina names are color coded by water type. **Green** = freshwater, **Yellow** = brackish water, **Blue** = saltwater

³ LRS = local reference site

Table 7. Median Metal (µg/L) and Total Suspended Solids (mg/L) Concentrations in Water (sorted by ascending order of marina median dissolved copper concentrations)

Marina ¹	Median Dissolved Copper Concentrations		Median Total Copper Concentrations		Median Dissolved Zinc Concentrations		Median Total Suspended Solids Concentrations	
	Marina	LRS ²	Marina	LRS	Marina	LRS	Marina	LRS
Folsom Lake Marina	0.5	0.3	0.7	0.6	2.8	2.5	<4	<4
Tahoe Keys Marina	0.6	0.2	1.2	0.2	2.3	2.2	<4	<4
San Francisco Marina	1.1	0.4	0.9	0.2	2.7	1.6	21.9	19.8
Alamitos Bay Marina	1.2	0.3	1.2	0.3	6.7	6.3	13.5	16.9
Coyote Point Marina	2.1	1.3	2.2	1.0	4.6	3.1	17.8	12.9
Pittsburg Marina	2.1	1.5	3.0	2.9	2.9	1.7	7.3	17.9
Antioch Marina	2.2	1.5	3.0	2.6	1.9	1.6	6.8	13.7
South Beach Harbor	2.2	0.7	1.9	0.4	4.4	1.3	16.2	17.3
Clipper Yacht Harbor	2.4	0.8	2.1	0.9	4.8	2.3	19.0	20.8
Marina Bay Yacht Harbor	2.6	1.7	2.7	1.7	4.1	2.8	13.0	16.4
Benicia Marina	2.7	1.7	4.1	4.5	2.7	1.4	23.0	54.7
Ballena Isle Marina	2.8	1.4	3.3	1.1	5.2	2.4	20.1	16.7
Sacramento Marina	3.0	0.7	4.2	2.4	2.8	2.5	4.3	19.6
Berkeley Marina	3.3	0.7	4.0	0.8	4.7	2.2	18.1	15.0
Village West Marina	3.4	1.8	5.6	3.6	5.1	3.2	12.5	19.4
Vallejo Marina	3.4	1.5	4.1	3.9	4.3	1.2	16.0	55.0
Santa Cruz Harbor	4.3	0.3	6.1	0.1	14.3	2.0	23.2	18.7
Monterey Harbor	4.9	0.2	5.3	0.1	18.5	1.7	14.1	16.3
Santa Barbara Harbor	5.7	0.1	5.8	0.1	13.9	1.9	18.2	18.0
Loch Lomond Marina	5.8	1.7	6.3	2.4	7.9	2.0	18.9	26.9
Downtown Shoreline Marina	6.6	0.7	6.4	0.2	20.3	3.9	18.5	15.3
Marina del Rey FB	12.4	1.0	13.3	0.3	49.1	5.6	15.8	17.3
Marina del Rey BB	13.6	1.0	14.7	0.3	50.0	5.6	18.4	17.3

¹ Marina names are color coded by water type. **Green** = freshwater, **Yellow** = brackish water, **Blue** = saltwater

² LRS = local reference site

Figure 4. Distribution of Dissolved Copper Concentrations in Freshwater Marina Areas

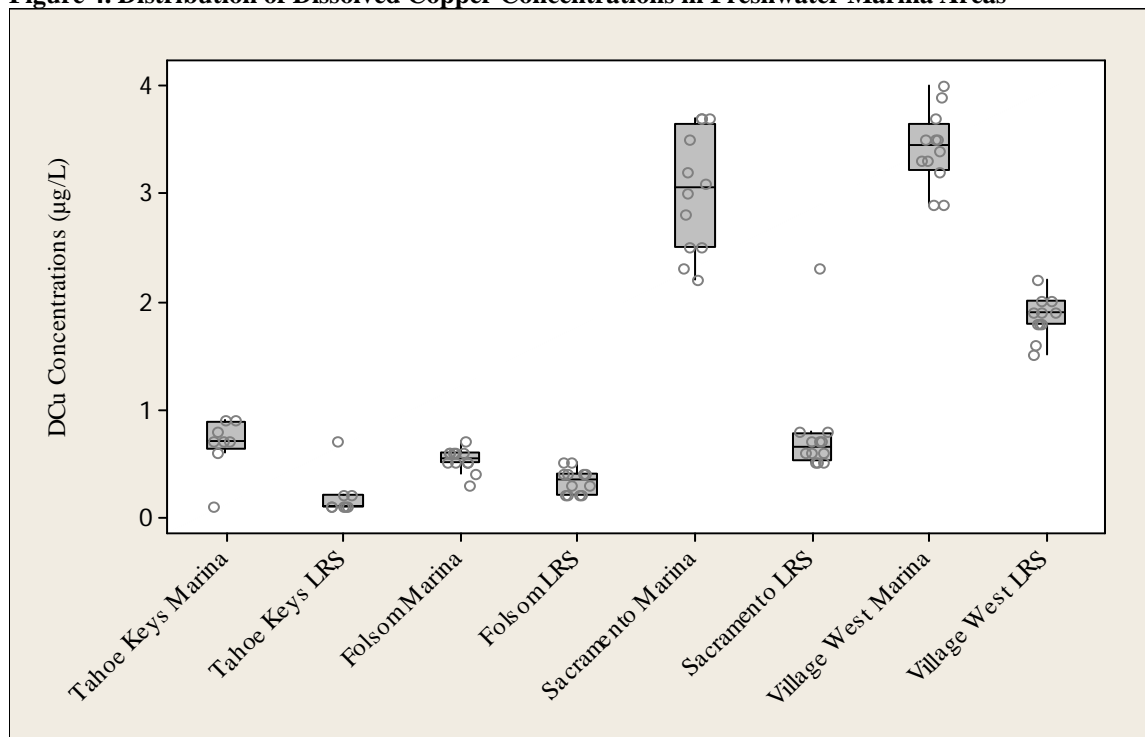


Figure 5. Distribution of Dissolved Copper Concentrations in Brackish Water Marina Areas

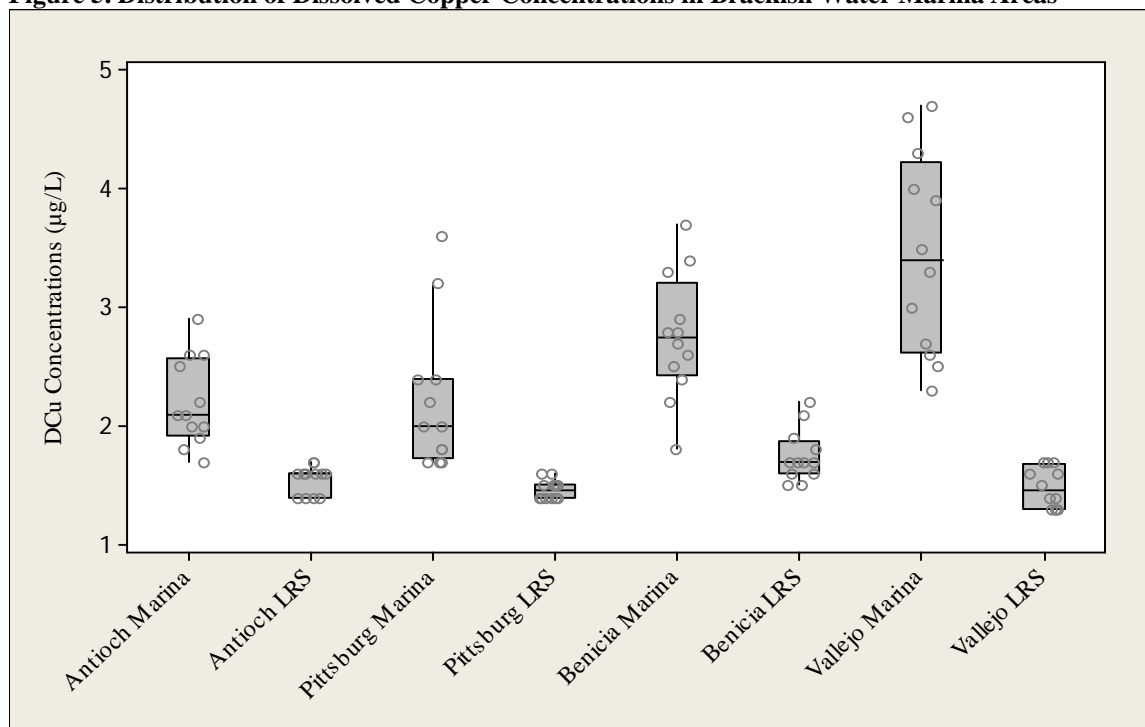


Figure 6. Distribution of Dissolved Copper Concentrations in Saltwater Marina Areas (San Francisco Bay Area)

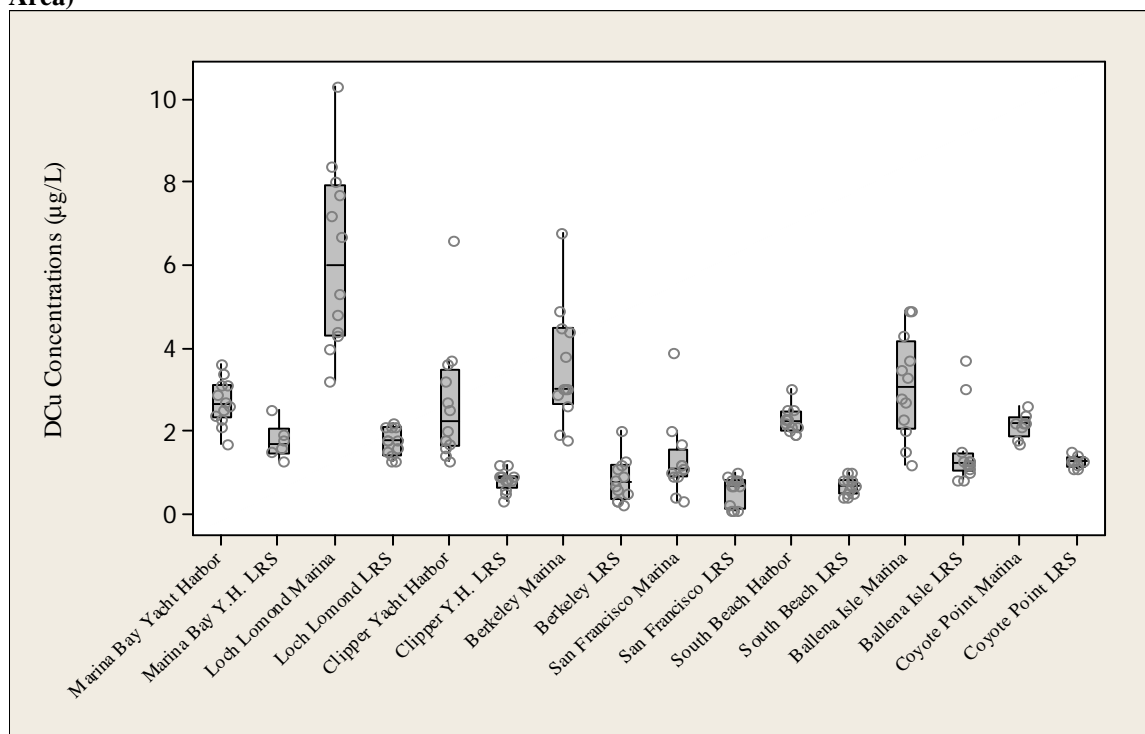


Figure 7. Distribution of Dissolved Copper Concentrations in Saltwater Marina Areas (Central and South Coast)

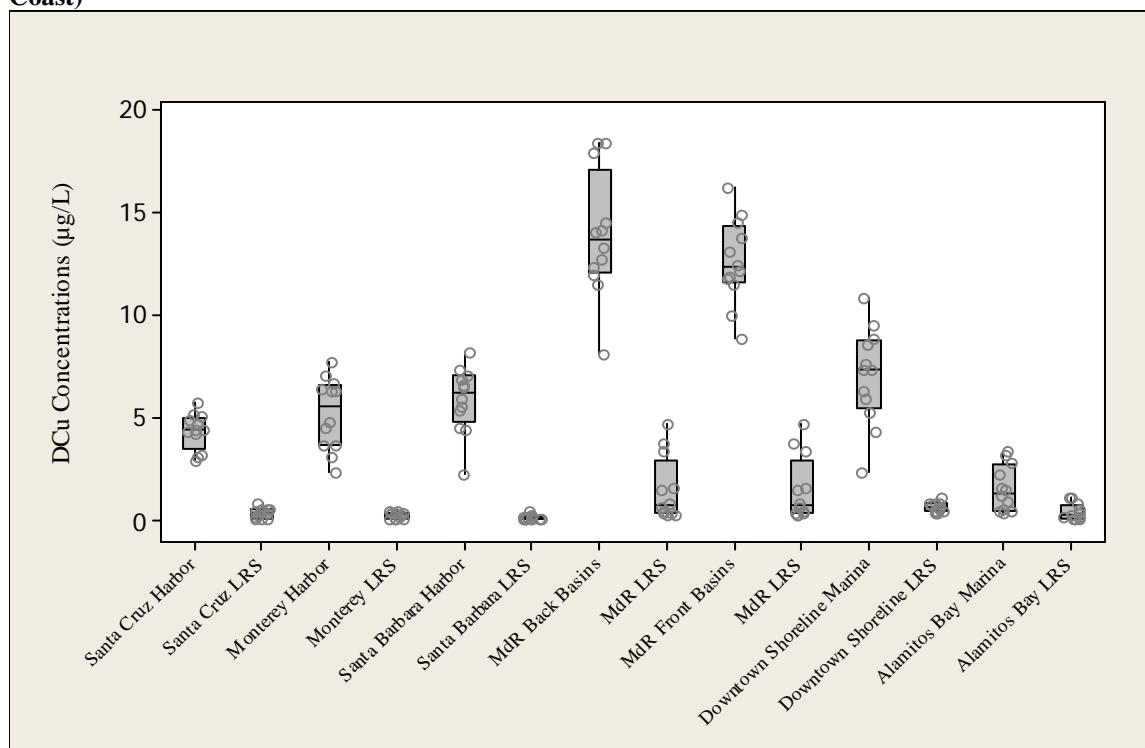
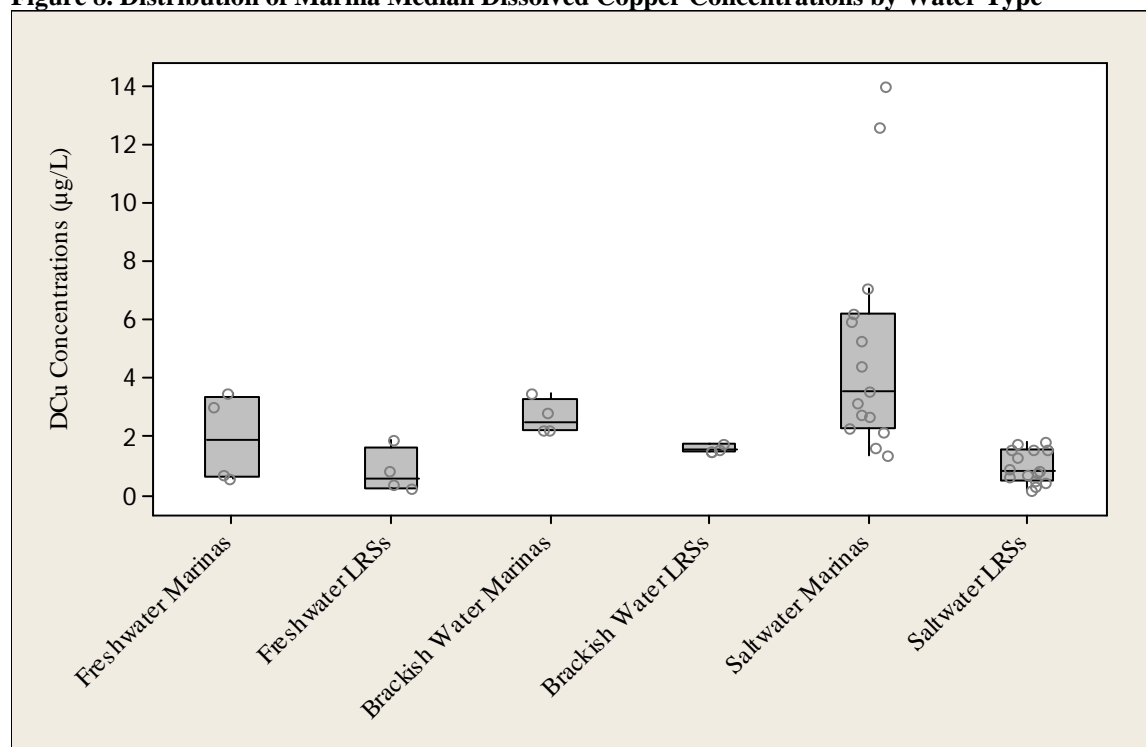


Table 8. Summary of Median Metal Concentrations (µg/L) in Water

	Median DCu Concentrations w/ 95% CI		Median TCu Concentrations w/ 95% CI		Median DZn Concentrations w/ 95% CI	
	Marina Sites	LRSs	Marina Sites	LRSs	Marina Sites	LRSs
Saltwater Sites	3.3 - 3.7 - 4.2	0.5 - 0.6 - 0.7	3.3 - 3.8 - 4.4	0.2 - 0.3 - 0.4	8.0 - 9.2 - 10.7	2.1 - 2.4 - 2.8
Brackish Water Sites	2.4 - 2.6 - 2.8	1.5 - 1.6 - 1.6	3.3 - 3.5 - 3.8	3.1 - 3.4 - 3.7	2.4 - 2.8 - 3.3	1.3 - 1.5 - 1.7
Freshwater Sites	1.1 - 1.4 - 1.9	0.4 - 0.5 - 0.7	1.7 - 2.2 - 2.9	0.8 - 1.1 - 1.6	2.5 - 3.1 - 3.9	2.1 - 2.6 - 3.2
All Water Sites	2.7 - 3.0 - 3.3	0.6 - 0.7 - 0.8	3.1 - 3.4 - 3.8	0.5 - 0.6 - 0.7	5.4 - 6.2 - 7.0	1.9 - 2.1 - 2.4

Figure 8. Distribution of Marina Median Dissolved Copper Concentrations by Water Type



times the LRS median concentrations. Brackish water marinas exhibited the smallest difference with marina median concentrations being about twice as high as the LRS median concentrations.

Overall, median DCu concentrations were 3.0 µg/L for all marina sites and 0.7 µg/L for all LRSs (Table 8). Median DCu concentrations in water were 3.7, 2.6, and 1.4 µg/L for salt, brackish, and freshwater marinas, respectively, while the respective LRS median DCu concentrations were 0.6, 1.6, and 0.5 µg/L.

There were significant differences in median DCu concentrations among the three water types (one-way ANOVA, $F_{2,64} = 8.90$, $p < 0.0005$), with freshwater marina median DCu concentrations being significantly less than those in salt and brackish water marinas (Tukey's Test, family error rate=0.05) (Figure 8,). In contrast, there was no significant difference between median DCu concentrations in salt and brackish water marinas. In Figure 8, plotted circles represent the median value for each marina and the horizontal line inside the box represents the water type median.

The fully-nested balanced ANOVA showed statistically significant differences between marinas and LRS DCu concentrations in saltwater marina areas (fully-nested balanced ANOVA, $F_{14,56} = 22.2$, $p < 0.0005$, Coyote Point Marina omitted), brackish water marina areas (fully-nested balanced ANOVA, $F_{4,16} = 36.3$, $p < 0.0005$), and freshwater marina areas, (fully-nested balanced ANOVA, $F_{3,12} = 33.9$, $p < 0.0005$, Tahoe Keys Marina omitted).

Total Copper

As was the case for DCu, 346, 96, and 88 TCu water samples were collected from salt, brackish, and freshwater areas, respectively. TCu concentrations were above the method detection limit (MDL = 0.1 µg/L) in 455 of 517 samples (88%), with concentrations ranging up to 20.2 µg/L (Appendix F). The sample with the highest TCu concentration came from one of MdR's back basins (Table 6).

Median TCu concentrations for individual marinas ranged from 0.7 µg/L at Folsom Lake Marina to 14.7 µg/L at MdR's back basins (Table 7). The median concentrations for 21 of 23 marinas were below 7 µg/L. The relative rank of marinas, based on the magnitude of their median TCu concentrations, is slightly different than that for DCu. The comparison of marina TCu concentrations by water type and region revealed similar patterns to DCu (Figures 9–12) with the primary exception of the relationship between the brackish water marinas and their LRSs (Figure 10).

Figure 9. Distribution of Total Copper Concentrations in Freshwater Marina Areas

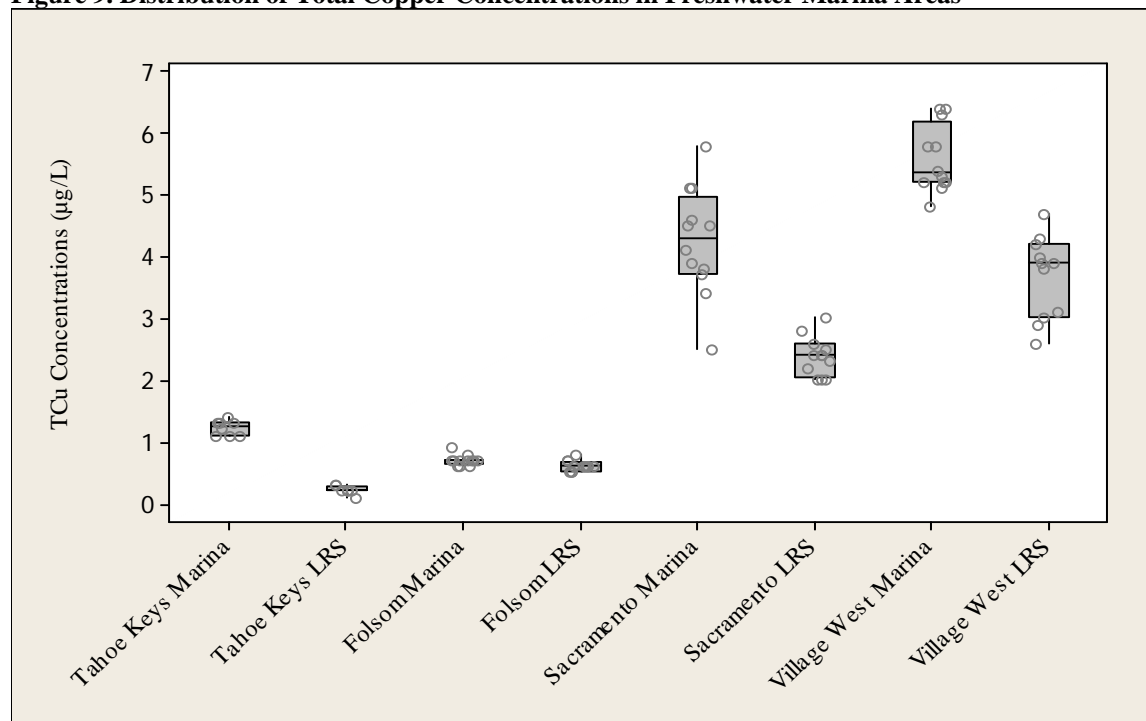


Figure 10. Distribution of Total Copper Concentrations in Brackish Water Marina Areas

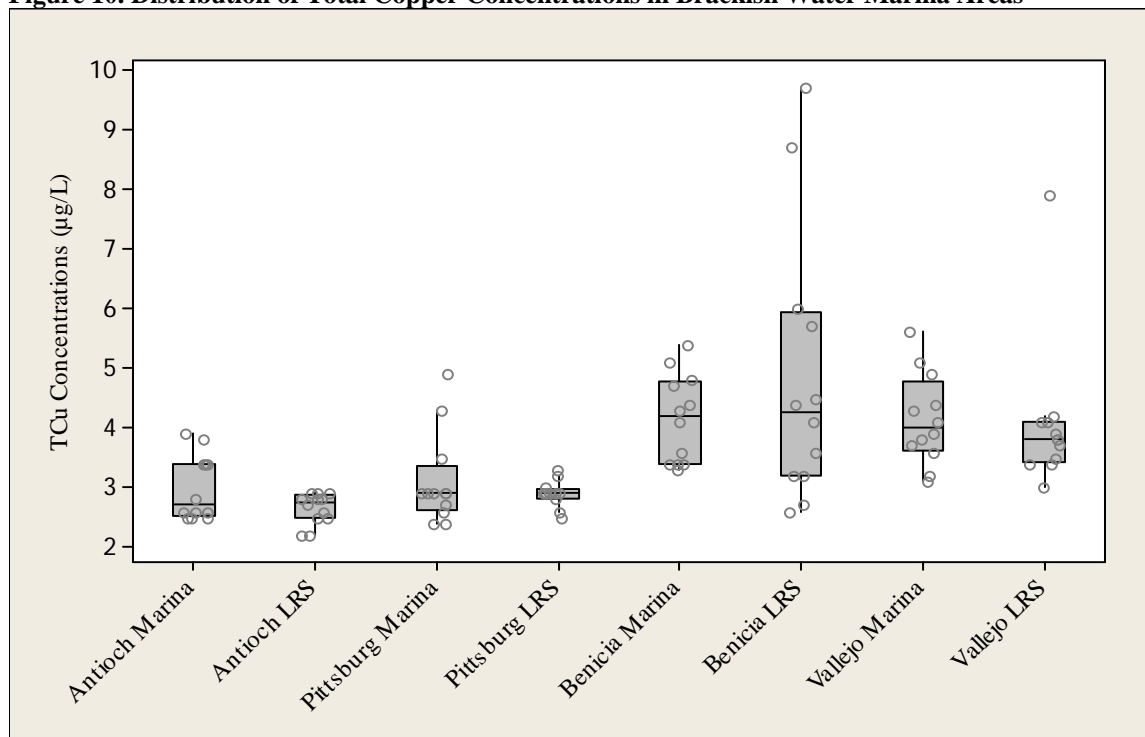


Figure 11. Distribution of Total Copper Concentrations in Saltwater Marina Areas (San Francisco Bay Area)

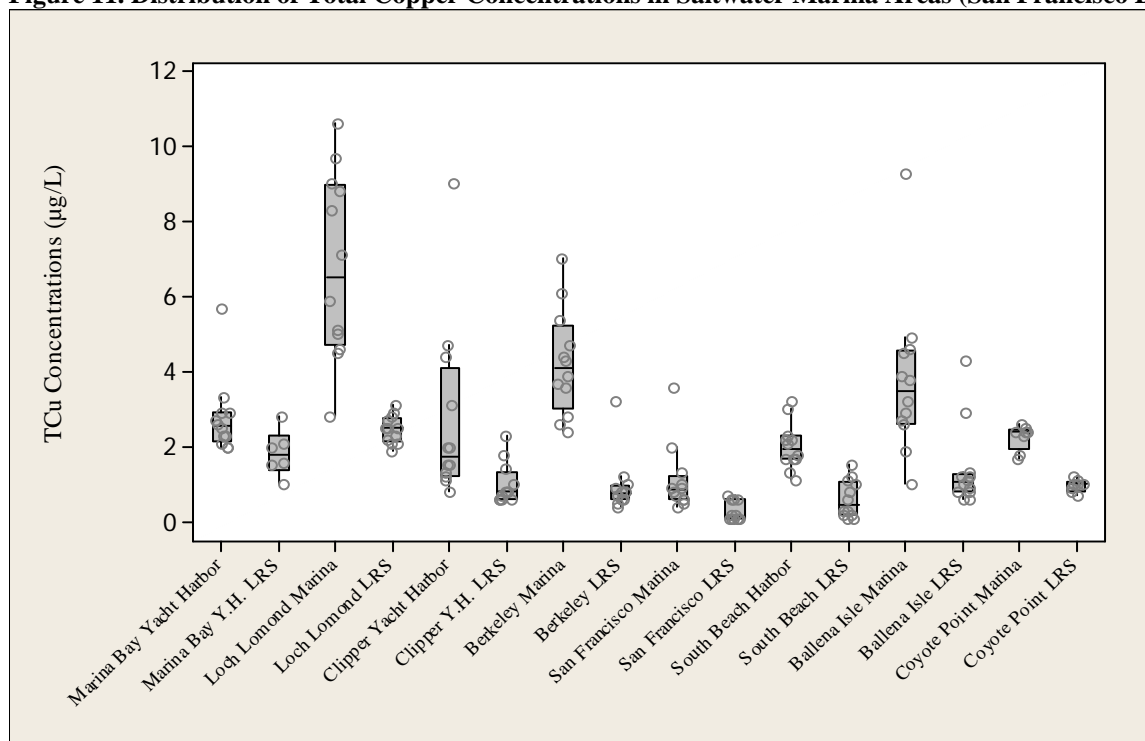


Figure 12. Distribution of Total Copper Concentrations in Saltwater Marina Areas (Central and South Coast)

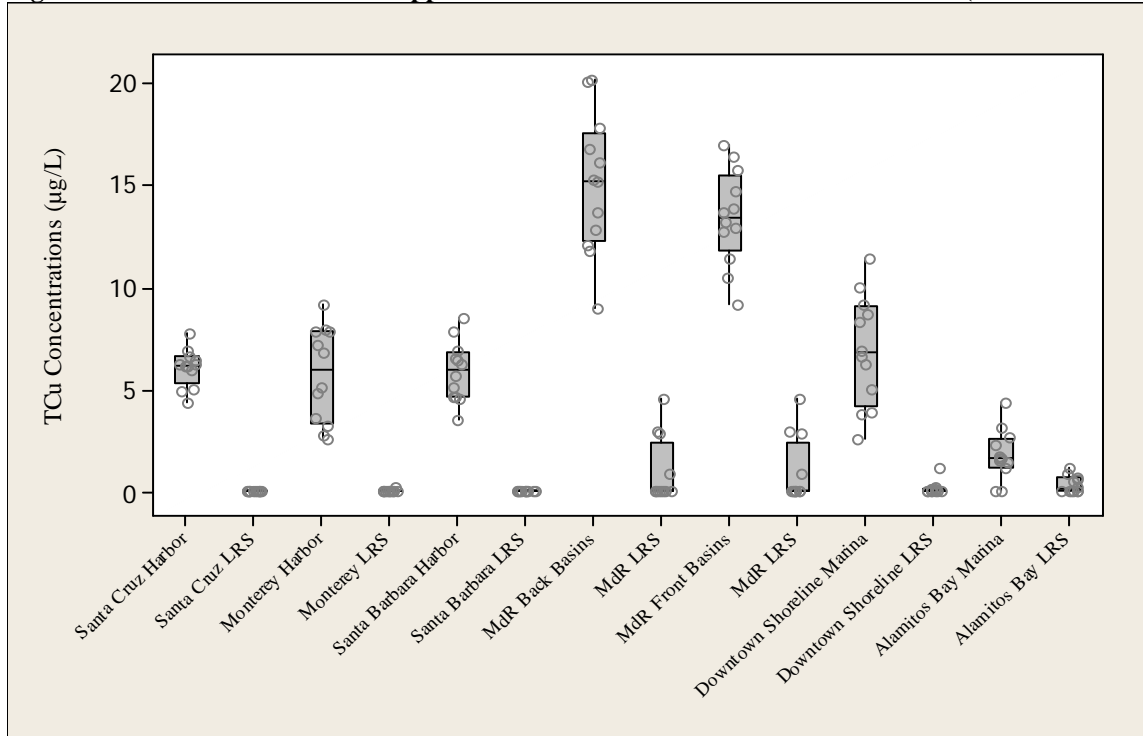
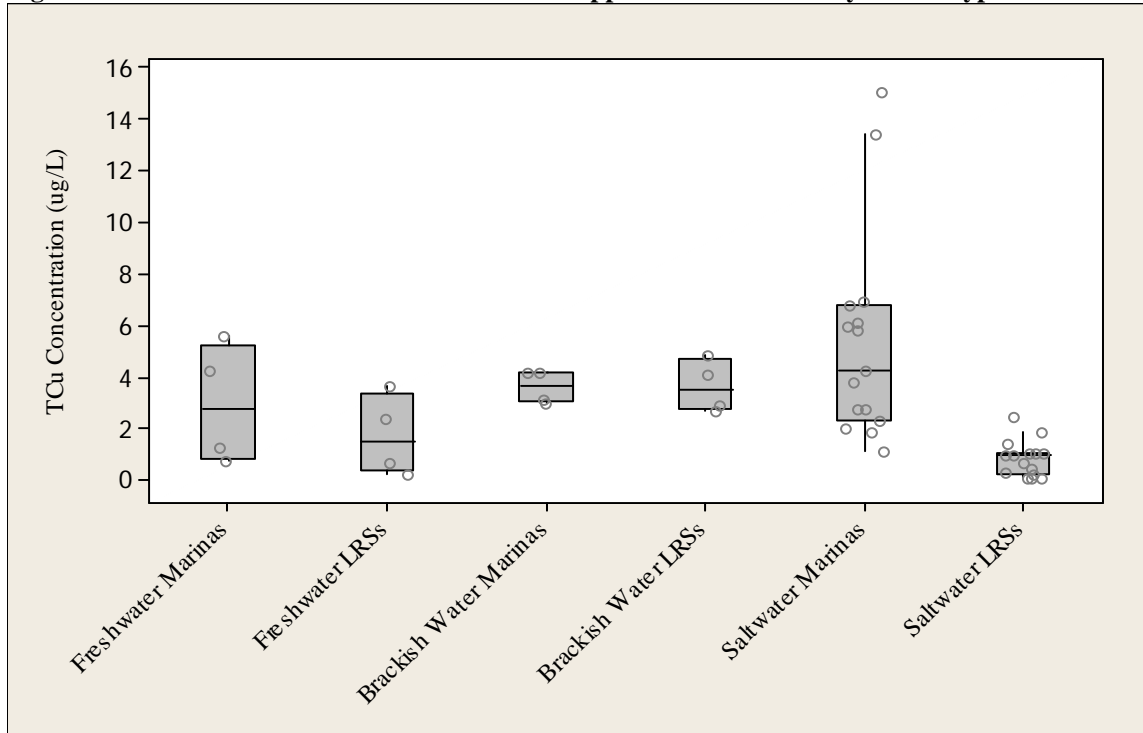


Figure 13. Distribution of Marina Median Total Copper Concentrations by Water Type



Overall, median TCu concentrations were 3.4 µg/L for all marina sites and 0.6 µg/L for all LRSs (Table 8). Median TCu concentrations in water were 3.8, 3.5, and 2.2 µg/L for salt, brackish, and freshwater marinas, respectively, while the respective LRS median TCu concentrations were 0.3, 3.4, and 1.1 µg/L.

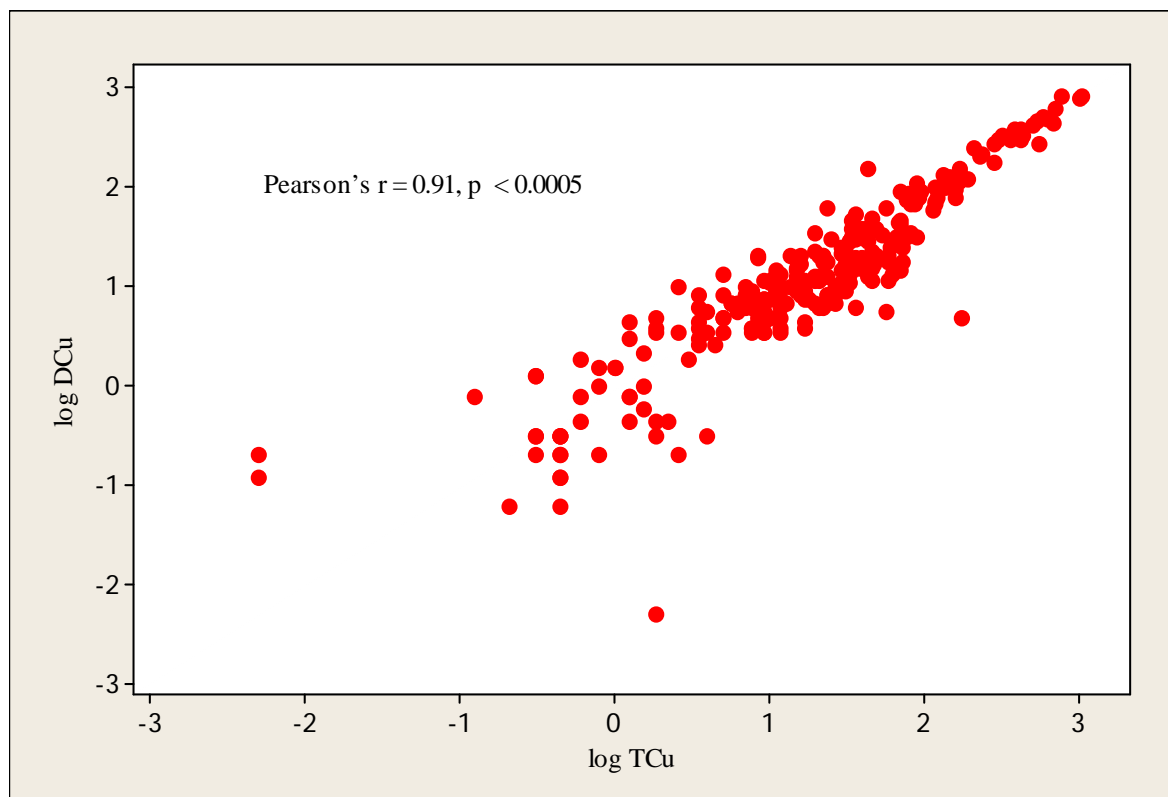
A test for differences in marina TCu concentrations among the three water types found no significant difference between water types, although the significance level was only slightly greater than the cutoff of 0.05 (one-way ANOVA, $F_{2,64} = 3.1$, $p = 0.051$). TCu concentrations tend to be similar among marinas of the three water types (Figure 13).

The TCu concentrations measured within both freshwater and saltwater marinas were significantly higher than those measured in the associated LRS (fully-nested balanced ANOVA; saltwater: $F_{14,56} = 60.8$, $p < 0.0005$, Coyote Point Marina omitted; freshwater: $F_{3,12} = 15.8$, $p < 0.0005$, Tahoe Keys Marina omitted) (Figure 13). In contrast, there was no significant difference between measurements taken in brackish water marina areas (fully-nested balanced ANOVA, $F_{4,16} = 0.4$, $p = 0.836$).

Median TCu concentrations were almost always higher inside of marinas compared to LRSs. At Benicia Marina, however, the median LRS TCu concentration was actually higher than the median marina concentration. At Benicia Marina, the corresponding TSS measurements were quite high (median LRS TSS concentration 54.7 mg/L) and could potentially serve to explain the high TCu concentrations at the LRSs for Benicia Marina. At Vallejo Marina, where the median LRS TSS concentration was also high (55.0 mg/L), the median LRS TCu concentration (3.9 µg/L) was almost as high as the median marina TCu concentration (4.1 µg/L).

There was a strong correlation between DCu and TCu concentrations (Pearson's $r = 0.91$, $p < 0.0005$, Figure 14). Overall analysis of dissolved-to-total copper ratios showed that about 92% of total copper is DCu. This percentage is consistent with the conversion factors (TCu to DCu) offered in the U.S. EPA's updated water quality criteria for copper (U.S. EPA, 2007). The criteria document suggests that the conversion factors of 0.96 and 0.909 be used for freshwater and saltwater, respectively. Thus, the observed correlation is a reflection of the fact that most of the copper in the system is dissolved.

Figure 14. Correlation Plot of Log Dissolved versus Log Total Copper Concentrations



Dissolved Zinc

A total of 346, 96, and 88 water samples were collected from salt, brackish, and freshwater areas, respectively. DZn concentrations were above method detection limit (MDL = 1.0 µg/L) in 465 of 517 samples (90%), with concentrations ranging up to 66.6 µg/L (Appendix F). The sample with the highest DZn concentration came from one of MdR's front basins (Table 6).

Median DZn concentrations for individual marinas ranged from 1.9 µg/L at Antioch Marina to 50.0 µg/L at MdR's back basins (Table 7). Median DZn concentrations were less than 8 µg/L in 17 of the 23 marinas studied.

The freshwater and brackish water marinas exhibited very low to low median DZn concentrations (Figures 15 and 16). DZn concentrations were generally similar among freshwater marinas and among brackish water marinas.

The eight San Francisco Bay Area saltwater marinas exhibited very low to moderate median DZn concentrations (Figure 17). Among these marinas, the highest median concentration was observed at Loch Lomond Marina (7.9 µg/L) and the low median concentration was observed at San Francisco Marina (2.7 µg/L). The remaining six Bay Area marinas exhibited median DCu concentrations that ranged between 4 and 6 µg/L.

The seven Central and South Coast saltwater marinas exhibited moderate to very high median DZn concentrations (Figure 18). Among these marinas, DCu concentrations at MdR's front and back basins (49.1 and 50.0 µg/L, respectively) were by far the highest. Alamitos Bay Marina exhibited the lowest median concentration (6.7 µg/L) in this region. The remaining four Central and South Coast marinas exhibited median DCu concentrations that ranged between 13 and 20 µg/L.

Figure 15. Distribution of Dissolved Zinc Concentrations in Freshwater Marina Areas

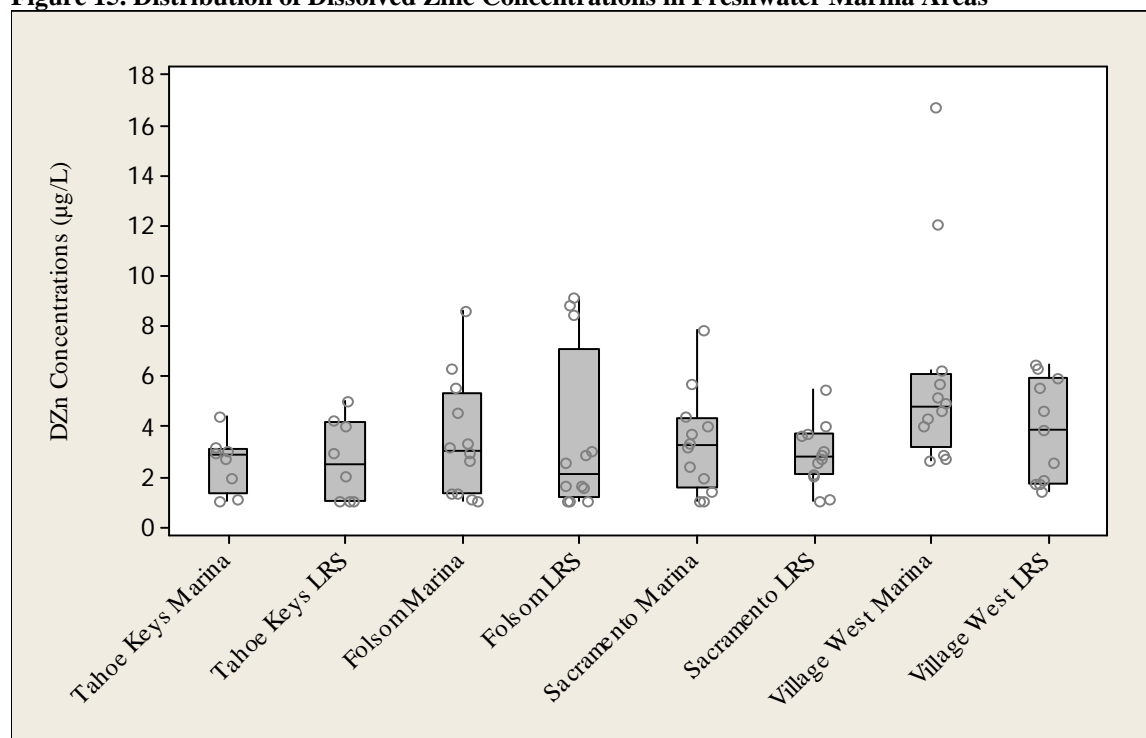


Figure 16. Distribution of Marina Dissolved Zinc Concentrations in Brackish Water Marina Areas

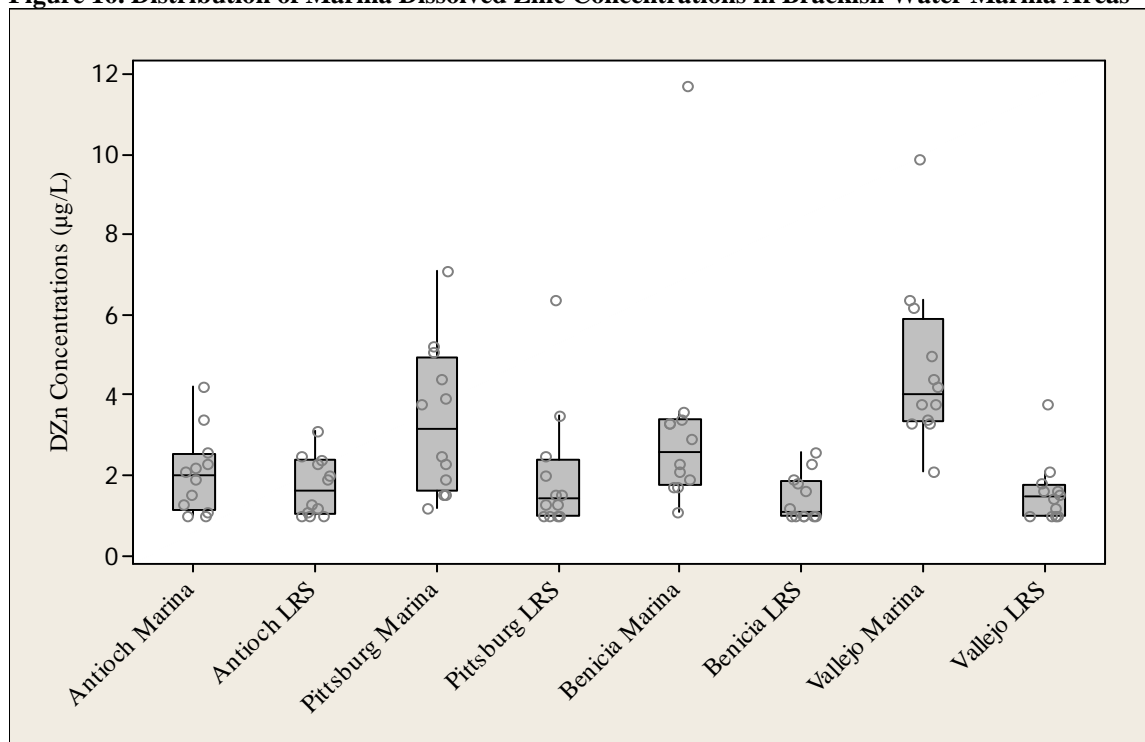


Figure 17. Distribution of Marina Dissolved Zinc Concentrations in Saltwater Marina Areas (San Francisco Bay Area)

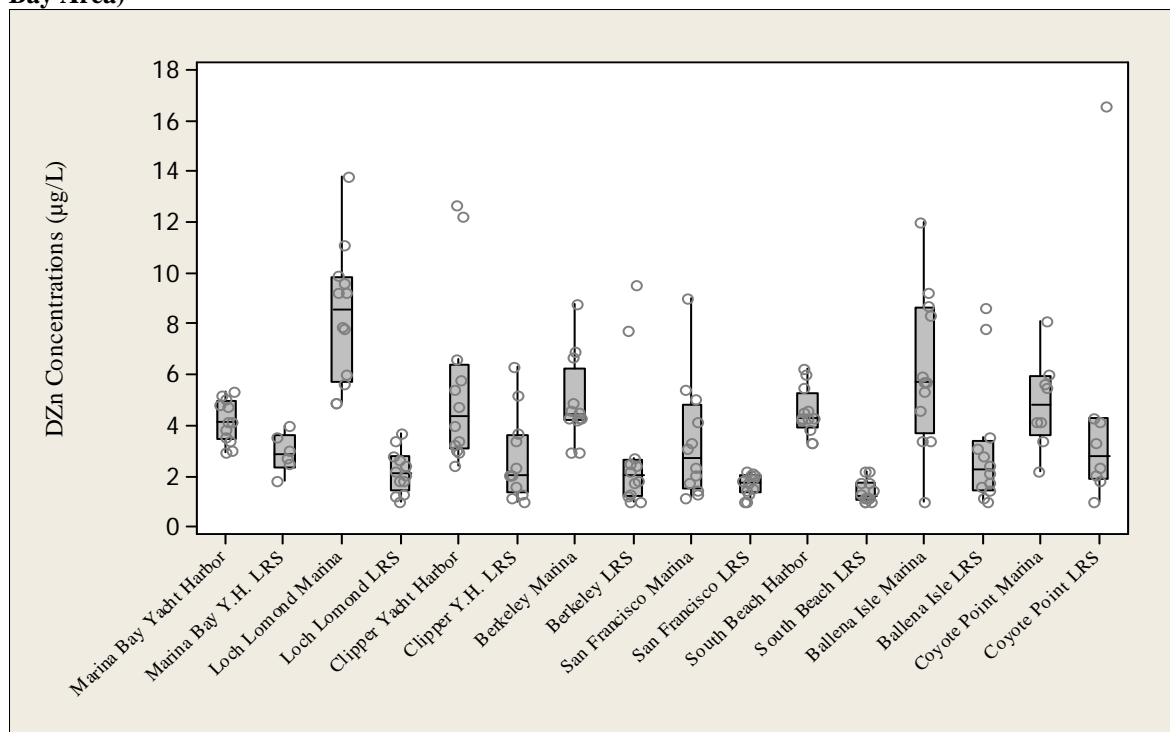


Figure 18. Distribution of Marina Dissolved Zinc Concentrations in Saltwater Marina Areas (Central and South Coast)

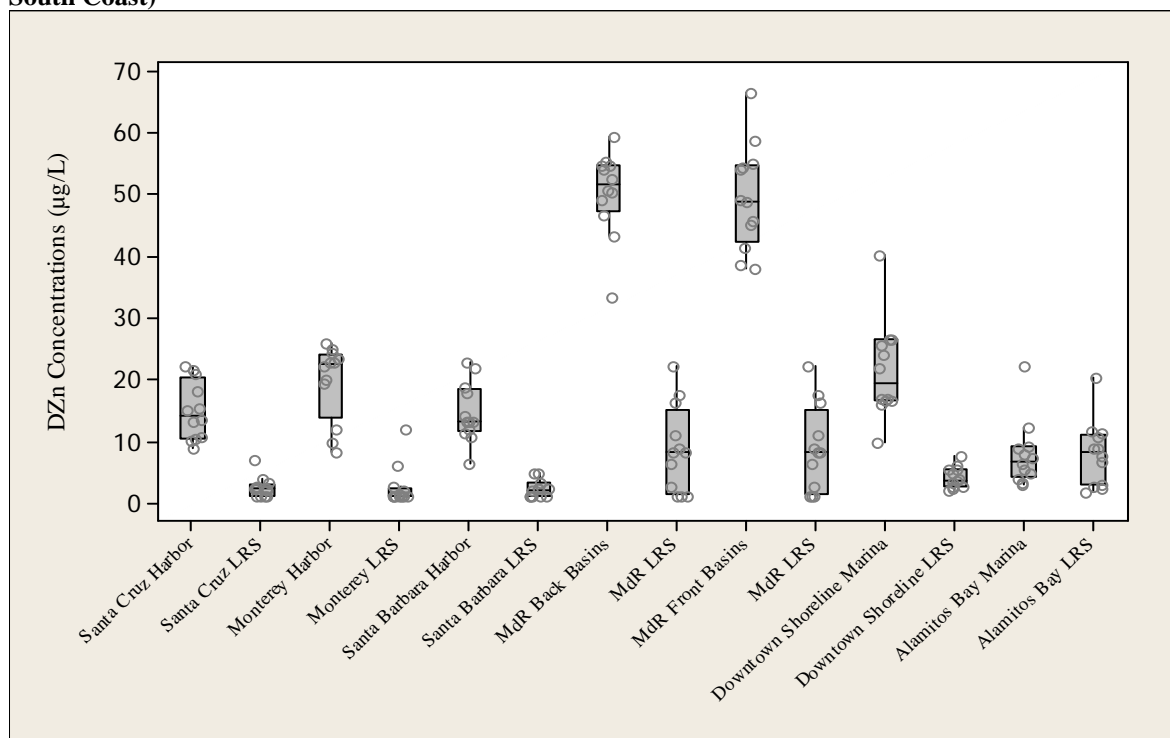
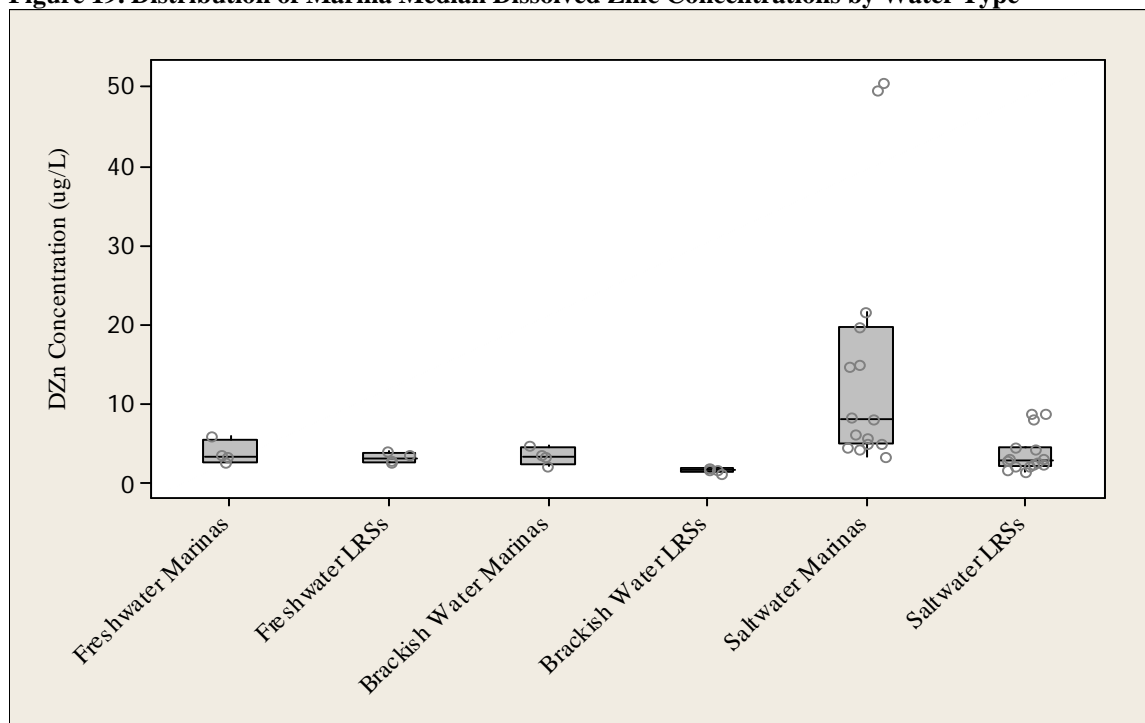


Figure 19. Distribution of Marina Median Dissolved Zinc Concentrations by Water Type



Overall, median DZn concentrations in water were 6.2 µg/L for all marina sites and 2.1 µg/L for all LRSs (Table 8). Median DZn concentrations were 9.2, 2.8, and 3.1 µg/L for salt, brackish, and fresh water marinas, respectively, while the respective LRS median DZn concentrations were 3.6, 1.5, and 2.6 µg/L.

There were significant differences in DZn concentrations among marinas of the three water types (one-way ANOVA, $F_{2,64} = 15.5$, $p < 0.0005$), with salt water marina DZn concentrations being significantly higher than those for brackish and freshwater marinas (Tukey's Test, family error rate = 0.05) (Figure 19). In contrast, there was no significant difference between DZn concentrations in brackish and freshwater marinas.

At all 23 marina areas, the median marina DZn concentrations were greater than the median LRS concentrations. In Figure 18, the median for Alamitos Bay Marina appears to be lower than the median for its LRSs. Note, however, that this is an artifact of the two different approaches used to calculate the sample median. Recall that the geometric mean median value is the one that is used for data analysis and discussion.

The difference in marina and LRS DZn concentrations is statistically significant for saltwater marina areas (fully-nested balanced ANOVA, $F_{14,56} = 22.9$, $p < 0.0005$, Coyote Point Marina omitted) and brackish water marina areas (fully-nested balanced ANOVA, $F_{4,16} = 5.4$, $p < 0.006$) (Figure 19). There is no statistically discernable difference for freshwater marina areas (fully-nested balanced ANOVA, $F_{3,12} = 0.3$, $p = 0.793$, Tahoe Keys Marina omitted).

Total Suspended Solids

TSS data are frequently useful in improving the understanding of metals data. Thus, these results are evaluated along with the metals results. TSS concentrations were above the detection limit (MDL = 4 mg/L) in 465 of 516 samples (90%) with concentrations ranging up to 150 mg/L (Appendix F). The sample with the highest TSS concentration in this study was from one the Benicia Marina LRS (Table 6).

Median TSS concentrations for individual marinas ranged from below the detection limit of 4 mg/L at Folsom Lake and Tahoe Keys marinas to 23.2 mg/L at Santa Cruz Harbor (Table 7). The median concentrations of 18 of 23 marinas were above 12 mg/L.

The freshwater marinas exhibited very low to low median TSS concentrations (Figure 20). The brackish water marinas showed low to moderate median TSS concentrations (Figure 21). The 15 saltwater marinas also showed low to moderate median TSS concentrations (Figures 22 and 23).

TSS concentrations were often higher outside of the marina than inside (Figures 20–23). Since marinas are constructed with the primary goal of protecting boats from turbulence caused by wind, currents, and tides, this observation seems logical. Median TSS concentrations for LRSs were higher in 13 out of 23 marina areas.

The two highest median TSS concentrations—54.7 and 55.0 mg/L were documented for the Benicia LRSs and the Vallejo LRSs, respectively. These high levels of TSS at these two areas can likely be attributed to particle flocculation, which is a common phenomenon in estuarine areas where freshwater meets more saline water. At the other two less-saline brackish water LRSs (Pittsburg and Antioch), the TSS ranges are similar to those of the two riverine freshwater LRSs (Sacramento Marina and Village West Marina).

Overall, median TSS concentrations in water were 13.5 mg/L for all marina sites and 17.4 mg/L for all LRSs (Table 8). Median TSS concentrations in water were 17.5, 11.6, and 5.6 mg/L for salt, brackish, and freshwater marinas, respectively, while the respective LRS median TSS concentrations were 17.6, 29.3, and 9.3 mg/L.

Figure 20. Distribution of Total Suspended Solid Concentrations in Freshwater Marina Areas

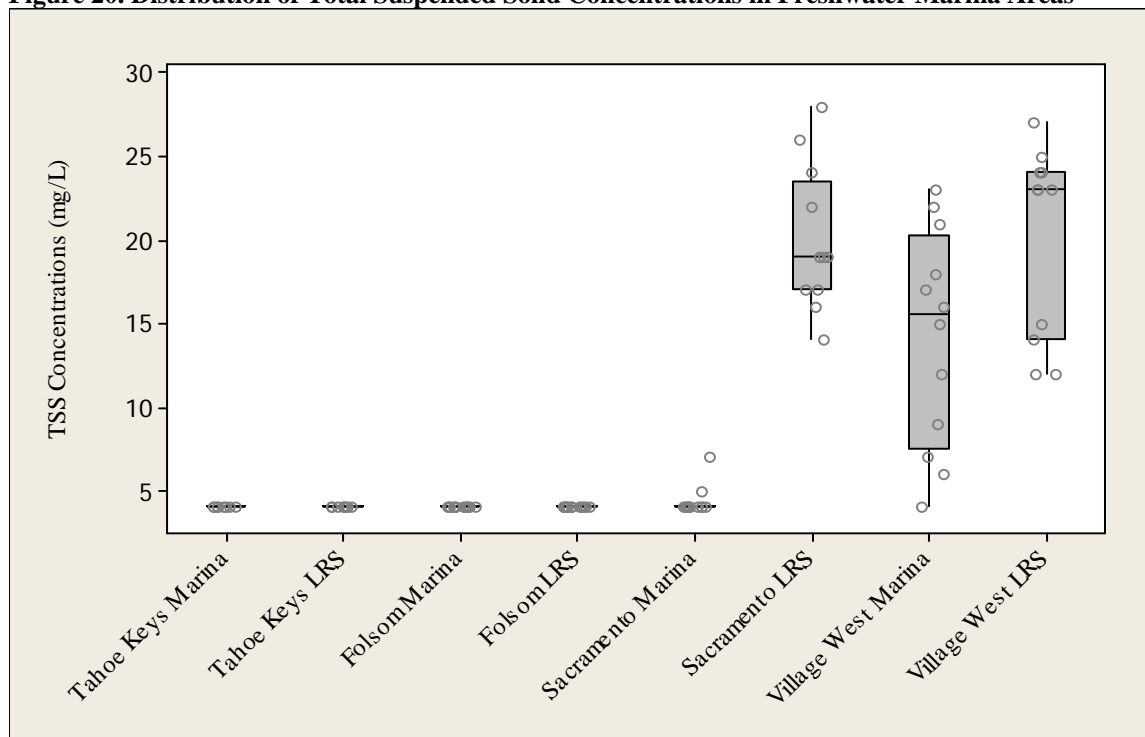


Figure 21. Distribution of Total Suspended Solid Concentrations in Brackish Water Marina Areas

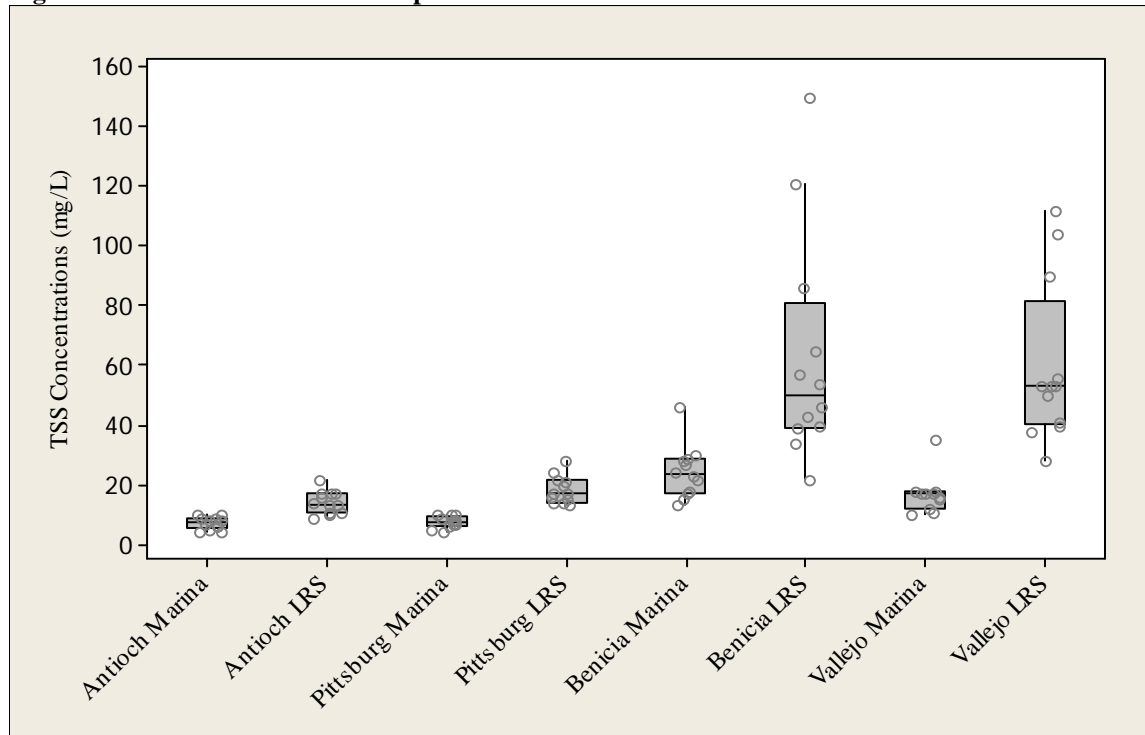


Figure 22. Distribution of Total Suspended Solid Concentrations in Saltwater Marina Areas (San Francisco Bay Area)

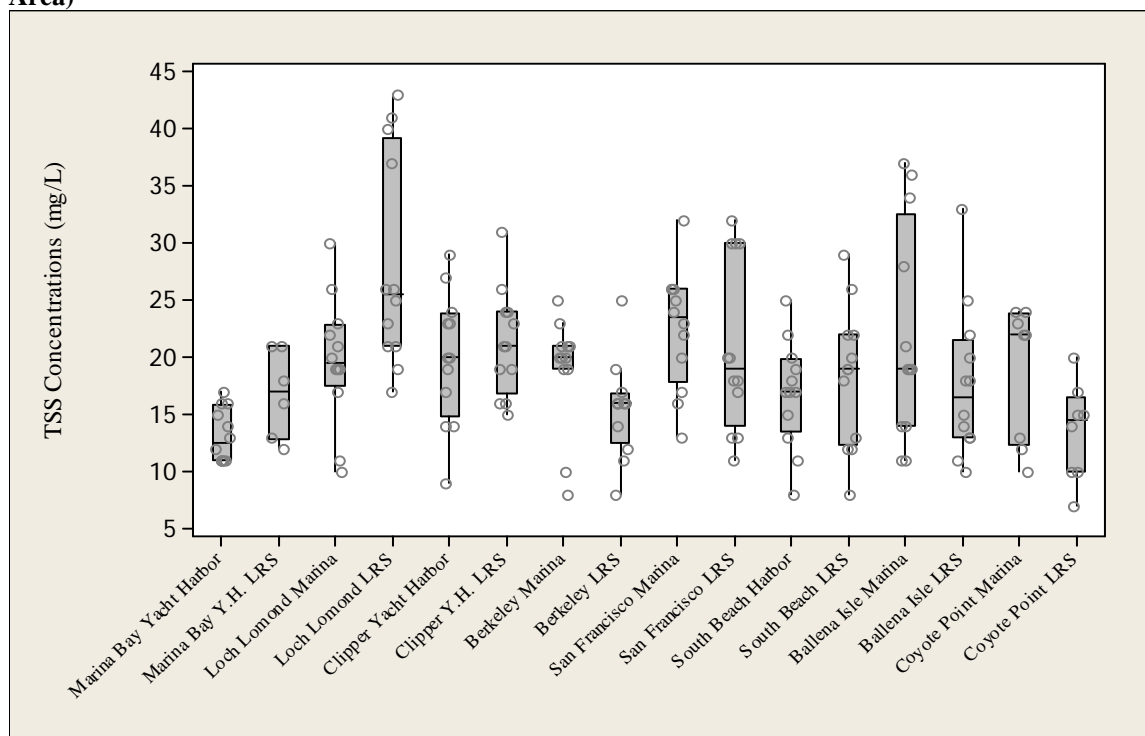


Figure 23. Distribution of Total Suspended Solid Concentrations in Saltwater Marina Areas (Central and South Coast)

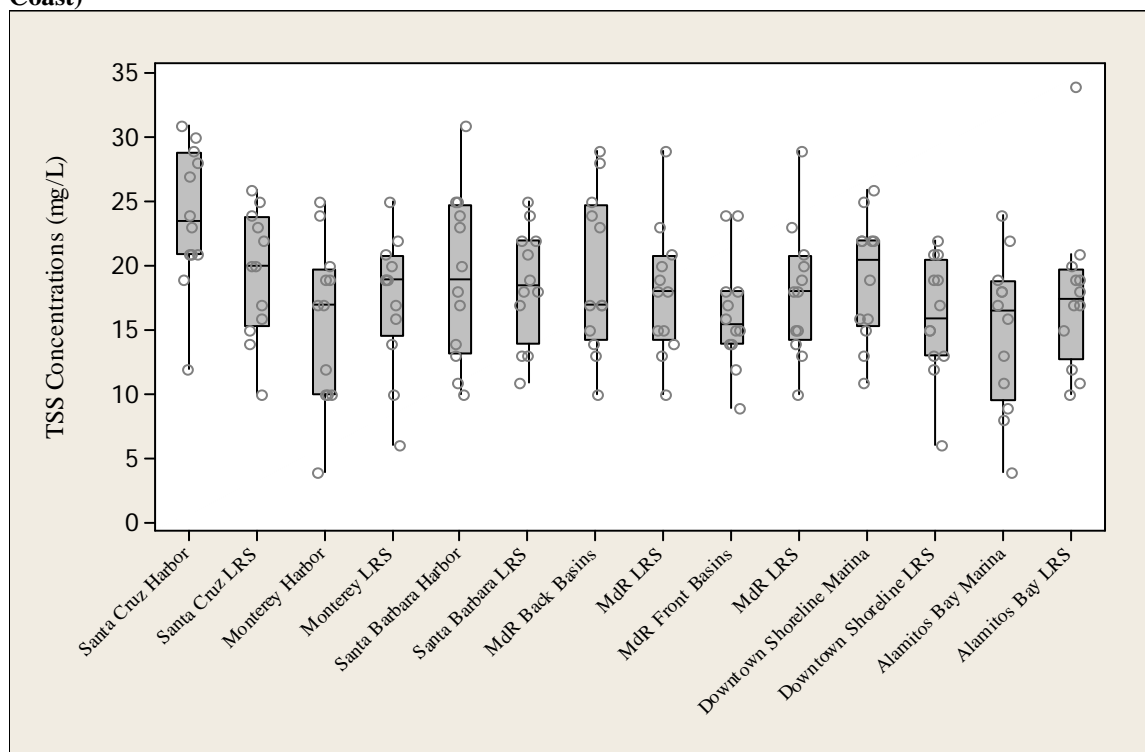
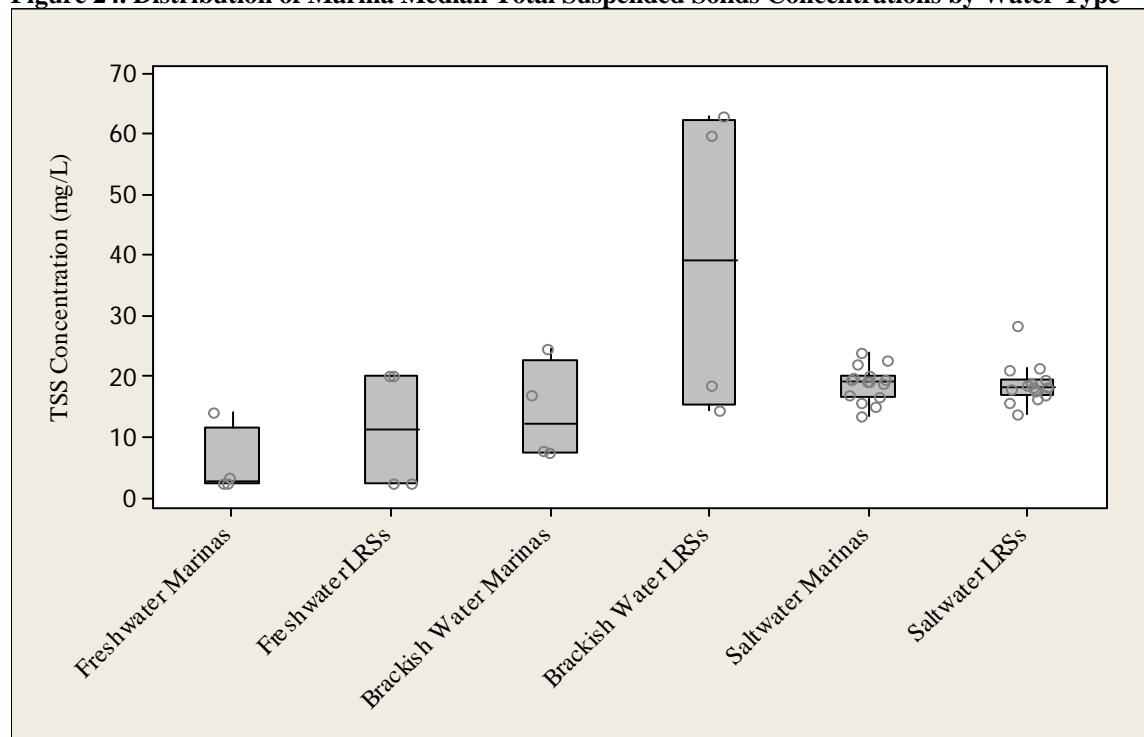


Figure 24. Distribution of Marina Median Total Suspended Solids Concentrations by Water Type



There were significant differences in TSS concentrations among marinas of the three water types (one-way ANOVA, $F_{2,64} = 51.6$, $p < 0.0005$), with TSS concentrations from marinas of each water types being significantly different than one another (Tukey's Test, family error rate = 0.05) (Figure 24). Median TSS concentrations in marinas were in the order of saltwater > brackish water > freshwater.

There was no statistical difference in marina and LRS TSS concentrations for saltwater marina areas (fully-nested balanced ANOVA, $F_{14,56} = 0.9$, $p = 0.601$, Coyote Point Marina omitted) (Figure 24). However, there was a statistical difference in marina and LRS TSS concentrations for brackish water marina areas (fully-nested balanced ANOVA, $F_{4,16} = 17.2$, $p < 0.0005$) and for freshwater marina areas (fully-nested balanced ANOVA, $F_{3,12} = 17.0$, $p < 0.0005$, Tahoe Keys Marina omitted). TSS concentrations in brackish and freshwater marinas were lower than TSS concentrations in their respective LRSs.

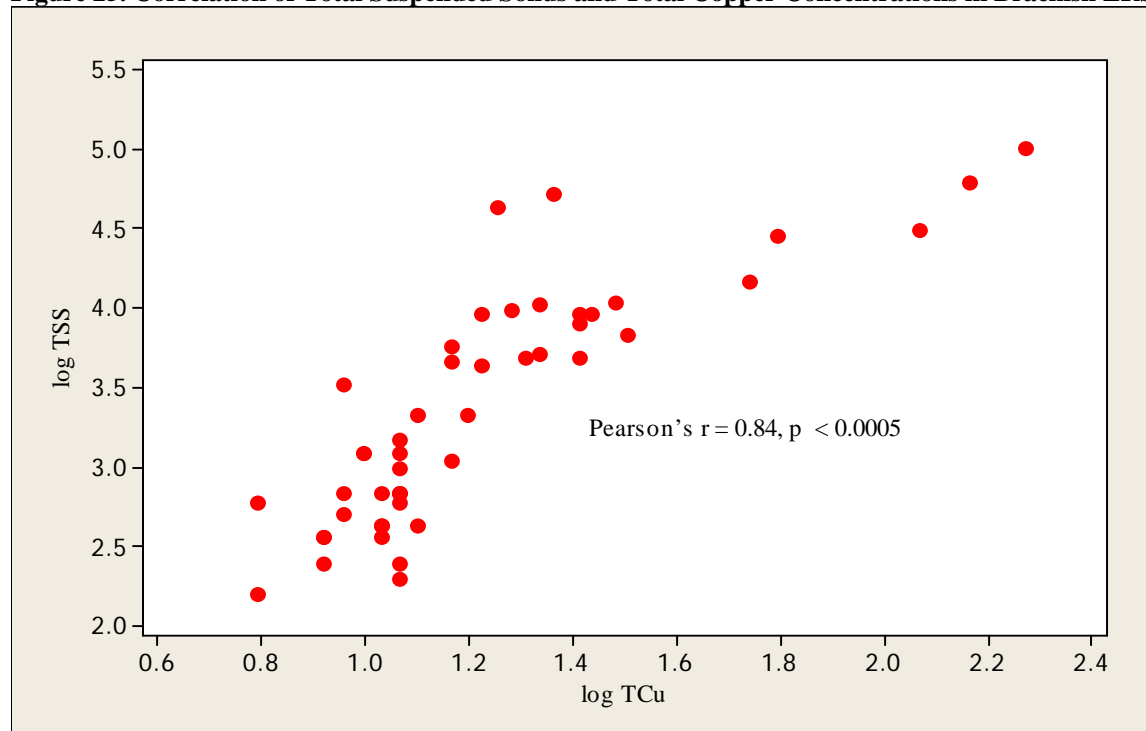
Correlations of Total Suspended Solids and Dissolved Organic Carbon with Metals

A correlation analysis was conducted on the TSS, DOC, and metals data to determine the presence of linear relationships among the variables. All pair-wise Pearson correlation coefficients and the non-parametric Spearman's rank-correlation coefficients were computed for the log-transformed dataset.

Across all data (all water types combined), there were no significant correlations between TSS and any of the three metal analytes (i.e., DCu, TCu, and DZn). Furthermore, no significant correlations were observed when the data were evaluated separately as marina and LRS datasets.

Within brackish marina areas, a few significant but weak relationships were observed. For example, there was a modest linear correlation between TSS and TCu in brackish water marina areas (marina sites + LRSs) (Pearson's $r = 0.56$, $p < 0.0005$) (Figure 25). A weak positive linear association of TSS-TCu also exists in brackish marinas (Pearson's $r = 0.51$, $p < 0.0005$). However, the most notable of the TSS-TCu correlations is the strong positive linear association in brackish LRSs (Pearson's $r = 0.84$, $p < 0.0005$) (Figure 25).

Figure 25. Correlation of Total Suspended Solids and Total Copper Concentrations in Brackish LRSs



It is possible that the observed positive relationship between TSS and TCu for brackish water LRSs is reflective of the tendency of metals in solution to bind to suspended solids in the water column. Thus, water with high amounts of suspended solids will tend to also have high amounts of metals associated with them. Recall that TSS at the Vallejo and Benicia LRSs (brackish water sites) exhibited TSS loads that were much higher than any other sites in this study (median TSS concentrations > 50 mg/L).

TSS can also serve to bind DCu and convert it to particulate copper (Morris, 1986; Ackroyd et al., 1986). The more TSS there are in a sample, a higher capacity generally exists to lower the DCu concentration in that sample. This binding effect may potentially explain the negative linear relationships that are observed for TSS and DCu (Pearson's $r = -0.78$, $p < 0.0005$) (Figure 26) and for TSS and DZn (Pearson's $r = -0.64$, $p < 0.0005$) (Figure 27) at the Benicia and Vallejo marina areas. Thus, at least for brackish waters, the magnitude of DCu may be significantly influenced by the amount of particulate matter that exists in these waters at any given time. By converting dissolved metals to particulate metals, suspended solids in natural water systems are moderating bioavailability of copper and other metals to aquatic organisms. Note that any significant decreases in TSS concentrations in these brackish marinas could result in a lower level of DCu conversion potentially leading to higher concentrations of observed DCu.

No significant correlations between TSS and metals were observed for saltwater samples. Correlation of freshwater TSS and metals data was not conducted since more than 50% of the freshwater TSS data were below detection limits (<4 mg/L).

Figure 26. Correlation of Total Suspended Solids vs. Dissolved Copper Concentrations at Benicia and Vallejo Marina Areas

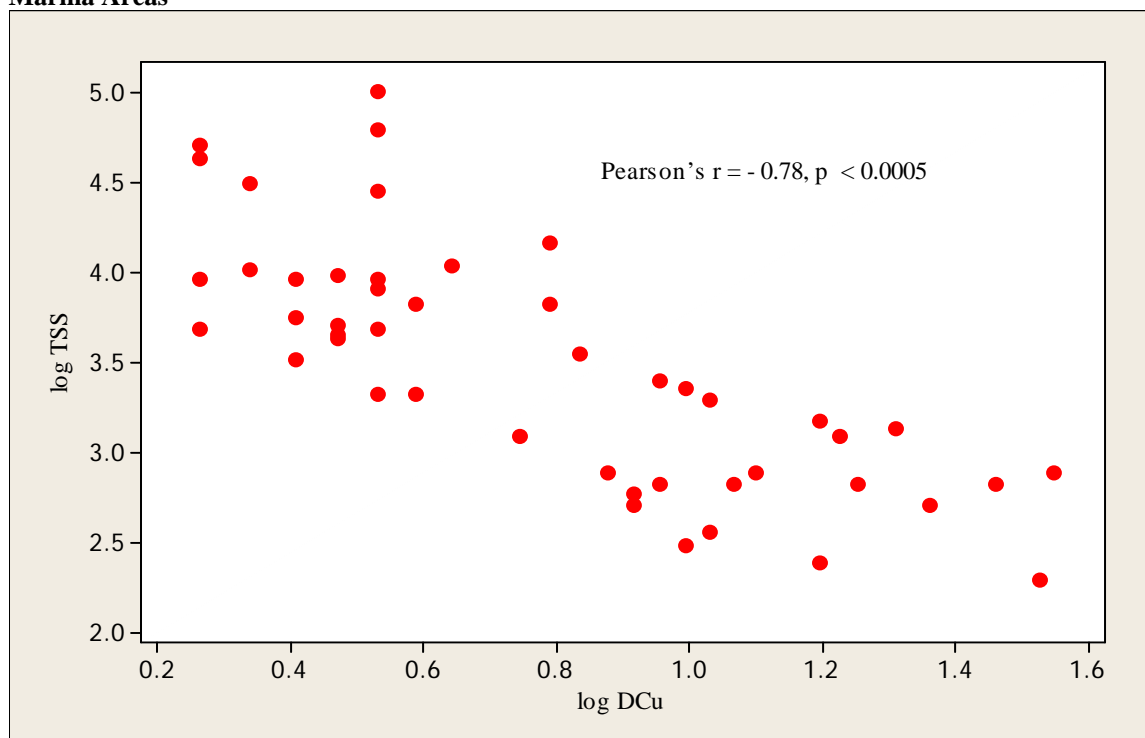
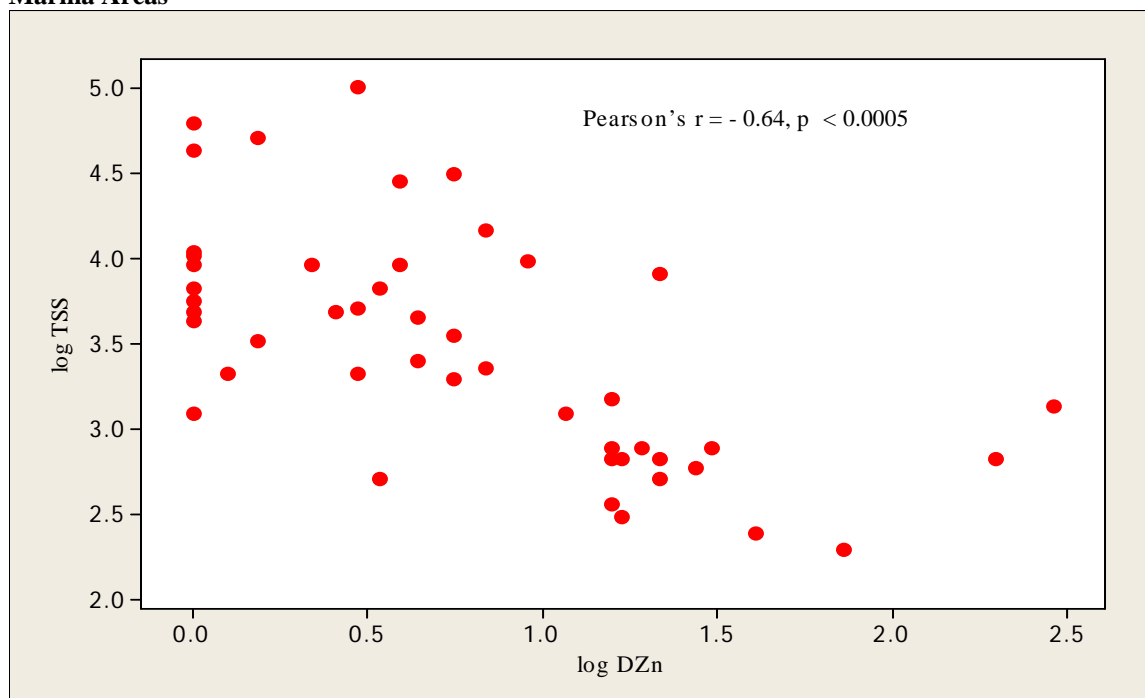


Figure 27. Correlation of Total Suspended Solids vs. Dissolved Zinc Concentrations at Benicia and Vallejo Marina Areas



Similar to the case of TSS, across all data (all water types combined), there were no significant correlations between DOC and any of the three metal analytes (i.e., DCu, TCu, and DZn). Furthermore, no significant correlations were observed when the data were evaluated separately as a marina dataset. However, there were weak positive correlations between DOC and DCu (Pearson's $r = 0.50$, $p < 0.0005$) and also TCu (Pearson's $r = 0.64$, $p < 0.0005$) for the LRS data.

By water type, a weak correlation was also observed between DOC and DCu in saltwater LRSs (Pearson's $r = 0.48$, $p < 0.0005$). Buck et al. (2007) and Kuwabara et al. (1989) both found positive correlations of DOC to DCu concentrations in the ambient waters of San Francisco Bay. This association is supported by the finding that in ambient water, the majority of DCu exists as a complex with dissolved organic matter (Buck and Bruland, 2005; Hurst and Bruland, 2005). This relationship between DOC and DCu is not likely to exist in many saltwater marinas since significant input of copper by marina sources greatly disturbs this equilibrium that supposed to exist in ambient water areas. Moreover, since DCu concentrations at LRSs could potentially be impacted by copper that is generated from the marinas, the DOC-DCu relationship could be weakened.

No correlations were observed between DOC and metals for brackish or freshwater.

Irgarol and M1

Water samples for Irgarol and M1 analysis were taken in the first (July to August) and third (September to November) sampling rounds. Forty five out of the anticipated 48 water samples for these analyses were collected from 11 marinas. Thirty-three samples were from eight saltwater marinas and 12 samples were from three brackish water marinas. Complete Irgarol and M1 results are presented in Appendix G.

Irgarol and M1 were detected in all 45 samples (limit of quantification [LOQ] of 0.1 ng/L or parts per trillion for both analytes). Irgarol detections ranged from 12 to 712 ng/L. The highest sample concentration of Irgarol was documented at Loch Lomond Marina in San Rafael. M1 detections ranged from 1.6 to 217.1 ng/L. The highest sample concentration of M1 was also documented at Loch Lomond Marina. M1 concentrations were always lower than Irgarol in the same sample.

Marina median concentrations were calculated for Irgarol for both sampling rounds (Figure 28). For the first round, marina median concentrations were highest at Loch Lomond Marina (539.0 ng/L), followed by MdR back basin #3/4 (277.6 ng/L), and Berkeley Marina (197.6 ng/L). The lowest marina median concentration was at Benicia Marina (30.0 ng/L). For the third round, Irgarol concentrations were noticeably lower. Median concentrations were highest at Loch Lomond Marina (148.1 ng/L), followed by Marina Bay Yacht Harbor (111.9 ng/L), and Ballena Isle Marina (98.9 ng/L). The lowest marina median concentration was at Alamitos Bay Marina (21.1 ng/L).

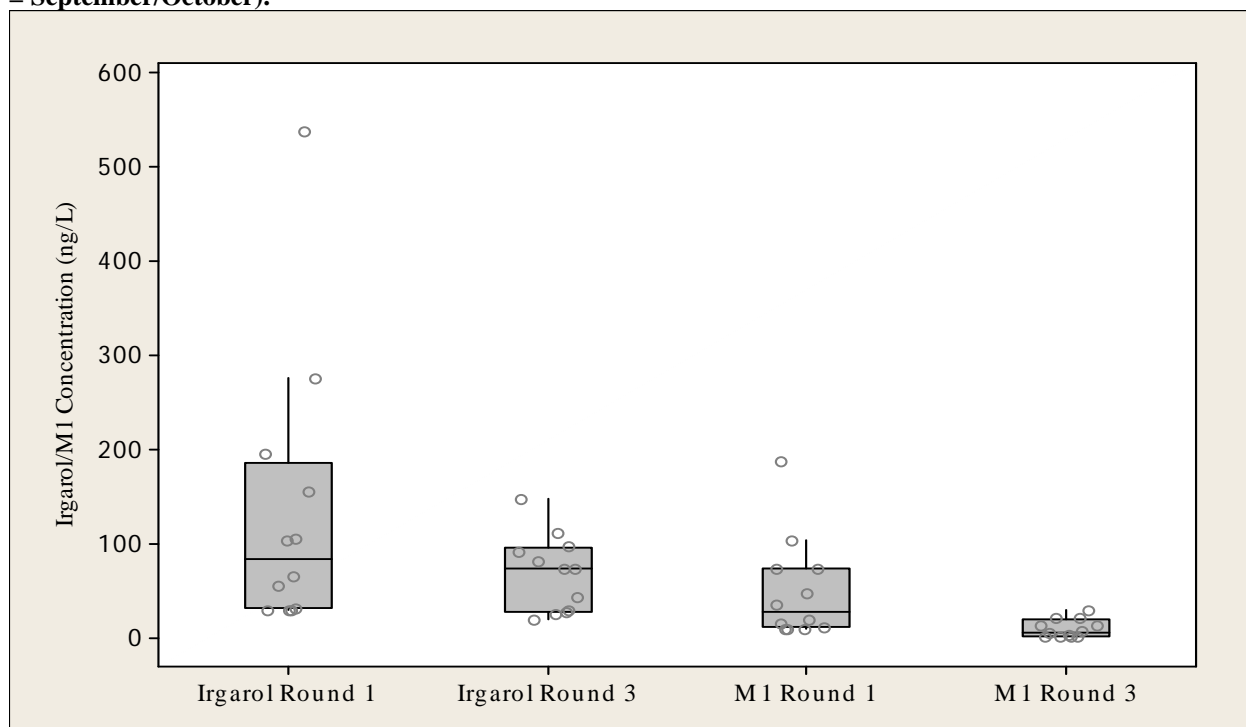
Marina median concentrations were also calculated for M1 (Figure 28). For the first round, marina median concentrations were highest at Loch Lomond Marina (189.0 ng/L), followed by MdR back basin #3/4 (104.2 ng/L), and Berkeley Marina (75.6 ng/L). For the third round, M1 concentrations (like Irgarol concentrations) were noticeably lower. Median concentrations were highest at Loch Lomond (148.1 ng/L), followed by MdR back basin #1/2 (22.0 ng/L), and MdR back basin #3/4 (22.0 ng/L).

The overall median Irgarol and M1 concentrations for all marina sites were 66.1 and 15.1 ng/L, respectively (Table 9). Median Irgarol concentrations for the first and third sampling rounds were 80.5 and 53.2 ng/L, respectively.

Table 9. Summary of Median Irgarol and M1 Concentrations (ng/L) in Water Samples (Shown with back-transformed lower and upper 95% Confidence Intervals)

Analyte	Overall Median Concentration w/ 95% CI	1st Round (July/August) Median Concentration w/ 95% CI	3rd Round (September/October) Median Concentration w/ 95% CI
Irgarol	50.1 - 66.1 - 87.1	51.9 - 80.5 - 124.8	38.9 - 53.2 - 74.8
M1	10.3 - 15.1 - 22.0	20.2 - 31.0 - 47.8	4.3 - 6.8 - 10.9

Figure 28. Marina Median Irgarol and M1 Water Concentrations by Rounds (Round 1 = July/August, Round 3 = September/October).



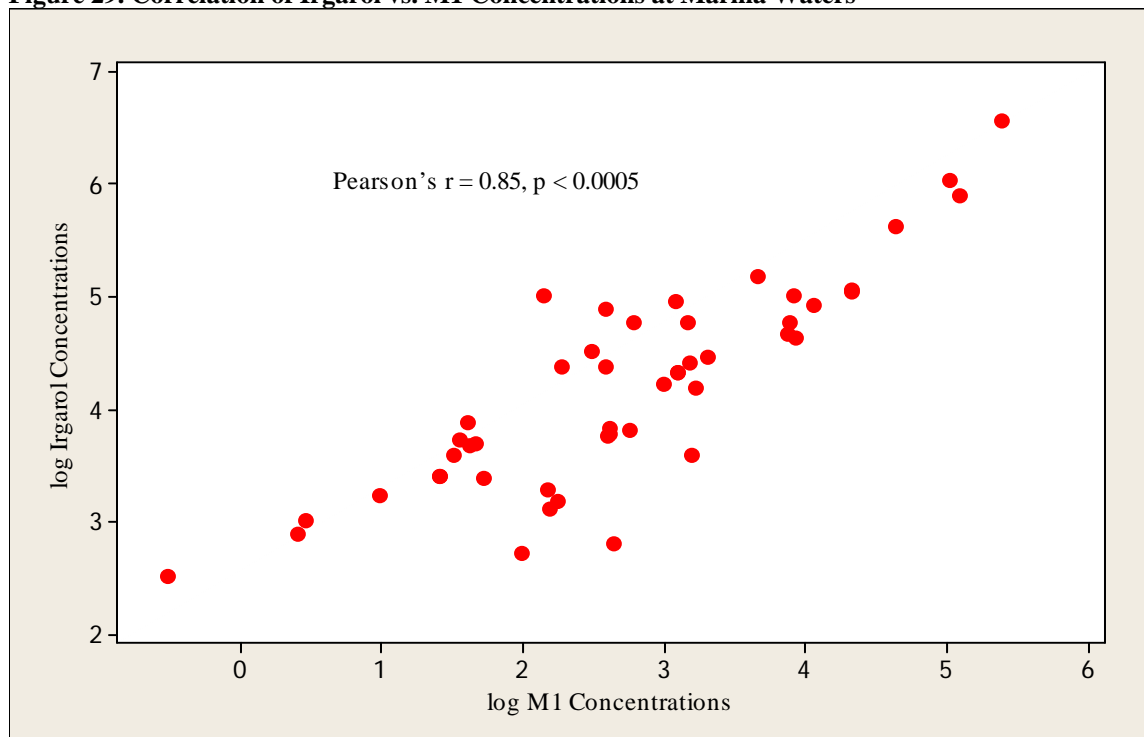
At almost all of the sampling sites, Irgarol and M1 concentrations were higher in the first round as compared to the third round. Paired t-tests on log-transformed Irgarol and M1 results yielded statistically significant differences between the first and third round of sampling for both Irgarol concentrations ($t_{11} = 2.4$, $p = 0.036$) and M1 ($t_{11} = 13.1$, $p < 0.0005$) concentrations.

ANOVA tests of results also showed that there was a statistically significant difference among marinas (fully-nested balanced ANOVA, $F_{11,23} = 5.0$, $p = 0.005$, with MdR grouped into 2 marinas). That is, Irgarol concentrations varied considerably among the marinas tested. Results for M1 did not show any statistically significant difference among marinas (fully-nested balanced ANOVA, $F_{11,23} = 1.7$, $p = 0.181$, with MdR being categorized as 2 marinas).

There was a significant log-log correlation between Irgarol and M1 concentrations (Pearson's $r = 0.85$, $p < 0.0005$) (Figure 29). This result is expected because M1 is the primary degradate of Irgarol. Assuming that there are no other appreciable sources of M1, the amount of M1 that is generated is dependent on the amount of Irgarol that is present and on environmental factors.

For the saltwater sites, the median concentrations for Irgarol and M1 were 83.7 and 20.1 ng/L, respectively. For brackish water sites (Benicia, Vallejo, and Pittsburg marinas), the median concentrations for Irgarol and M1 were 33.2 and 6.8 ng/L, respectively. Based on the results of two-sample t-tests of log-transformed concentration data, saltwater marinas exhibited higher concentrations of both Irgarol ($t_{22} = 2.7$, $p = 0.013$) and M1 ($t_{22} = 2.2$, $p = 0.037$) as compared to brackish water marinas.

Figure 29. Correlation of Irgarol vs. M1 Concentrations at Marina Waters



Total Copper - Sediment

Twenty three of the anticipated 180 sediment samples were analyzed for TCu (Appendix H). Sediment collection was limited to three freshwater marinas: Folsom Lake, Sacramento Marina, and Village West Marina. No sediment was collected from the remaining 20 marina sites due to logistical and safety issues.

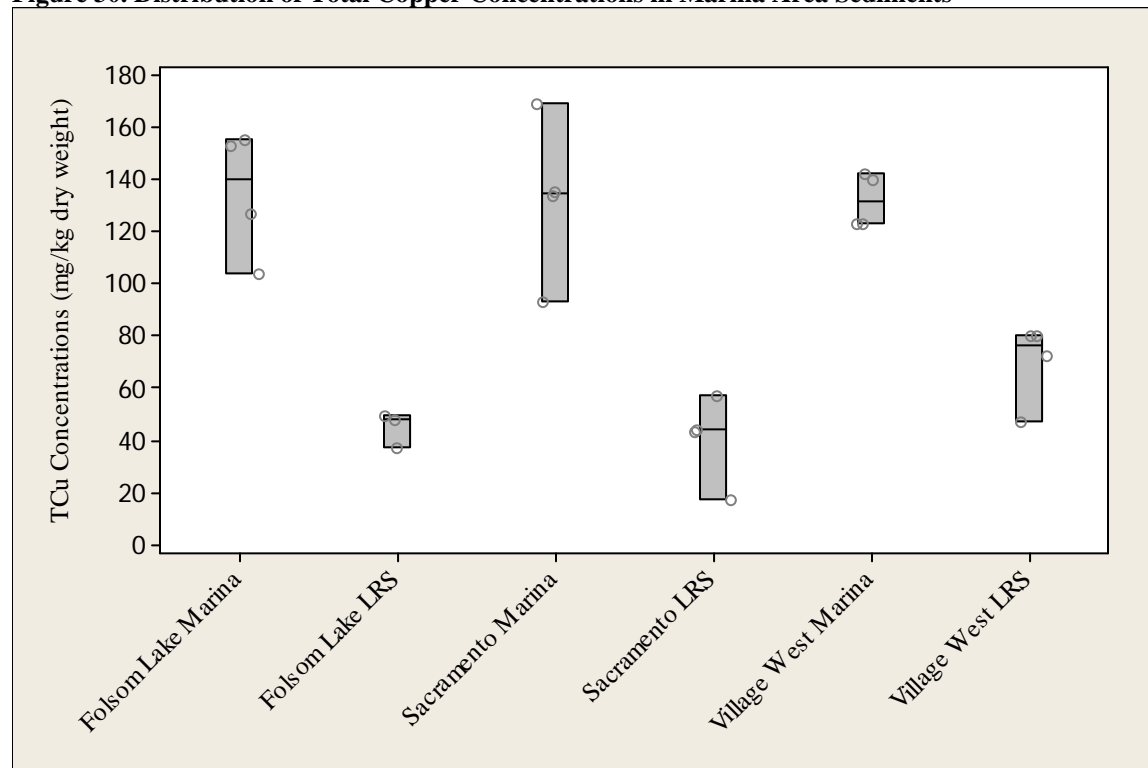
At the three sites, DPR's field crew used a sampling vessel owned by the Central Valley Regional Water Quality Control Board (CVRWQCB) with the assistance of its staff. This particular vessel was equipped with a manually-operated winch, which allowed field crew to collect sediment samples. Instead of canceling the entire sediment collection, DPR chose to collect as many samples as possible using this vessel.

Sediment TCu concentrations were log-normally distributed, and ranged from 17 to 167 mg/kg. Note that TCu in sediment refers to the concentration of total copper in the sediment and not in the interstitial or pore water in the sediment. The highest TCu concentration was documented at Sacramento Marina and the lowest was documented at an LRS of that marina. For the three marinas where sediment samples were collected, median TCu concentrations in sediment were 131.5 mg/kg for the three freshwater marina sites and 48.5 mg/kg for their associated LRSs (Table 10).

Paired t-tests were used to test the equivalence of marina and LRS sediment TCu concentrations for each marina. There were significant differences in TCu concentrations between marina sites and LRSs for all three marina areas: Folsom Marina/LRS ($t_5 = 8.18$, $p < 0.0005$), Sacramento Marina/LRS ($t_6 = 4.31$, $p = 0.005$), and Village West Marina/LRS ($t_6 = 4.96$, $p = 0.003$). In all cases, TCu concentrations in marina sediment were higher inside the marina than in the adjacent LRSs (Figure 30).

Table 10. Summary of Median Metal Concentrations (mg/kg dry weight) in Sediment Samples

	Median TCu Concentrations w/ 95% CI		Median TZn Concentrations w/ 95% CI	
	Marina Sites	LRSs	Marina Sites	LRSs
3 Freshwater Marina Areas	118.2 - 131.5 - 146.3	36.2 - 48.5 - 64.8	151.3 - 182.5 - 220.2	49.2 - 78.3 - 124.7

Figure 30. Distribution of Total Copper Concentrations in Marina Area Sediments

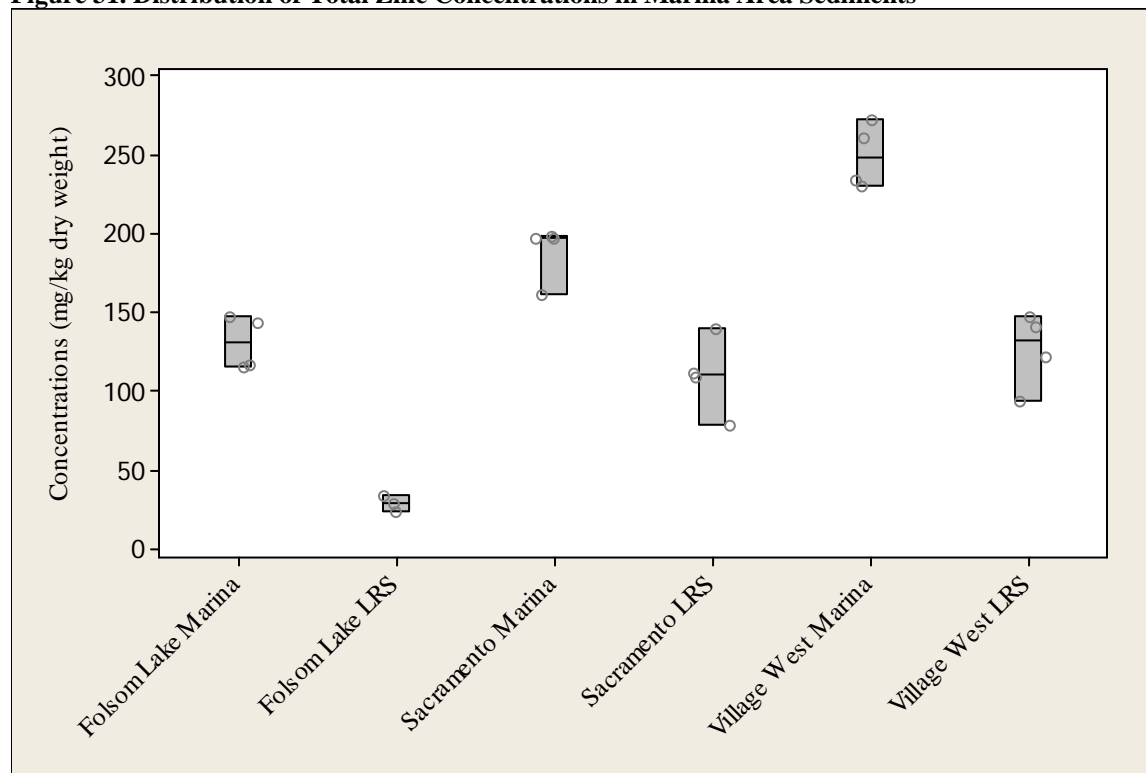
Total Zinc - Sediment

Twenty three of the anticipated 180 sediment samples were collected and analyzed for TZn (Appendix H).

TZn concentrations ranged from 23 to 273 mg/kg. The highest concentrations were documented at Village West Marina and the lowest at an LRS adjacent to the Folsom Lake Marina. For the three marinas where sediment was collected, median TZn concentrations in sediment were 182.5 mg/kg for the marina sites and 78.3 mg/kg for the associated LRSs (Table 10).

Paired t-tests were used to test the equivalence of marina and LRS sediment TZn concentrations for each marina. There were significant TZn concentration differences between marina and LRS for all three marina areas—Folsom Marina/LRS ($t_5 = 12.56$, $p < 0.0005$), Sacramento Marina/LRS ($t_6 = 4.28$, $p = 0.005$), and Village West Marina/LRS ($t_6 = 6.28$, $p = 0.001$). In all cases, TZn concentrations in marina sediment were higher inside the marina than in the adjacent LRSs (Figure 31).

Figure 31. Distribution of Total Zinc Concentrations in Marina Area Sediments



Toxicity

All of the anticipated 48 toxicity samples were collected for toxicity tests on mussel embryo development. One water sample (from Pittsburg Marina) was, however, excluded from testing because it was not saline enough to meet minimum test requirements.

Eight of 47 samples (17%) exhibited statistically significant toxicity (Table 11). Seven of the eight toxic samples came from Marina del Rey (MdR) in Los Angeles. The remaining toxic sample originated from Marina Bay Yacht Harbor (MBYH) in Richmond. The complete toxicity test results are available in Appendix G while the toxicity data report from SCCWRP is in Appendix I.

Table 11. Water Samples with Statistically Significant Toxic Endpoints

Sample Number	Location	Concentration of DCu in associated metal sample (µg/L)	Percent Normal-Alive			
			Sample Mean	Percent of Control	Standard Deviation	Number of Replicates
111	MBYH #1	1.7	72	88	5.1	4
118	MdR FB #2	12.5	55	64	11.1	4
119	MdR BB #3	12.4	61	72	6.9	4
120	MdR FB #1	13.1	67	79	11.8	4
121	MdR BB #2	18.4	4	4	1.9	4
123	MdR BB #4	14.2	66	78	10.8	4
178	MdR BB #1	11.5	37	44	7.6	4
179	MdR FB #4	11.9	49	57	7.1	4

Toxicant Identification Evaluation (TIE)

Two samples (sample numbers 121 and 179) were tested using Phase I TIE procedures (Appendix I). Both of the selected samples were subjected to treatments designed to selectively remove or neutralize classes of compounds (Table 12). Treated samples were then retested to determine whether changes in toxicity occurred as a result of the treatments. A control sample, using laboratory seawater, was included with each type of treatment to verify that the manipulation itself was not causing toxicity. Samples for each TIE manipulation were tested at 100% sample strength.

Each sample was subjected to four treatments:

- Ethylenediaminetetraacetic acid (EDTA) addition, which chelates metals and reduces the toxicity caused by them.
- Sodium thiosulfate (STS) addition, which reduces oxidants and decreases the toxicity of some metals, including copper.
- Centrifugation, which removes particles and reduces the toxicity associated with suspended solids.
- C-18 column extraction, which removes non-polar organic compounds and reduces the toxicity caused by them.

Table 12. Toxicant Identification Evaluation Treatment Results

Sample Number	Treatment	Percent Normal-Alive			
		Sample Mean	Percent of Control	Standard Deviation	Number of Replicates
121	Baseline*	1	1	1.1	4
121	EDTA	91	93	6.8	3
121	STS	55	57	1.3	3
121	Centrifuge	6	6	1.5	3
121	C-18 Column	80	82	3.6	3
179	Baseline*	14	14	4.1	4
179	EDTA	92	92	10.4	3
179	STS	82	83	1.7	3
179	Centrifuge	37	38	8.3	3
179	C-18 Column	62	63	54.0	3

* Results are different from the analogous sample in the previous table since baseline toxicity tests were redone for the TIEs.

A decrease in sample toxicity after the EDTA and STS treatments suggested that a cationic metal was responsible for the majority of the toxicity. Ideally, if metals were the primary cause of the toxicity, the C-18 column treatment would have had little effect on the observed toxicity of the baseline samples; however, the intermediate toxicity reduction that was observed in the C-18 results suggested that non-polar organics were causing some of the toxicity. Follow up discussions with SCCWRP personnel revealed that the C-18 columns used by SCCWRP have been documented to also remove a small amount of trace metals along with the non-polar organics. The sequestration of metals by C-18 columns has been noted in a recent SCCWRP study (Schiff et al., 2007). In that study, the columns were estimated to have removed 45% of the copper out of the sample solution. This level of copper removal could account for the intermediate reduction of toxicity that was observed for the two C-18 TIE samples.

Overall, based on results of the TIEs and the complications with the C-18 columns, it is likely that cationic metals are the cause of the toxicity. Copper concentrations in these samples were high enough to exceed the toxicity test's range of effects (i.e., EC₅₀'s). Zinc concentrations were below its range of effects. Therefore, we believe that copper is the most likely cause of toxicity in the two TIE samples from MdR.

Comparisons to Water Quality Standards

Two water quality indicators of AFP pollution (copper and zinc) were compared to available water quality standards. There are no applicable water quality standards for Irgarol or M1, however, there are established standards for copper and zinc. The most relevant water quality standards for copper and zinc in the State of California are specified in the CTR (U.S. EPA, 2000). The CTR contains two standards—the criterion maximum concentration (CMC), which is the acute standard defined as the highest concentration of a pollutant to which aquatic life can be exposed for a short period of time without deleterious effects, and the criterion continuous concentration (CCC), which is the chronic

standard defined as the highest concentration of a pollutant to which aquatic life can be exposed for an extended period of time without deleterious effects. For both copper and zinc, the CMC and CCC are defined as a 1-hour average and a 4-day average, respectively.

Considering the specific way the CTR defines compliance assessment for copper and zinc standards and the way the samples in this study were taken, a direct comparison of this study's analytical results to numeric standards may not be the most fitting approach from a compliance standpoint. However, since the goal of this study is water quality assessment and not regulatory compliance, such a comparison is still informative in determining the relative level of metal pollution at a number of sites across California.

CTR Freshwater CMC and CCC Water Quality Standards - Copper

Freshwater DCu results were compared to the CTR's hardness-based CMC and CCC standards to determine if there were any exceedances (Appendix J). CMC and CCC equations and conversion factors that are established in the CTR were used to calculate the site-specific copper water quality standards (U.S. EPA, 2000) used for the comparison.

Note that U.S. EPA defines freshwater as water that contains salinity at 1 part per thousand and below at locations where this occurs 95% or more of the time. In brackish water areas that are between 1 and 10 parts per thousand in salinity, the freshwater criteria could still apply if they are more stringent than the saltwater criteria. Based on these definitions, freshwater CCC and CMC were calculated for the following six marinas: Tahoe Keys, Folsom Lake, Sacramento, Village West, Antioch, and Pittsburg. Benicia and Vallejo marinas are likely to experience salinity that is higher than 10 parts per thousand for most of the year and were thus left out of this determination.

None of the DCu concentrations in the 135 freshwater samples collected from six different marina areas exceeded the acute or chronic CTR standards for copper.

CTR Freshwater CMC and CCC Water Quality Standards - Zinc

Freshwater DZn results were compared to the CTR's hardness-based CMC and CCC zinc standards to determine if there were any exceedances (Appendix K). CMC and CCC equations and conversion factors that are established in the CTR were used to calculate the site-specific zinc water quality standards (U.S. EPA, 2000) used for the comparison. The same salinity considerations as those presented in the previous section for DCu apply here.

None of the DZn concentrations in the 135 freshwater samples collected from six different marina areas exceeded the acute or chronic CTR standards for zinc.

CTR Saltwater CMC and CCC Water Quality Standards - Copper

Salt and brackish water DCu results were compared to the CTR's fixed saltwater CMC and CCC standards to determine if there were any exceedances. The CTR states that the saltwater criteria apply at salinities of 10 parts per thousand and above at locations where this occur 95% or more of the time. Moreover, the saltwater criteria could also apply at salinities between 1 and 10 parts per thousand if these criteria are more stringent than the freshwater criteria. Therefore, our evaluation of exceedances of the saltwater standards includes the salt and brackish water marinas as classified by this study (see Table 1). Thus, Tahoe Keys Marina, Folsom Marina, Sacramento Marina, and Village West Marina were excluded from consideration against saltwater standards.

For salt and brackish waters, the CTR standards for copper are fixed. The copper CMC is 4.8 µg/L and represents a short-term (1-hour) average that is not to be exceeded more than once every three years on the average. The copper CCC is 3.1 µg/L and represents a 4-day average that is not to be exceeded more than once every three years on the average.

In salt and brackish water areas, DCu concentrations in 16 of 19 marinas exceeded the CCC. The marina areas where DCu concentrations did not exceed the chronic standard (and thus not the acute standard either) were Antioch, South Beach Harbor, and Coyote Point. DCu concentrations in 10 of the 16 marinas that exceeded the CCC also exceeded the CMC. These 10 marinas were Loch Lomond Marina, Clipper Yacht Harbor, Berkeley Marina, Ballena Isle

Marina, Santa Cruz Harbor, Monterey Harbor, Santa Barbara Harbor, MdR front basins, MdR back basins, and Downtown Shoreline Marina.

Of the 388 samples taken from the 19 salt and brackish water marina areas, 118 or 30% exceeded the CCC. Of these 118 samples, 67 had high enough DCu concentrations to also exceed the CMC. Overall, this number is equivalent to about 17% of all salt and brackish water samples from this study that exceeded the CMC. Focusing specifically on marina samples, 114 of 224 (51%) samples from salt and brackish water marinas exceeded the CCC. Furthermore, 67 of 224 (30%) of samples from salt and brackish water marinas exceeded the CMC.

Marina samples taken from MdR had the greatest frequency of CCC and CMC exceedances by far among all the marinas. In fact, all of the marina samples (12 of 12 samples) from MdR's Front and Back Basins were well above the CMC. Four marinas exhibited DCu concentrations that were above the CMC in more than half of the samples taken at that particular marina. These marinas were Loch Lomond Marina (8 of 12 samples), Monterey Harbor (8 of 12 samples), Santa Barbara Harbor (9 of 12 samples), and Downtown Shoreline Marina (10 of 12 samples).

Only 4 of the 118 samples that had DCu concentrations above the CCC were LRS samples. DCu concentrations in these samples ranged between 3.4 and 3.8 µg/L. Moreover, three of these four samples came from MdR's LRS #1, which after a thorough evaluation of metals data, appeared to resemble a marina site rather than an LRS. Of the four LRSs at MdR, this LRS is the closest to the MdR marina sites. TCu, DCu, and DZn concentrations from MdR LRS #1 tended to be at an intermediate level between MdR's eight basin sites and the three LRSs farthest away from the marina area. Metal concentrations from MdR's LRS #2–4 were typically very low. The remaining LRS sample that exceeded the CCC was a sample taken from Ballena Isle Marina's LRS #7.

Note that site specific objectives (SSOs) that are higher than the CTR are awaiting approval by U.S. EPA (R. Looker, personal communication, 2008). The CCC, as proposed in the SSOs, is 6.0 µg/L and the CMC is 9.4 µg/L. Once these SSOs are adopted, they will supercede the CTR criteria as the enforceable water quality standards for much of San Francisco Bay, where many of the marinas in this study is located. This means that DCu concentrations in these marinas will be in compliance with water quality standards more frequently. The establishment of SSOs will make this section's comparison of DCu results with water quality standards somewhat obsolete. An updated comparison with the new SSOs will undoubtedly result in a lower frequency of exceedances.

CTR Saltwater CMC and CCC Water Quality Standards - Zinc

Salt and brackish water DZn results were compared to the CTR's fixed saltwater CMC and CCC standards to determine if there were any exceedances. For salt and brackish waters, the CTR standards for zinc are also fixed values. The zinc CMC is 90 µg/L and represents a short-term (1-hour) average that is not to be exceeded more than once every three years on the average. The zinc CCC is 81 µg/L and represents a 4-day average that is not to be exceeded more than once every three years on the average.

CTR saltwater CCC and CMC for zinc were never exceeded in any of the 388 samples taken from the 19 salt and brackish water marinas. Even though DZn concentrations at MdR marina sites were some of the highest DZn concentrations observed in this study, the highest DZn concentration documented there (66.6 µg/L), did not even exceed the CCC.

Comparisons to Toxicity Benchmark Values

In certain cases, water quality standards do not exist for comparison with measured concentrations. For example, there are currently no numeric standards for metals in sediment and there are no standards for Irgarol and M1. Therefore, non-regulatory toxicity thresholds or benchmarks are used instead to provide reference points to help determine the potential impacts of measured concentrations.

Comparison of Sediment Concentrations to NOAA's Biological-Effects Guidelines - Copper

Since no numeric sediment quality standards currently exists for metals, sediment TCu concentrations were compared to NOAA's Effects Range Low (ERL) and Effects Range Medium (ERM) concentrations (Long and Morgan, 1991;

Long et al., 1995). ERLs and ERMs are screening level tools developed by NOAA to assess the potential impacts of sediment pollutants. The ERL value represents the 10th percentile of ranked data for which there was an observed effect for a sediment pollutant. The ERM value represents the 50th percentile of the same ranked dataset. Concentrations below the ERL are not expected to be toxic to sediment-dwelling organisms. Toxic effects may occasionally occur when measured concentrations are between the ERL and ERM thresholds. The likelihood of toxic effects increases significantly if a pollutant concentration regularly exceeds the ERM.

For copper, the ERL is 34 mg/kg dry weight and the ERM is 270 mg/kg dry weight. Of the 23 sediment samples taken, TCu concentrations in 22 of the samples exceeded the copper ERL. Even though TCu concentrations from inside the marinas are generally higher than TCu concentrations from the LRSs, the LRS concentrations were high enough to also exceed the copper ERL. The only sample that did not exceed this threshold was from an LRS associated with the Sacramento Marina. None of the sediment samples collected exceeded the ERM. Past placements of sediment pollutant data on the SWRCB's CWA 303d impaired water bodies list have been primarily based on ERM exceedances.

Although no sediment data were generated in this study for salt and brackish water marinas, California's RWQCBs conducted sediment quality assessments in the 1990's, as part of their California Bay Protection Toxic Clean Up Programs. A number of marinas along California's Central and South Coast (including some that are included in this study) did show sediment concentrations that were above the NOAA ERM values (Singhasemanon, 2005).

Comparison of Sediment Concentrations to NOAA's Biological Effects Guidelines - Zinc

NOAA's ERL and ERM values for zinc are 150 and 410 mg/kg dry weight, respectively. Of the 23 samples taken, TZn concentrations in eight of the samples exceeded the zinc ERL. Interestingly, all eight samples were taken from marina sites (specifically, from Sacramento Marina and Village West Marina). None of the samples taken from Folsom Lake Marina exceeded the ERL. None of the samples exceeded the ERM.

Comparison of Irgarol Concentrations to Toxicological Endpoints and Aquatic Toxicity Benchmarks

A variety of toxicological endpoints (e.g., EC₅₀s and LC₅₀s) and aquatic toxicity benchmarks are available in the scientific literature for comparison with measured Irgarol concentrations. As an *s*-triazine herbicide, Irgarol tends to be much more toxic to the aquatic flora than to the aquatic fauna. Thus, the toxicity referred to in this sub-section focuses specifically on sub-lethal effects on aquatic plants and algae.

Since Irgarol acts as an inhibitor of photosynthesis, growth inhibition of phytoplankton appears to be one of the most commonly-observed effects of Irgarol. For the green algae *Navicula pelliculosa*, an EC₅₀ of 136 ng/L for growth inhibition has been documented for Irgarol (Hughes and Alexander, 1993). DeLorenzo and Serrano (2006) documented similar growth-rate inhibition for the marine phytoplankton species *Dunaliella tertiolecta* at an EC₅₀ of 270 ng/L. Devilla et al. (2005) determined the EC₅₀ for growth inhibition of Irgarol to be 160 and 250 ng/L for the phytoplankton-*Synechococcus* sp. and *Emilinia huxleyi*, respectively. Dahl and Blanck (1996) documented a lowest observed effects concentration (LOEC) of 63 ng/L for reduced photosynthetic activity in marine periphyton communities. They also noted an LOEC of about 250 ng/L where a change in community structure was seen and an LOEC of about 1,000 ng/L where a reduction in biomass was observed.

Irgarol concentrations at many of the marinas in this study are high enough to exceed some of the toxicological values cited here. These marinas were Pittsburg Marina, MBYH, Loch Lomond Marina, Berkeley Marina, South Beach Harbor, MdR front and back basins, and Downtown Shoreline Marina. In contrast, Irgarol concentrations at Vallejo Marina, Benicia Marina, San Francisco Marina, and Alamitos Bay Marina were all below the lowest of these toxicological values (63 ng/L).

Hall et al. (1999) derived an aquatic-plant toxicity benchmark value of 136 ng/L for Irgarol in a ecological risk assessment (ERA) for European waters. In our study, Irgarol concentrations in 11 of the 45 samples (24%) collected for Irgarol analysis exceeded this plant toxicity benchmark.

Hall and Gardinali (2004) conducted a similar ERA for U.S. waters (Chesapeake Bay and Southeastern Florida). In this study, the authors used a larger aquatic plant toxicity dataset (16 toxicological values) and also included

toxicological data, which contained mortality as endpoints. The Irgarol benchmark value that was derived (251 ng/L) was higher than the Hall et al. (1999) benchmark of 136 ng/L. Four of the 45 samples (9%) collected for Irgarol analysis in our study contained concentrations that were above 251 ng/L. Two of these four samples were collected from Loch Lomond Marina. The remaining samples with Irgarol concentrations above 251 ng/L were collected from Berkeley Marina and Mdr's back basins.

In 2007, Hall et al. (2007) generated another benchmark value of 193 ng/L. Comparison of this benchmark yielded the same results as the comparison with the 251 ng/L benchmark value from Hall and Gardinali (2004).

Another aquatic toxicity benchmark known as the Environmental Risk Limit (ERL) is being utilized in the Netherlands. This ERL is also based on a plant toxicity dataset and is set at dataset's 5th percentile value (protective of 95% of all aquatic plant species). Van Wezel and van Vlaardingen (2004) calculated an ERL for Irgarol in water to be 24 ng/L. Forty out of 45 samples from our study (89%) contained Irgarol concentrations above the Dutch ERL for Irgarol.

Comparison of M1 Concentrations to Toxicological Endpoints

M1 is much less toxic to aquatic plants and animals than its parent Irgarol. Hall and Gardinali (2004) established a plant aquatic benchmark for M1 at 12,500 ng/L (10th percentile value or protective of 90% of all aquatic plant species) based on 8 toxicological values. None of the M1 results from our study exceeded this threshold. The highest M1 concentration documented in our study was 217 ng/L suggesting very low ecological risk from M1 exposures at these sites.

BLM-Associated Water Quality Data

Water quality data that are primarily used in the subsequent sections' metal bioavailability and toxicity prediction models (the freshwater BLM, DOC Model, and saltwater BLM) can be divided into two categories: laboratory-analyzed constituents and *in-situ* measurements. Unlike the presented results for metals, TSS, toxicity/TIE, and Irgarol/M1, the BLM-associated parameters were not summarized and discussed as a narrative. Instead, these parameters were simply tabulated to show their ranges and median values on a marina-area specific basis.

Laboratory-Analyzed Constituents

Most of the BLM-associated water quality constituents were quantified using laboratory instruments. These constituents included alkalinity, calcium, chloride (salinity), dissolved organic carbon, magnesium, potassium, sodium, and sulfate (complete results are in Appendix G). Results were within expected ranges for the various water types. The marina median and range for each constituent are presented in Table 13 and Table 14, respectively.

In-Situ Measurements

In addition to the eight constituents listed in the previous section, two additional water quality constituents—pH and temperature were needed to run the BLM. These two constituents were directly quantified *in situ* (probe placed directly in the water) using field water quality meters. Data of several water quality constituents that were not necessarily needed for modeling input but were nevertheless collected as general water quality and water type indicators were DO, EC, and turbidity. *In-situ* measurements results are also shown in Appendix G.

Table 13. Marina Median Concentrations of Biotic Ligand Model-Related Constituents (in mg/L)¹

Marina ²			Alkalinity		Calcium		Magnesium		Potassium		Sodium		Chloride		Sulfate	
	M	LRS	M	LRS	M	LRS	M	LRS	M	LRS	M	LRS	M	LRS	M	LRS
Folsom Lake Marina	1.3	1.2	22.4	22.2	4.7	4.7	1.5	1.5	0.6	0.6	1.5	1.8	1.1	1.1	1.5	1.5
Tahoe Keys Marina	0.9	0.6	45.2	43.3	8.9	8.4	2.3	2.2	1.2	1.7	5.8	5.5	1.7	1.7	1.5	1.7
San Francisco Marina	0.9	1.0	109	109	387	397	1197	1236	369	378	9166	9499	17994	18200	2486	2518
Alamitos Bay Marina	0.9	0.9	113	113	433	437	1356	1367	411	413	10489	10595	19670	19718	2683	2701
Coyote Point Marina	1.7	1.6	112	111	364	368	1122	1134	348	350	8494	8544	16696	16739	2356	2359
Antioch Marina	1.9	1.8	62.7	62.1	18.2	15.3	23.9	16.4	7.9	5.2	150	92.3	279	163	44.6	29.3
DOC Pittsburg Marina	1.8	1.7	64.6	65.1	26.4	32.2	47.1	61.8	15.5	20.9	331	437	623	865	97.9	126
South Beach Harbor	0.9	1.0	108	108	380	388	1176	1203	362	370	9085	9255	17406	17863	2395	2463
Clipper Yacht Harbor	1.0	1.1	109	108	386	385	1205	1200	366	367	9392	9444	17565	17520	2404	2413
Marina Bay Yacht Harbor	1.1	0.8	104	105	375	373	1150	1148	356	357	8776	8847	17183	17262	2360	2388
Benicia Marina	2.0	2.0	78.5	81.7	147	181	411	518	135	167	3282	4077	6682	8279	898	1121
Sacramento Marina	1.4	1.0	57.2	58.3	10.6	10.7	5.4	5.5	0.9	0.9	7.0	7.1	3.9	3.7	4.7	4.9
Ballena Isle Marina	1.4	1.4	112	111	365	367	1127	1130	342	345	8949	8743	16708	16591	2263	2252
Village West Marina	3.7	3.6	70.0	71.3	18.2	18.4	8.7	8.8	2.5	2.5	28.9	29.5	32.7	33.1	29.5	29.8
Vallejo Marina	2.2	2.2	87.4	85.1	210	197	600	563	191	180	4725	4443	9379	8904	1269	1207
Berkeley Marina	1.0	1.0	105	106	377	377	1153	1153	356	358	8854	8926	17061	17376	2345	2408
Santa Cruz Harbor	1.0	1.0	118	115	429	433	1338	1350	410	414	10398	10430	19718	19715	2699	2694
Monterey Harbor	1.0	1.0	115	114	437	436	1363	1361	412	410	10382	10392	19707	19782	2690	2693
Santa Barbara Harbor	0.8	0.7	115	113	431	430	1351	1352	407	409	10420	10447	20118	20309	2763	2777
Loch Lomond Marina	1.3	1.3	98.5	98.1	325	327	1001	1011	314	314	7741	7803	14930	14855	2039	2041
Downtown Shoreline Marina	1.0	1.4	113	116	430	415	1341	1284	409	394	10335	9984	19400	18478	2666	2552
Marina del Rey FB	1.0	1.0	117	115	431	430	1359	1358	413	414	10584	10596	19704	19613	2713	2697
Marina del Rey BB	1.1	1.0	117	115	428	430	1347	1358	411	414	10590	10596	19690	19613	2718	2697

¹ Ordered by ascending marina median DCu concentrations. Values > 100 are rounded to the nearest one. Values < 100 are rounded to the nearest tenth.

² Marina names are color coded by water type. **Green** = freshwater, **Yellow** = brackish water, **Blue** = saltwater.

Table 14. Ranges of BLM-Related Constituent Concentrations (in mg/L) for Each Marina Area¹

			Alkalinity		Calcium		Magnesium		Potassium		Sodium		Chloride		Sulfate	
Marina ²	M	LRS	M	LRS	M	LRS	M	LRS	M	LRS	M	LRS	M	LRS	M	LRS
Folsom Lake Marina	0.9 - 1.6	0.9 - 1.6	21 - 26	21 - 24	4.5 - 4.9	4.5 - 4.9	1.4 - 1.6	1.4 - 1.5	0.6 - 0.6	0.6 - 0.6	1.8 - 1.9	1.8 - 1.9	1.1 - 1.1	1.0 - 1.1	1.4 - 1.5	1.4 - 1.5
Tahoe Keys Marina	0.7 - 1.2	0.5 - 0.7	42 - 49	39 - 46	8.9 - 9.0	7.8 - 8.7	2.3 - 2.3	2.0 - 2.3	1.2 - 1.3	1.6 - 1.7	5.6 - 6.0	5.1 - 5.8	1.5 - 1.8	1.7 - 1.8	1.4 - 1.6	1.4 - 1.9
San Francisco Marina	0.6 - 2.1	0.6 - 1.5	107 - 113	107 - 113	337 - 407	387 - 414	1030 - 1250	1210 - 1280	322 - 383	365 - 389	7690 - 9570	9210 - 9830	17614 - 18400	17700 - 18482	2380 - 2663	2270 - 2672
Alamitos Bay Marina	0.8 - 1.1	0.8 - 1.0	110 - 115	110 - 117	425 - 444	429 - 449	1340 - 1390	1350 - 1410	399 - 429	399 - 438	10200 - 10700	10320 - 10800	19284 - 20400	19258 - 20400	2507 - 2810	2589 - 2820
Coyote Point Marina	1.5 - 1.8	1.5 - 1.8	110 - 114	109 - 113	353 - 378	354 - 381	1080 - 1170	1080 - 1180	342 - 362	337 - 363	7680 - 9200	9120 - 9120	15993 - 17400	16062 - 17500	2310 - 2410	2318 - 2420
Antioch Marina	1.6 - 2.3	1.4 - 2.4	56 - 73	56 - 70	16.5 - 20.4	13.5 - 18.3	20.3 - 31.0	13.2 - 22.4	6.2 - 11.7	4.4 - 6.9	129 - 201	68.0 - 137	200 - 389	123 - 240	33.5 - 58.5	24.0 - 39.5
Pittsburg Marina	1.5 - 2.3	1.5 - 2.3	61 - 72	58 - 80	21.8 - 38.7	19.8 - 192.1	35.6 - 86.8	29.0 - 554.6	11.5 - 29.5	12.4 - 180.7	245 - 656	182 - 4345	426 - 1331	391 - 8412	68.0 - 180	57.9 - 1117
South Beach Harbor	0.7 - 1.5	0.6 - 1.5	107 - 110	106 - 110	371 - 392	376 - 397	1150 - 1210	1170 - 1220	351 - 370	359 - 377	8720 - 9310	9020 - 9460	17115 - 17882	17468 - 18534	2210 - 2531	2300 - 2682
Clipper Yacht Harbor	0.9 - 1.5	0.9 - 1.5	107 - 111	106 - 110	374 - 403	375 - 399	1166 - 1250	1170 - 1240	358 - 376	356 - 377	8780 - 9790	9250 - 9700	16800 - 18100	16989 - 18100	2312 - 2476	2322 - 2480
Marina Bay Yacht Harbor	0.7 - 6.4	0.6 - 1.2	99 - 107	99 - 107	369 - 382	369 - 378	1120 - 1170	1120 - 1160	341 - 373	345 - 371	8320 - 9349	7860 - 9177	15994 - 17857	16842 - 17636	2134 - 2513	2365 - 2406
Benicia Marina	1.7 - 2.3	1.6 - 2.3	74 - 92	76 - 89	139 - 157	161 - 202	379 - 444	456 - 570	129 - 141	156 - 190	3087 - 3520	3590 - 4693	6032 - 7458	7328 - 9311	773 - 1020	1000 - 1238
Sacramento Marina	0.9 - 1.4	0.2 - 1.3	52 - 61	50 - 70	10.2 - 11.2	9.7 - 13.1	5.0 - 5.9	4.8 - 7.2	0.9 - 1.0	0.9 - 1.1	6.3 - 7.9	5.6 - 9.3	3.6 - 4.3	2.6 - 5.1	4.6 - 4.9	4.4 - 5.8
Ballena Isle Marina	1.3 - 1.6	1.2 - 1.6	107 - 116	107 - 115	357 - 373	356 - 377	1110 - 1150	1110 - 1150	333 - 350	336 - 352	8700 - 9140	8640 - 9190	16340 - 18000	16364 - 17000	2150 - 2350	2140 - 2335
Village West Marina	3.3 - 4.4	3.2 - 3.8	59 - 76	62 - 76	15.8 - 20.0	16.2 - 19.8	7.2 - 9.8	7.3 - 9.9	2.1 - 3.0	2.2 - 2.7	24.4 - 32.3	25.3 - 32.2	26.4 - 32.2	26.3 - 36.4	25.6 - 32.2	25.6 - 32.0
Vallejo Marina	1.8 - 2.5	1.6 - 3.6	84 - 91	78 - 92	200 - 222	181 - 216	576 - 633	523 - 614	186 - 200	172 - 189	4511 - 4920	3996 - 4730	8739 - 10369	8048 - 10334	1162 - 1430	1065 - 1431
Berkeley Marina	0.8 - 1.2	0.7 - 2.7	99 - 109	102 - 108	372 - 380	364 - 385	1130 - 1170	1130 - 1180	344 - 371	347 - 366	8152 - 9199	8606 - 9187	16362 - 17833	16543 - 18302	2215 - 2471	2206 - 2521
Santa Cruz Harbor	0.6 - 1.7	0.7 - 1.9	113 - 127	111 - 118	413 - 447	409 - 455	1280 - 1380	1280 - 1400	393 - 432	404 - 432	10100 - 10700	9900 - 10800	19403 - 20059	19300 - 20171	2650 - 2741	2600 - 2748
Monterey Harbor	0.7 - 1.6	0.5 - 1.8	111 - 120	111 - 117	422 - 454	419 - 456	1300 - 1420	1300 - 1420	399 - 430	393 - 425	10100 - 10800	9900 - 10800	19443 - 20100	19298 - 20521	2650 - 2741	2608 - 2796
Santa Barbara Harbor	0.7 - 1.0	0.6 - 0.9	112 - 119	111 - 115	426 - 439	413 - 439	1330 - 1380	1300 - 1390	389 - 433	391 - 437	9927 - 11000	10057 - 10800	19500 - 20833	19400 - 21285	2550 - 3008	2600 - 3081
Loch Lomond Marina	1.0 - 1.7	1.2 - 1.6	92 - 103	94 - 103	313 - 344	312 - 394	969 - 1053	957 - 1232	304 - 332	297 - 379	6970 - 8210	7210 - 9560	14300 - 16120	14417 - 15606	1912 - 2150	1911 - 2160
Downtown Shoreline Marina	0.9 - 1.2	0.9 - 2.9	110 - 116	109 - 128	425 - 434	345 - 434	1330 - 1350	1010 - 1360	402 - 417	316 - 414	10057 - 10530	7720 - 10500	18971 - 19900	14800 - 19300	2564 - 2750	2080 - 2670
Marina del Rey FB	0.7 - 1.1	0.7 - 1.7	113 - 129	112 - 118	421 - 437	417 - 438	1340 - 1390	1320 - 1390	401 - 421	400 - 428	10393 - 10700	10400 - 10800	19300 - 20414	18468 - 20100	2635 - 2760	2454 - 2800
Marina del Rey BB	1.0 - 1.9	0.7 - 1.7	114 - 120	112 - 118	417 - 435	417 - 438	1320 - 1380	1320 - 1390	394 - 421	400 - 428	10367 - 11000	10400 - 10800	19300 - 20400	18468 - 20100	2604 - 2790	2454 - 2800

¹ Ordered by ascending marina median DCu concentrations. Values > 100 are rounded to the nearest one. Values < 100 are rounded to the nearest tenth.

² Marina names are color coded by water type. **Green** = freshwater, **Yellow** = brackish water, **Blue** = saltwater.

Predictive Toxicity Models

Biotic Ligand Model - Freshwater

Since relatively few of the samples met the operating parameter requirements for the freshwater BLM (Table 4) (mainly pertaining to the salinity-related constituents), only 53 samples were analyzed using this model. Most of these samples were from the four freshwater sites; however, some of the samples came from the Antioch site, which on some occasions contained sodium and chloride concentrations within the BLM operating range. Recall that the Antioch Marina has been classified in this study as a brackish water site due to the range of salinity at this location over the course of a year. The Pittsburg Marina and sites with greater salinity than Pittsburg had sodium and chloride concentrations that were above the operating range of the freshwater BLM. They, however, were evaluated using the interim saltwater BLM and will be discussed in a later sub-section.

Appendix L contains the freshwater BLM results for samples that met the criteria of the operating parameter above. The BLM-generated, unit-less, toxic unit (TU) values for freshwater sites ranged from 0.03–9.42. The model predicted that seven of 53 freshwater samples evaluated would meet or exceed the 1-TU threshold (Table 15). All seven samples were collected from the Sacramento Marina area and the most significant exceedances occurred during the second sampling event in August 2006. The BLM output columns shown include:

- Site and sample information (i.e., station name, sampling date, site, and event)
- The Final Acute Value (FAV) for copper (calculated from the 4 lowest genus mean acute values adjusted to account for site-specific BLM input parameters)
- CMC (Calculated as $\frac{1}{2}$ the FAV and rounded to the nearest tenth to facilitate comparison with DCu.)
- Measured DCu concentrations
- TU (Measured DCu/CMC. For TU equal to or greater than 1, the model predicts toxicity.)

The freshwater BLM did not predict acute toxicity from DCu at the following marina areas: Tahoe Keys, Folsom Lake, Antioch, Pittsburg, and Village West. Note that at this time, toxicity thresholds generated by the freshwater BLM are not enforceable water quality criteria or standards.

Table 15. Freshwater BLM Output for Samples with Predicted Toxicity ($TU \geq 1$)

Station Name	Sampling Date	Site ¹	Event	FAV	CMC	Measured DCu (µg/L)	Toxic Units
Sacramento Marina	7/21/2006	1	1	7.3459	3.7	3.7	1.00
Sacramento Marina	8/16/2006	1	2	0.8178	0.4	3.0	7.50
Sacramento Marina	8/16/2006	2	2	0.7435	0.4	3.5	8.75
Sacramento Marina	8/16/2006	3	2	0.6129	0.3	2.8	9.33
Sacramento Marina	8/16/2006	4	2	0.7626	0.4	2.3	5.75
Sacramento Marina	8/16/2006	5	2	0.6971	0.3	0.6	2.00
Sacramento Marina	9/12/2006	8	3	1.4317	0.7	0.7	1.00

¹ Sites 1–4 are marina sites. Sites 5–8 are LRSs.

The relatively large magnitude of the TU values for the second event suggests that copper concentrations could have had a significantly toxic effect on the more sensitive aquatic organisms at that site. BLM input data for the second sampling event at Sacramento Marina do not appear to exhibit distinctly different characteristics from data for the first sampling event, in which only one sample slightly exceeded the 1-TU threshold, with the exception of the pH data. Upon more detailed evaluation, it is likely that the lower pH values recorded during the second sampling event (6.0–6.5) compared to those during the first event (7.3–7.7) had a large impact in reducing the FAV and CMC values for

that event. Lower pH conditions tend to favor the presence of more-bioavailable free copper ions (sometimes referred to as labile copper or free dissolved copper), which have greater impact on biotic ligands. At higher pH levels, copper tends to be bound with both inorganic (e.g., carbonates) and organic (e.g., fulvic and humic acids) complexes in solution and is generally less available to interact with biotic ligands.

An evaluation of the water quality field data sheet for the second sampling event, however, revealed that the pH levels were measured using pH strips (i.e., litmus paper) since the pH meter was not functional that day. This was the only time when pH strips were used in the study. Historical pH data from a downstream monitoring station (Sacramento River at Hood) showed that pH levels typically ranged between 6.8 and 7.7 during the study's entire sampling period (CDEC, 2008). Thus, the pH readings for the second sampling event is likely to be less accurate than the pH readings made using the frequently calibrated pH meters. Consequently, the freshwater BLM's toxicity predictions for the Sacramento Marina for this particular event are likely to be less reliable as well.

Even if the toxicity predictions for the second sampling event at the Sacramento Marina were considered to be unreliable, there are still predictions of toxicity from the first and third sampling event. Even though the predicted TUs are relatively low (both at around 1 TU), these predictions suggest that the DCu could be bioavailable enough at the Sacramento Marina area to be occasionally toxic to freshwater organisms.

DOC Model - Salt and Brackish Water

Appendix M contains the complete results from the DOC model. Table 16 shows the FCC and FAC output ranges for the 19 salt and brackish water marinas evaluated. Applicable saltwater CTR CCC/CMC and range of measured DCu concentrations are also shown for comparison. The DOC-model generated FCC and FAC values are threshold values that are used to predict toxic effects. They are not enforceable water quality objectives or standards.

Table 16. DOC Model FCC and FAC Output Ranges (µg/L)

Station Name	FCC Range	FAC Range	CTR CCC¹	CTR CMC¹	Range DCu
Alamitos Bay Marina	3.0–3.8	4.7–5.9	3.1	4.8	ND–3.6
Antioch Marina	4.4–6.0	6.9–9.4	3.1	4.8	1.4–3.0
Ballena Isle Marina	4.0–4.8	6.3–7.5	3.1/6.0	4.8/9.4	0.1–5.0
Benicia Marina	4.8–5.9	7.5–9.3	3.1/6.0	4.8/9.4	ND–3.7
City of Berkeley	3.0–6.5	4.6–10.2	3.1/6.0	4.8/9.4	0.2–7.2
Clipper Yacht Harbor	3.1–4.7	4.8–7.3	3.1/6.0	4.8/9.4	0.3–6.6
Coyote Point Marina	4.6–5.2	7.2–8.0	3.1/6.0	4.8/9.4	1.0–2.6
Downtown Shoreline Marina	3.3–6.9	5.1–10.7	3.1	4.8	0.4–10.9
Loch Lomond Marina	3.6–5.0	5.6–7.8	3.1/6.0	4.8/9.4	1.3–10.3
Marina Bay Yacht Harbor	2.8–11.0	4.3–17.1	3.1/6.0	4.8/9.4	1.3–3.6
Marina del Rey Back Basin	3.6–5.3	5.6–8.2	3.1	4.8	8.1–18.4
Marina del Rey Front Basin	2.9–5.0	4.5–7.8	3.1	4.8	0.3–16.2
Monterey Harbor	2.5–5.1	3.9–7.9	3.1	4.8	ND–7.8
Pittsburg Marina	4.5–6.0	7.1–9.3	3.1	4.8	1.4–3.2
San Francisco Marina	2.6–5.5	4.1–8.7	3.1/6.0	4.8/9.4	ND–3.9

Station Name	FCC Range	FAC Range	CTR CCC ¹	CTR CMC ¹	Range DCu
Santa Barbara Harbor	2.6–3.7	4.0–5.7	3.1	4.8	ND–8.2
Santa Cruz Harbor	2.7–4.9	4.2–7.6	3.1	4.8	ND–5.8
South Beach Harbor	2.7–4.6	4.2–7.1	3.1/6.0	4.8/9.4	0.4–3.0
Vallejo Municipal Marina	4.7–7.8	7.3–12.1	3.1/6.0	4.8/9.4	1.3–4.7

¹ CTR's CCC and CMC for the San Francisco Bay Area Marinas will be replaced by Site Specific Objectives pending U.S. EPA approval. Once approved, the new chronic and acute water quality objectives for these marinas will be 6.0 and 9.4 µg/L, respectively.

Out of the 412 salt and brackish water samples that had DOC results, 86 contained high enough concentrations of DCu to equal or exceed the DOC-model predicted FCC and 54 of those also exceeded the FAC. Both FCC and FAC exceedances are highlighted in Appendix M. The majority of the samples that exceeded toxicity thresholds came from Central and South Coast marinas, most notably MdR's front and back basins, Downtown Shoreline Marina, Santa Barbara Harbor, Monterey Harbor, and Santa Cruz Harbor. Bay Area marinas also had occasional exceedances, namely Loch Lomond Marina, Clipper Yacht Harbor, Berkeley Marina, and Ballena Isle Marina.

Eighty five of the 86 samples that exceeded the lower FCC threshold came from inside of marinas. Only one LRS sample exceeded this same threshold. This sample came from MdR's LRS #1, which has been noted as an LRS site with characteristics that make it more like a marina site.

In comparison to the CTR's fixed CCC and CMC for the same sites, the DOC model FCCs and FACs are generally higher. Thus, measured DCu concentrations tend to exceed CTR standards more frequently than DOC-model predicted toxicity thresholds. Occasionally, the opposite is true. This is most noticeable at San Francisco Marina, Santa Cruz Harbor, Monterey Harbor, and Santa Barbara Harbor. This phenomenon is likely a reflection of the relatively low DOC concentrations at these locations. Due to the potential of DOC concentrations to fluctuate at each site, a particular concentration of measured DCu could exceed FCCs and FACs one day and be below them the next.

A comparison of the Bay Area marinas' FCCs and FACs to water quality standards needs to be done with the understanding that site specific objectives (SSOs) could be adopted that would result in the CCC being raised to 6.0 µg/L and the CMC to 9.4 µg/L. Subsequently, DCu concentrations in Bay Area marinas will likely exceed the FCCs and FACs more frequently than the SSOs.

Since the study's toxicity tests involved the exact same test species, toxic endpoint, and exposure period as the toxicity tests on which the DOC model's function is based, it is possible to directly compare model-predicted results to our toxicity results. A comparison of the results from the DOC model with the study's actual toxicity results showed good agreement in 42 of 47 outcomes. In other words, the DOC model predicted acute toxicity when statistically significant toxicity was observed in toxicity tests, or it predicted that no acute toxicity would occur for samples with no observed toxicity. Five inconsistent outcomes were, however, observed. The model predicted acute toxicity at one Loch Lomond Marina site, one MdR back basin site, and two Downtown Shoreline Marina sites when no acute toxicity was observed for samples tested from these sites. In one case, in a Marina Bay Yacht Harbor sample, the model predicted no toxicity and yet low level acute toxicity was observed in the actual sample. Overall, the DOC model predicted water column toxicity well (89% success rate) when compared to actual result of acute toxicity tests on copper-sensitive *M. galloprovincialis*. When the model and toxicity results disagree, it is due to the tendency of the model to over-predict toxicity rather than under-predict.

Biotic Ligand Model - Salt and Brackish Water

The output of the saltwater BLM is presented in Appendix N. Saltwater BLM results that were greater than one toxic unit (TU) are presented in Table 17. Sixty seven of 373 samples (for which output could be calculated) or 18% of the samples contained a high enough concentration of DCu to reach or exceed the 1-TU threshold. Key BLM output columns shown include: predicted EC₅₀ for *M. galloprovincialis*, observed DCu concentrations, and TUs. Note that the TUs calculated for the saltwater BLM in Table 17 and Appendix N are based on the predicted EC₅₀'s for *M. galloprovincialis* and not on the CMC as was the case for the freshwater BLM. In this case, exceedances over one TU, as determined by the saltwater BLM, suggests that adverse risks to *M. galloprovincialis* may exist from the exposure of copper. At this time, the predicted EC₅₀'s for *M. galloprovincialis* that are generated by the saltwater BLM are not enforceable water quality criteria or standards.

Table 17. Saltwater BLM Output for Samples with Predicted Toxicity (TU ≥ 1)

Station Name	Date	Site	Event	Water Type	Observed DCu (µg/L)	Predicted EC50 <i>M. galloprovincialis</i>	Toxic Units
Berkeley Marina	7/24/2006	1	1	Salt	6.8	5.2	1.31
Berkeley Marina	9/18/2006	1	3	Salt	3.8	3.2	1.19
Downtown Shoreline Marina	8/1/2006	1	1	Salt	7.4	3.9	1.90
Downtown Shoreline Marina	8/1/2006	2	1	Salt	6.3	3.9	1.62
Downtown Shoreline Marina	8/1/2006	3	1	Salt	7.7	4.7	1.64
Downtown Shoreline Marina	8/29/2006	1	2	Salt	5.3	5.3	1.00
Downtown Shoreline Marina	8/29/2006	2	2	Salt	7.4	4.3	1.72
Downtown Shoreline Marina	8/29/2006	3	2	Salt	8.9	4.2	2.12
Downtown Shoreline Marina	9/26/2006	1	3	Salt	10.9	4.6	2.37
Downtown Shoreline Marina	9/26/2006	2	3	Salt	9.5	4.7	2.02
Downtown Shoreline Marina	9/26/2006	3	3	Salt	8.6	4.2	2.05
Downtown Shoreline Marina	9/26/2006	4	3	Salt	6	4.8	1.25
Marina del Rey Back Basin	8/2/2006	1	1	Salt	18.4	4.8	3.83
Marina del Rey Back Basin	8/2/2006	2	1	Salt	17.9	4.5	3.98
Marina del Rey Back Basin	8/2/2006	3	1	Salt	14.5	4.5	3.22
Marina del Rey Back Basin	8/2/2006	4	1	Salt	14.1	4.8	2.94
Marina del Rey Back Basin	8/30/2006	1	2	Salt	11.5	4.5	2.56
Marina del Rey Back Basin	8/30/2006	2	2	Salt	18.4	4.6	4.00
Marina del Rey Back Basin	8/30/2006	3	2	Salt	12.4	4.7	2.64
Marina del Rey Back Basin	8/30/2006	4	2	Salt	14.2	4.6	3.09
Marina del Rey Back Basin	9/27/2006	1	3	Salt	12.7	4.6	2.76
Marina del Rey Back Basin	9/27/2006	2	3	Salt	13.3	4.6	2.89
Marina del Rey Back Basin	9/27/2006	3	3	Salt	8.1	8.1	1.00
Marina del Rey Back Basin	9/27/2006	4	3	Salt	12	4.3	2.79
Marina del Rey Front Basin	8/2/2006	1	1	Salt	16.2	4.8	3.38
Marina del Rey Front Basin	8/2/2006	2	1	Salt	14.5	4.6	3.15
Marina del Rey Front Basin	8/2/2006	3	1	Salt	14.9	4.4	3.39
Marina del Rey Front Basin	8/2/2006	4	1	Salt	13.8	3.2	4.31
Marina del Rey Front Basin	8/2/2006	5	1	Salt	4.7	4.2	1.12
Marina del Rey Front Basin	8/30/2006	1	2	Salt	13.1	4.5	2.91
Marina del Rey Front Basin	8/30/2006	2	2	Salt	12.5	4.2	2.98
Marina del Rey Front Basin	8/30/2006	3	2	Salt	11.8	4.5	2.62

Station Name	Date	Site	Event	Water Type	Observed DCu (µg/L)	Predicted EC50 <i>M. galloprovincialis</i>	Toxic Units
Marina del Rey Front Basin	8/30/2006	4	2	Salt	11.9	5	2.38
Marina del Rey Front Basin	9/27/2006	1	3	Salt	12.2	4.3	2.84
Marina del Rey Front Basin	9/27/2006	2	3	Salt	11.5	3.9	2.95
Marina del Rey Front Basin	9/27/2006	3	3	Salt	8.9	4.6	1.93
Marina del Rey Front Basin	9/27/2006	4	3	Salt	10	4.1	2.44
Monterey Harbor	8/10/2006	1	1	Salt	6.3	4.7	1.34
Monterey Harbor	8/10/2006	2	1	Salt	7.1	4.4	1.61
Monterey Harbor	8/10/2006	3	1	Salt	4.6	3.9	1.18
Monterey Harbor	8/10/2006	4	1	Salt	4.8	4.1	1.17
Monterey Harbor	9/8/2006	1	2	Salt	3.7	3	1.23
Monterey Harbor	9/8/2006	2	2	Salt	3.7	3.2	1.16
Monterey Harbor	10/19/2006	3	3	Salt	7.8	6.7	1.16
Loch Lomond Marina	7/25/2006	1	1	Salt	10.3	5.8	1.78
Loch Lomond Marina	7/25/2006	2	1	Salt	8.4	5.8	1.45
Loch Lomond Marina	7/25/2006	3	1	Salt	7.2	5.7	1.26
Loch Lomond Marina	7/25/2006	4	1	Salt	8	5.5	1.45
Loch Lomond Marina	8/22/2006	1	2	Salt	7.7	7.5	1.03
Loch Lomond Marina	9/19/2006	1	3	Salt	6.7	4.5	1.49
Santa Barbara Harbor	8/3/2006	2	1	Salt	6.5	3.6	1.81
Santa Barbara Harbor	8/3/2006	3	1	Salt	6.6	4.2	1.57
Santa Barbara Harbor	8/3/2006	4	1	Salt	4.6	3.3	1.39
Santa Barbara Harbor	8/31/2006	1	2	Salt	5.6	3.5	1.60
Santa Barbara Harbor	8/31/2006	2	2	Salt	6.9	3.2	2.16
Santa Barbara Harbor	8/31/2006	3	2	Salt	8.2	3.4	2.41
Santa Barbara Harbor	8/31/2006	4	2	Salt	7.4	3.3	2.24
Santa Barbara Harbor	9/28/2006	1	3	Salt	4.5	4.3	1.05
Santa Barbara Harbor	9/28/2006	2	3	Salt	7.1	4.1	1.73
Santa Barbara Harbor	9/28/2006	3	3	Salt	6	4	1.50
Santa Barbara Harbor	9/28/2006	4	3	Salt	5.4	4.6	1.17
Santa Cruz Harbor	8/9/2006	3	1	Salt	4.3	3.5	1.23
Santa Cruz Harbor	9/7/2006	1	2	Salt	5.1	2.7	1.89
Santa Cruz Harbor	9/7/2006	2	2	Salt	5.8	3	1.93
Santa Cruz Harbor	9/7/2006	3	2	Salt	4.4	3.1	1.42
Santa Cruz Harbor	9/7/2006	4	2	Salt	4.5	2.9	1.55
Clipper Yacht Harbor	8/25/2006	3	2	Salt	6.6	4.4	1.50

For samples that equaled or exceeded the toxicity threshold, TUs ranged from 1.00–4.36. The majority of the samples that exceeded the *M. galloprovincialis* site-specific predicted EC₅₀s were from Central and South Coast marinas. This observation is similar to the DOC model results. MdR's front and back basins had the most occurrences of samples that reached or exceeded one TU. The magnitude of TU values appeared to also be highest at MdR. TUs for MdR were often 3–4 times the *Mytilus* sp. EC₅₀ values. Bay Area marinas also had occasional exceedances, but these occurrences were primarily isolated to Loch Lomond Marina and Berkeley Marina.

Sixty six samples with predicted toxicity were collected from marina sites and one sample was collected from an LRS. This sample is the same sample (MdR LRS #1) that exceeded the DOC model's toxicity threshold. As previously

asserted, this LRS site has characteristics that are more like a marina site than an LRS. Overall, it is clear that water samples from saltwater marinas have the potential to be acutely toxic to *M. galloprovincialis*.

Predictions were fairly consistent between the saltwater BLM (i.e., exceedances of *M. galloprovincialis* EC₅₀) and the DOC model (i.e., exceedances of FCCs or FACs). That is, both models tend to predict acute toxicity or the lack of toxicity for the same sample. This is not entirely surprising since DOC, which is a major determinant in the bioavailability of copper in saline water, is an input in both models. Note that chronic toxicity cannot be compared here since the draft saltwater BLM used for this report does not currently generate a CCC output.

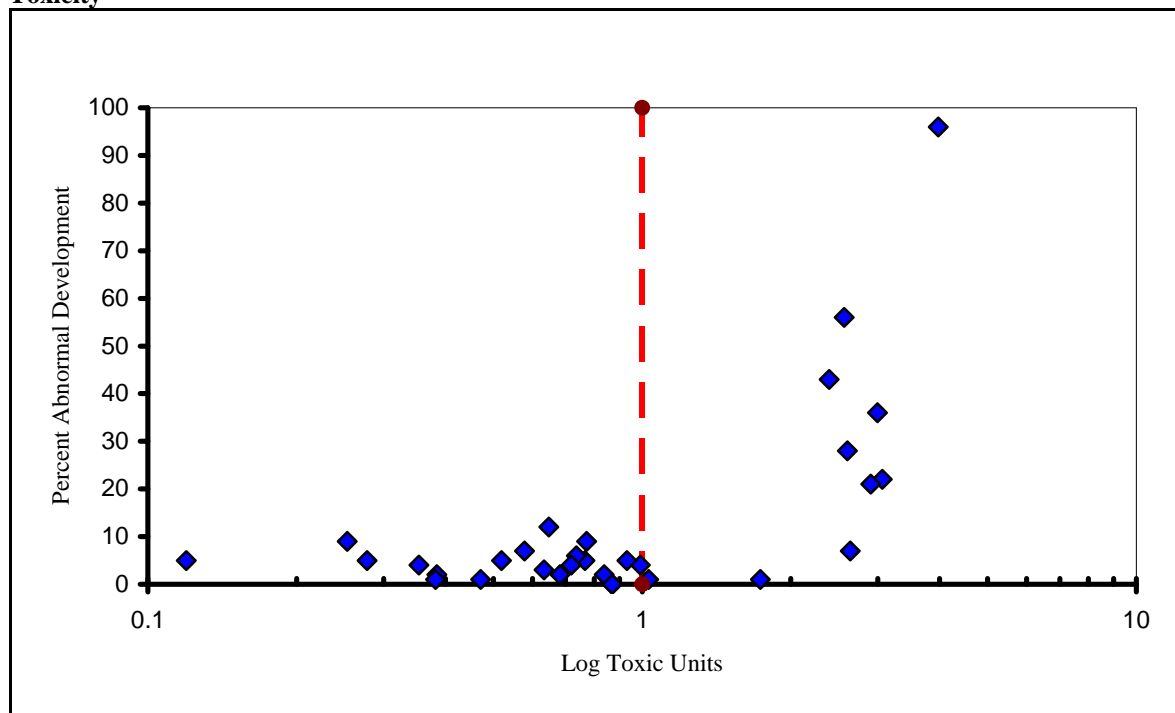
The saltwater BLM predicted acute toxicity more frequently than the DOC model. There were 14 occasions where the saltwater BLM predicted the exceedance of an acute toxicity threshold and the DOC model did not. In contrast, there were only two occasions where the DOC model predicted the exceedance of an acute toxicity threshold and the saltwater BLM did not. This suggests that the DOC model is more conservative than the saltwater BLM in predicting acute toxicity. There is an assumption made here that both models' toxicity thresholds (i.e., FACs and BLM predicted EC₅₀'s) are similar enough to allow this comparison.

Since site-specific CCCs and CMCs are not yet available from the saltwater BLM, it is not possible to accurately compare the current model output with the CTR's water quality criteria. However, considering the importance of DOC in mediating the bioavailability of copper, it is likely that the comparison of the saltwater BLM criteria to the existing CTR water quality criteria will be similar in result to the comparison of the DOC model's FACs and FCCs to the same criteria. In other words, the saltwater BLM-predicted CCCs and CMCs are likely to be higher than the fixed acute (3.1 µg/L) and chronic (4.8 µg/L) CTR standards for many sites. However, at sites where DOC tends to be low (i.e., San Francisco Marina, Santa Cruz Harbor, Monterey Harbor, and Santa Barbara Harbor), it is possible that the saltwater BLM-generated criteria could be lower than the existing standards.

A subset of the saltwater BLM-predicted toxicity results were directly compared to the study's toxicity results. A comparison of samples that had both predicted and actual toxicity results showed 35 of 40 matching outcomes. That is, the saltwater BLM predicted acute toxicity when statistically significant toxicity was observed in toxicity tests, or it predicted that no toxicity would occur for samples with no observed toxicity. Five contradicting outcomes were observed. The model predicted acute toxicity at a Loch Lomond Marina site, one MdR Back Basin site, and two Downtown Shoreline Marina sites when no acute toxicity was observed in these samples. In one case, for a Marina Bay Yacht Harbor sample, the model predicted no toxicity and yet acute toxicity was observed in the sample. Interestingly, these five anomalous results are identical to those observed between the DOC model predictions and actual toxicity results.

Overall, the saltwater BLM predicted EC₅₀'s for *M. galloprovincialis* were generally in good agreement with actual toxicity (88% success rate). Like the DOC model, however, the saltwater BLM also tends to over-predict toxicity on occasions. This tendency can be seen when toxicity results were plotted against the BLM-predicted TUs (Figure 32). Note the red vertical line on the graph, which denotes the 1-TU threshold. Interestingly, significant abnormal development (which includes larval mortality) does not appear to take place until the predicted TU is greater than 2. This suggests that toxicity predictions by the saltwater BLM, particularly at levels between 1 and 2 TUs, may not always translate to notable toxicity to *M. galloprovincialis* in laboratory tests. With this in mind, of the 67 samples that were above the 1-TU threshold, only 29 of them were also above the 2-TU threshold. These 29 samples were collected from four marinas—Santa Barbara Harbor, MdR back basins, MdR front basins, and Downtown Shoreline Marina. Thus, if this subset of samples were analyzed for toxicity to *M. galloprovincialis*, they would likely exhibit statistically significant toxicity. Future interpretation and linkage of BLM toxicity predictions to actual toxicity results should consider this observation.

Figure 32. BLM-Predicted Toxic Units (Observed DCu/Predicted *M. galloprovincialis* EC₅₀) vs. Observed Toxicity



IV. Discussion

Occurrence and Magnitude

DCu, TCu, and DZn were frequently detected. The high frequency of detection is not surprising considering (1) the ubiquitous nature of copper and zinc (2) that monitoring was conducted in marina areas, which have historically been known to exhibit elevated concentrations of metals, and (3) the relatively low detection limits used for quantification.

Water Column – Copper

DCu concentrations in salt and brackish water marinas were frequently higher than those found in freshwater marinas. This difference is statistically significant. Marinas in California's South Coast exhibited low to very high median DCu concentrations among results for all the marinas. MdR's front and back basins had the two highest median concentrations at 12.4 and 13.6 µg/L, respectively. The highest sample concentration of DCu was detected in two samples from the back basins of MdR. Both samples contained 18.4 µg/L of DCu. Downtown Shoreline Marina had the third highest median concentration in the study at 6.6 µg/L. The remaining South Coast marina, Alamitos Bay Marina, exhibited a relatively low median DCu concentration of 1.2 µg/L. This marina is located only a few miles from Downtown Shoreline Marina and is similar in size. This deviation, however, could potentially be created by the dilution effect caused by the routine pumping of a high volume of water from the marina for cooling use at a nearby power-generating facility (M. Sandoval, personal communication, 2007). During peak pumping periods, a volume that is roughly equivalent to the capacity of Alamitos Bay could be emptied out from the basin.

Elevated DCu concentrations in South Coast marinas have also been documented in two recent studies. In 2005, SCCWRP conducted a monitoring study of 12 yacht basins in four Southern California harbors (Dana Point Harbor, Oceanside Harbor, Mission Bay, and San Diego Bay) as part of SDRWQCB's Harbor Monitoring Program (SCCWRP, 2006). DCu concentrations ranged from below the detection limit to 21.0 µg/L with a mean concentration of 7.0 µg/L. In 2006, the Santa Ana RWQCB conducted a metal monitoring study in LNB. DCu concentrations in the marinas sampled ranged from 1.3–11 µg/L with a mean concentration of 4.2 µg/L. The marinas investigated in both of

these studies are located farther south along the California coast than the southernmost site in this DPR study. If the copper results from the three studies were pooled together, they would show that elevated DCu concentrations are common among California South Coast marinas.

The three Central Coast marinas in this study exhibited moderately high median DCu concentrations. Santa Barbara Harbor, Monterey Harbor, and Santa Cruz Harbor had median concentrations of 5.7, 4.9, and 4.3 µg/L, respectively. These median concentrations are the fifth through seventh highest values documented among the 23 marinas studied. The highest DCu concentration documented among these three Central Coast marinas was detected in a sample from Santa Barbara Harbor at 8.2 µg/L.

Eight Bay Area marinas were examined in this study and most of them exhibited moderate median DCu concentrations between 2.1–3.3 µg/L. The higher-end exception to this range is Loch Lomond Marina in San Rafael where the median concentration was 5.8 µg/L. The lower-end exception is San Francisco Marina where the median concentration was 1.1 µg/L.

The brackish water marinas—the Vallejo, Benicia, Pittsburg, and Antioch marinas—exhibited low to moderate median DCu concentrations of 3.4, 2.7, 2.2 and 2.1 µg/L, respectively. The freshwater marinas—the Village West, Sacramento, Folsom Lake, and Tahoe Keys marinas—exhibited moderate to very low median concentrations of 3.4, 3.0, 0.5, 0.6 µg/L. We observed the lowest median DCu concentrations in this study at the two lake marinas at Tahoe Keys and Folsom Lake.

The median TCu and DCu concentrations for each marina tend to be similar in magnitude. That is, marinas that exhibit high DCu concentrations tend to also exhibit high TCu concentrations. So, the ranking of marinas from the lowest to the highest median TCu concentrations closely resembles the ranking for DCu. This observation is largely explained by the fact that the TCu measurement accounts for the DCu load as well as the particulate copper load. U.S. EPA derived a recommended multiplier of 0.91 as a conversion factor of DCu from TCu in saltwater environments (U.S. EPA, 2007). The freshwater multiplier is 0.96 (Stephan, 1995). In other words, DCu tends to make up over 90% of TCu. The overall ratio of DCu to TCu for this study is 0.92, which is a good indicator that DCu and TCu were within the expected range in this study. Despite this relationship between the DCu and TCu, statistical analysis (one-way ANOVA tests) of TCu data only showed a marginal difference between the TCu concentrations of salt and freshwater marinas.

Water Column – Zinc

DZn concentrations were generally 2–4 times larger than DCu and TCu concentrations in the same sample. Consequently, median DZn concentrations were usually higher than those for DCu or TCu at each marina. Mdr's front and back basins exhibited the two highest median DZn concentrations at 49.1 and 50.0 µg/L, respectively. The highest DZn concentration documented in the study was detected in one of the front basins of Mdr at the concentration of 66.6 µg/L. The lowest marina median DZn concentrations are often associated with the fresh and brackish water samples. The difference between DZn concentrations in saltwater marinas and DZn concentrations in brackish and freshwater marinas is statistically significant.

The ranking of lowest to highest median DZn concentrations is also very similar to the analogous ranking for DCu and TCu. The primary exception was Alamitos Bay which ranked much higher for zinc than copper. Note, however, that the LRSs at Alamitos Bay Marina (median DZn of 6.3 µg/L) exhibited similar DZn concentrations as the marina sites (median DZn of 6.7 µg/L). Thus, the flushing activity that is unique to this marina would not necessarily serve to effectively dilute the DZn load in the marina. This could explain why DZn concentrations are still relatively high compared to DCu and TCu concentrations in Alamitos Bay Marina.

Overall, larger saltwater marinas tend to rank highly for metal concentrations. Smaller saltwater marinas and fresh and brackish water marinas tend to make up the intermediate and lower rankings. This observation suggests that factors relating to water types and marina size may play a major role in determining the magnitude of copper and zinc in marina waters.

As previously noted for Alamitos Bay Marina, site specific hydrological factors (i.e., flushing) appear to be an influential factor (Katz, 1998) and may serve to explain why Alamitos Bay Marina (affected by industrial pumping) and San Francisco Marina (located at the mouth of San Francisco Bay) exhibited rather low median DCu and TCu

concentrations relative to their size. Poor flushing may also explain why Loch Lomond and Ballena Isle marinas, which are both smaller marinas, exhibited higher concentrations of copper and zinc when compared to larger marinas in the Bay Area.

Water Column – Irgarol/M1

The biocide Irgarol and its primary degrade M1 were detected in all 45 samples. Irgarol and M1 concentrations ranged from 12–712 and 2–217 ng/L, respectively. The highest Irgarol and M1 concentrations were found in a sample from Loch Lomond Marina in San Rafael. M1 concentrations were also always lower than Irgarol in the same sample. M1 concentrations also correlated well with Irgarol at each site reaffirming the parent compound-degrade relationship between the two analytes.

Irgarol and M1 concentrations were higher in saltwater marinas than brackish water marinas. Similar to our evaluation of copper, Irgarol concentrations in a particular marina are likely dictated by the amount of use in that marina and the level of site-specific flushing at that location. DPR's product data show that 68 products (including several manufacturing use products) are registered with DPR (DPR, 2005b). Almost all of the end-use products are for AFP use with boat hulls being the most common application site.

Irgarol and M1 concentrations were higher in the first versus the third sampling round. Assuming that all of the Irgarol in the water column originated from AFP sources, then the difference between the two sampling rounds can be attributed to the differences in the release of Irgarol from boat hulls (whether through leaching or underwater hull-cleaning) during the time of sample collection in the first round versus the third round. Many factors could have an influence on the release rates between the two rounds including use, elapsed time from application and hull cleaning, and seasonal changes in flushing and water temperature.

In 2005, Sapozhnikova et al. (2007) conducted an assessment of Irgarol and M1 in San Diego Bay Area marinas. Irgarol and M1 concentrations in that study ranged from 1–304 ng/L and 1–68 ng/L, respectively. In 2006, Hall et al. (2007) quantified Irgarol and M1 concentrations in 15 California marina areas. Alamitos Bay Marina, MdR, Ballena Isle Marina, and Berkeley Marina were also studied in Hall et al. (2007). Irgarol and M1 concentrations in this study ranged from 1–339 ng/L and below detection to 74 ng/L, respectively. Hall et al. (2007) also assessed local reference sites in addition to marina sites. Both Irgarol and M1 concentrations were much lower at local reference sites than at marina sites. This supports our previous assertion that the main source of Irgarol and M1 are from AFP use.

Sediment – Copper and Zinc

Only 23 of the anticipated 180 sediments samples were taken in this study. These samples were taken from three freshwater marinas. For TCu, both the highest (169 mg/kg dry weight) and lowest concentrations (17 mg/kg dry weight) were detected at Sacramento Marina and one of its associated LRSs, respectively. For TZn, the highest concentration (273 mg/kg dry weight) was detected at Village West Marina and the lowest concentration (23 mg/kg dry weight) was detected at an LRS of Folsom Marina. The availability of sediment metals data, particularly those from studies where sediment samples are not depth-composited, is very limited for freshwater marinas in California. Sediment metals data that do exist are mainly from saltwater marinas. Pap (2004) documented the range of sediment TCu concentrations in four Bay Area marinas (Ballena Isle, Loch Lomond, Berkeley, and Corinthian Club) to be 38.2–151 mg/kg dry weight. Sediment TZn concentrations in the Pap (2004) study ranged from 82.7–219 mg/kg dry weight. These ranges are fairly similar to the ranges observed for TCu and TZn at the three freshwater marinas in our study. Orange County Coast Keeper's study in LNB documented sediment TCu concentrations in the range of 16–365 mg/kg dry weight and TZn concentrations in the range of 69–692 mg/kg dry weight (Orange County Coast Keeper, 2007). These ranges from LNB marinas are somewhat higher than the ones observed in Pap (2004) and our study.

Comparison to Water Quality Standards or Biological Effects Thresholds

Copper

The CTR contains the enforceable water quality standards for copper in California. These standards have been in place for California since 2000 when U.S. EPA promulgated them in the absence of a state-established water quality standards.

The comparison of freshwater DCu results to the CTR's hardness-based CCC (chronic) and CMC (acute) standards for copper suggested that DCu concentrations in freshwater marina areas (marinas sites and LRSs) were not likely to represent a significant risk to freshwater aquatic organisms. Both the CTR chronic and acute standards for DCu in freshwater were never exceeded in the 135 DCu samples evaluated from six different marinas and associated LRSs. Note that some samples from two of the brackish water marinas contained low enough salinity that it was possible to evaluate them with the freshwater standards.

DCu results from the study's salt and brackish water marina areas were also compared to the CTR fixed saltwater standards. Of the 388 combined salt and brackish water samples, DCu concentrations in 30% and 17% of them exceeded the chronic and acute copper standards, respectively. Almost all of the samples that exceeded CTR standards were marina samples. For marina samples only, the DCu concentrations in 51% and 30% of the salt and brackish water marina samples combined exceeded the chronic and acute standards, respectively.

DCu concentrations in 16 of 19 marina areas exceeded the chronic saltwater CTR standard of 3.1 µg/L. The marina areas where DCu concentrations did not exceed the chronic standards were Antioch Marina, South Beach Harbor, and Coyote Point Marina. Copper concentrations in 10 of the 16 marina areas that exceeded the CCC also exceeded the CMC standard of 4.8 µg/L. These 10 marina areas were Loch Lomond, Clipper Yacht Harbor, Berkeley Marina, Ballena Isle Marina, Santa Cruz Harbor, Monterey Harbor, Santa Barbara Harbor, MdR front basins, MdR back basins, and Downtown Shoreline Marina.

As defined by the CTR, exceedances of CTR saltwater standards indicate that concentrations of DCu are high enough to present a significant risk to the aquatic organisms and their uses. The exceedance of CTR standards for copper has historically been used to support the declaration of beneficial use impairments by the San Diego RWQCB. Therefore, water bodies across the state that exceed these standards can certainly be placed on the CWA 303(d) impaired water bodies list by other RWQCBs as well. TMDL development is a possibility for all water bodies that are on the CWA 303(d) list. The adoption of a site-specific objectives for the San Francisco Bay will, however, likely impact the future 303(d) listing process for Bay Area marinas.

Zinc

The CTR also established specific water quality standards for zinc. None of the 135 freshwater DZn samples collected in this study exceeded the CTR's hardness-based freshwater chronic and acute standards for zinc. Moreover, none of the 388 DZn samples from salt and brackish water marinas contained high enough DZn concentrations to exceed the CTR's saltwater fixed chronic and acute standards of 81 and 90 µg/L, respectively. Therefore, DZn concentrations in all the marina areas in this study were not likely to present an adverse risk to freshwater aquatic organisms.

Irgarol/M1

There are no water quality standards for Irgarol or M1. Thus, a comparison of sample concentrations to various biological effect thresholds is a more informative way to put Irgarol and M1 data into perspective. Since Irgarol acts as an inhibitor of photosynthesis, growth inhibition of phytoplankton appears to be one of its most commonly-observed biological effects. Irgarol concentrations at some of the marinas in this study are high enough to exceed some of the toxicological values for growth and reproduction inhibition endpoints. Thus, there are instances where simple risk quotients ($EC_{50}/\text{observed concentration}$) would be greater than one.

For a more complete assessment of potential risks, it is more informative to compare environmental concentrations to aquatic benchmark values than to EC_{50} or LC_{50} values. Hall et al. (1999) derived an aquatic-plant toxicity benchmark value for Irgarol in an ecological risk assessment (ERA) for European waters. The benchmark threshold represents the 10th percentile of the available and accepted plant toxicity dataset that contained nine toxicological values. For this particular assessment, the benchmark value was calculated to be 136 ng/L. When compared with measured environmental concentrations (i.e., 90th percentile value of various station types), varying levels of ecological risks were established with risks in marinas being the highest among the station types. Hall et al. (1999) determined that Irgarol concentrations at 24% of the marina sites and 10% of all the sites evaluated exceeded the 136 ng/L benchmark. In our study, Irgarol concentrations in 11 of the 45 samples (also 24%) collected for Irgarol analysis exceeded this same plant toxicity benchmark.

Similar ERAs were conducted by Hall and Gardinali (2004) and Hall et al. (2007). Both these ERAs used a larger aquatic plant toxicity dataset (16 toxicological values) than the 1999 assessment and also included LC₅₀ data. The Irgarol benchmark values that were derived in Hall and Gardinali (2004) and Hall et al. (2007) were 251 ng/L and 193 ng/L, respectively. Four of the 45 samples (9%) collected for Irgarol analysis in our study contained Irgarol concentrations that were above these higher and more robust benchmarks. In all three of these ERAs, ecological risks from Irgarol were assessed to be generally low. However, the ERAs found that risks in marina areas were notably higher.

For additional perspective, an aquatic toxicity benchmark known as the Environmental Risk Limit (ERL) (not to be mistaken with the identical abbreviation that stands for Effects Range Low that is used in the context of sediment quality guideline) is used in the Netherlands. The Dutch Irgarol ERL of 24 ng/L is also based on a plant toxicity dataset and is set at dataset's 5th percentile value (protective of 95% of all aquatic plant species). Recall that the benchmark values used by Hall et al. (1999) and Hall and Gardinali (2004) utilized the 10th percentile value. The more protective percentile value used for the ERL and the difference in the toxicity dataset analyzed resulted in a significantly lower benchmark value. Forty out of 45 samples from our study (89%) contained Irgarol concentrations above the Dutch ERL for Irgarol.

Considering the overlap of measured marina Irgarol concentrations with phytoplankton and periphyton EC₅₀ ranges and aquatic benchmark values, there appears to be risk from Irgarol exposure to these assemblages in some of the saltwater marinas in this study. However, at this point, it is not clear what biological and/or ecological impacts are occurring due to Irgarol exposure in these marinas. A more focused study on the impact of Irgarol to marina biological assemblages should reveal if ERA predictions are representative of real-world conditions.

M1 is considerably less toxic to aquatic organisms than Irgarol. As a consequence, its aquatic benchmark value (12,500 ng/L) is much higher than that for Irgarol. None of the samples in this study contained M1 concentrations that were close to this benchmark. Thus, ecological risks from M1 exposure to aquatic plants in the marinas in this study are extremely low.

Marina versus Local Reference Site

Water Column

Copper and zinc concentrations were frequently higher in marina samples than in LRS samples taken from adjacent areas. For DCu, this difference is statistically significant for marinas in all three water types. For TCu, this difference is statistically significant in saltwater and freshwater marinas. For DZn, the difference is statistically significant for salt and brackish water marinas. The discrepancy between marina and LRS concentrations of copper and zinc strongly support the assertion that sources of metals from inside of marinas and/or factors that are related to the residence time and flushing dynamics (as compared to LRSs) are mainly responsible for the observed difference.

Two basic factors could potentially explain why elevated metal concentrations often exist in many of the marinas in this study. Metals loading from the marina's confines could serve as a localized source, which could distinctly elevate water column and sediment concentrations of copper and zinc in the immediate vicinity of the marina. Moreover, since the primary basis of marina placement, construction, and design is to provide shelter and protection for mooring boats from wind, currents, and tides, marina areas tend to be poorly flushed compared to the larger body of water with which they are associated.

In 2005, DPR conducted a review of California copper monitoring studies that could have relevance to the evaluation of copper AFP pollution. The review showed that a number of studies had documented elevated concentrations of copper (as well as zinc) in marina water and sediment versus the local background levels (Singhasemanon, 2005). Two large marina studies that were recently conducted in LNB and along California's South Coast (sampling sites between Dana Point Harbor and the U.S./Mexico border) also documented this phenomenon (Orange County Coast Keeper, 2007; Schiff et al., 2007).

Marina-related metal studies are typically conducted during dry periods to help reduce the interference of metal contaminants associated with rain runoff. Storm discharge data from the LNB metals study documented high metal concentrations in runoff water that discharged directly into several marinas (Orange County Coast Keeper 2007).

During periods of wet weather, it is likely that metal loads introduced via runoff and sediment disturbance and transport overshadow metal sources from within the marina.

When LRS and marina metal concentrations are not statistically different as in the cases of TCu in brackish water marina areas and DZn in freshwater marina areas, this suggests that loading might not be high enough in the marinas to be distinct from the LRSs or that site-specific flushing characteristics are good enough to keep metal concentrations low. For the case of TCu in brackish water marina areas, the LRS median concentrations ranged from 73–110% of the associated marina median TCu concentrations. Based on the strong correlation of TCu to TSS in brackish water marina areas and based on the relationships established in the Equilibrium Partitioning Theory, the high TCu concentrations observed in the LRSs are likely linked to the high TSS concentrations that co-occur there. For DZn, the lack of statistical difference in freshwater marina areas may potentially be explained by the lack of loading within the marinas. This will be further explored in the next sub-section.

Sediment

It is difficult to draw clear conclusions from the sediment data considering that only three freshwater marina areas were sampled and that sediment from salt and brackish water marina areas were not collected and analyzed. Sediment concentrations of TCu and TZn in the three freshwater marinas sampled were statistically higher than the concentrations in their respective LRSs. Results from Pap (2004), which looked at five S.F. Bay Area (saltwater) marina areas, also showed higher sediment metal concentrations inside of marinas versus outside. The same two factors that likely explain the differences in water column concentrations may also play a major role in this observed difference. The loading and marina flushing dynamics may be somewhat different for metals in the sediment versus metals in the water column. For example, higher sediment concentrations of total metals in marinas may be an artifact of greater association of particulate metals with finer sediment particles and organic matter that is typically more prevalent inside of marinas compared to the more well-flushed LRSs, where the sediment is likely to be larger-grained.

Marina Sources of Copper

Wood Preservatives

There are many possible metal sources within a marina. Copper-containing wood preservatives that are used in the marina environment represent a potential copper source. Marina survey responses that were provided to DPR by marina managers (Appendix A) suggested that pilings and other marina-associated structures that are continually or occasionally immersed in the water could leach wood preservatives into marina waters. Creosote, copper borate azol (CBA), chromated copper arsenate (CCA), Copper-Green®, and ammoniacal copper zinc arsenate (ACZA) were identified as being historically or currently used in a few of the marinas. Benicia Marina, Vallejo Marina, Berkeley Marina, Ballena Isle Marina, South Beach Harbor, and Santa Barbara Harbor also reported that there were creosote-treated piles in their marinas, particularly in association with older construction. Considering that creosote is a product of coal tar distillation, the leachate of concern from creosote use is polyaromatic hydrocarbons (PAHs), and does not contain copper in any appreciable amount (U.S. EPA, 2003).

CBA, CCA, Copper-Green®, and ACZA, however, do leach copper and have the potential to contribute to copper levels in the marinas. Berkeley Marina reported that limited replacement piles for wood and all other wood treated at the marina are treated with CBA. Antioch Marina reported that some of its wood is treated with CCA although none of the wood is submerged. Copper-Green®, a copper naphthenate compound, is reportedly used for the treatment of the ends of pressure-treated wood in Monterey Harbor. The survey response suggests, however, that there is limited use of wooden materials in the marina area and that the treated materials are not submerged in marina waters. Lastly, Santa Barbara Harbor reported that wooden walers, stringers, and deck boards at the marina are treated with ACZA. Again, these are above-water uses, and continuous and direct leaching into the water column is unlikely although contamination associated with rain events or structural washing and rinsing is still possible.

Considering the wood preservative use information that were submitted by marina managers via the marina survey, it is unlikely that copper-treated wood had a significant direct influence on the water column concentrations of copper observed during the study. Note that survey responses also suggest that the recent trend in marina construction appears to be in incorporating more concrete and pressure-treated wood (without added preservatives) on newer structures.

Background Load

A sizable portion of the copper load in the marina's water column can be attributed to the local background load of copper. For example, at the Ballena Isle Marina area, the measured median DCu concentrations were 2.8 µg/L in the marina and 1.4 µg/L for the LRSs. Assuming that the copper load measured at the LRSs originated from non-marina sources and not the marina itself, then local background sources of copper from San Francisco Bay could have contributed as much as 50% of the load characterized at Ballena Isle Marina. An inverse perspective to this is that copper sources within Ballena Isle Marina caused the copper concentrations to be twice as high as the local background level. Thus, if loading from all the marina sources suddenly ceases, then the marina concentrations of copper should approach those of the LRS concentrations. Since the background metal load of each marina area is unique, it was necessary to take LRS samples at all the marinas. This observation also assumes that the copper concentrations measured at the LRSs are a good approximation of the local water body's background load.

Marina Sediment

The marina's underlying sediment also represents a potential intermediary source despite the popular view that it simply acts as a sink for heavy metals. A sizable portion of copper in the marina sediment could have originated from sources within the marina as well as from sources external to the marina that are deposited via (1) wet deposition (rain runoff and flows generated from rain events), (2) dry deposition, and (3) deposition via currents or wave action.

Once deposited, sediment-bound copper can be reintroduced into the water column via diffusion or particle resuspension and subsequent desorption. In fact, desorption from resuspended particles could be a significant source of DCu to the water column as demonstrated by Gee and Bruland (2002) for the southern portion of S.F. Bay. In the Gee and Bruland (2002) study, even with the accounting of regional point-source discharges, a significant portion of DCu in the South Bay was still attributable to DCu that was released from suspended bay sediment. Thus, a significant net movement of copper from the sediment to the water column is therefore possible.

Before generally transposing the finding for South S.F. Bay to the marina environment, it is necessary to consider the differences between the open bay environment and the typical marina environment. South S.F. Bay is a large water body with a significantly large sediment-water column surface area for diffusion and partitioning interaction. Moreover, the S.F. Bay is shallow and relatively vulnerable to perturbations from the wind and water movement. The scale of sediment-water column interface in a marina is much smaller and the marina sediment bed is, by design, much more protected from perturbations compared to the exposed sediment in the open bay. Furthermore, there is a potentially substantial source of copper in the marina (i.e., boat antifouling paints that are designed to leach copper directly into the water column) to factor into the source calculation.

So, although the marina sediment may not appear to be the chief contributor to the copper concentrations in the marina water column, it does not mean that contributions from the sediment are necessarily fixed or that sediment contributions will remain small. Since copper concentrations in the water column and sediment are continually seeking a state of equilibrium, sediment desorption could become a more significant pathway for copper release into the water column if copper concentrations in the marina sediment are high enough and/or if loading from the other marina inputs to the water column sharply declined. This potential shift in contributions was specifically noted as a peer review comment in the SIYB TMDL (SDRWQCB, 2005).

Note that the background load of copper in the LRS should, to some extent, account for copper that is released through the sediment diffusion and resuspension process, at least for the larger water body in which the marina resides. In this way, the magnitude of sediment contributions may be partially accounted for by the LRS results.

Antifouling Paints

AFPs that are applied to boat hulls are one of the most commonly identified major sources for copper in the marina environment (Jones and Bolam, 2007; Srinivasan and Swain, 2007; Pap 2004; Hall and Anderson, 1999; Matthiessen et al., 1999; Hall et al., 1998; Katz, 1998; Goh and Chou, 1997; McPherson and Peters, 1995; Claisse and Alzieu, 1993; Young et al., 1979).

There are over 170 copper AFP products (including a few manufacturing use products) currently registered with DPR in 2007. However, reporting of AFP applications (with the exception of TBT since it is a restricted use pesticide) is

not required by DPR. Therefore, it is difficult to develop a good understanding of the use pattern and use amount for copper or any other types of non-TBT AFPs.

Researchers have attempted to estimate copper loading from AFP sources. In 1979, SCCWRP estimated that as much as 180 metric tons of copper were applied annually to boat hulls in Southern California (Young et al., 1979). Furthermore, it estimated that this load represented at least twice the amount that enters the Southern California coastal waters from storm runoff and aerial deposition. At that time, TBT AFPs were still commonly used. Thus, this particular copper AFP use estimate undoubtedly represents a smaller fraction than what is being used in recent years. With the additional restrictions put on TBT AFPs in the U.S. and abroad, copper AFPs have become the most popular AFP for recreational boats (Young et al., 1979; Claisse and Alzieu, 1993). Today, more than 95% of AFPs registered for sale and use in California contain copper biocides.

In recent years, U.S. EPA has generated a more contemporary estimate of copper loading from AFP use in the Lower Newport Bay (LNB) area, which harbors approximately 10,000 boats. The Agency estimated that boat AFPs contribute more than 62,000 lbs. of copper (via passive leaching and underwater hull cleaning) into LNB waters annually (U.S. EPA, 2002). U.S. EPA believed that this load could account for as much as 80% of all copper input into LNB.

Two copper source loading studies for San Diego Bay were conducted by the U.S. Navy and by private researchers in the late 1990s (Johnson et al., 1998; PRC, 1997). Both of these studies concluded that AFPs accounted for the majority of DCu loading to the Bay. For SIYB, SDRWQCB estimated that passive leaching and underwater hull cleaning of boat hulls painted with copper AFPs combine to contribute 98% to the basin's copper load (SDRWQCB, 2005).

Field observations and anecdotal evidence show that AFPs are regularly used on boats that operate in salt and brackish waters. The use of copper AFPs is necessary to combat continual hull-fouling pressures (particularly hard fouling) that exist in the salt and brackish aquatic environment. Moreover, the largest marinas in California tend to be located in saltwater areas. Thus, we expected to see the highest copper concentrations in saltwater marinas. The eight highest marina median DCu concentrations are from saltwater marinas. The marinas with the largest assemblages of boats (i.e., Mdr front and back basins) exhibited the greatest marina median DCu and TCu concentrations. And although two saltwater marinas—San Francisco and Alamitos Bay marinas—exhibited very low DCu concentrations, the hydraulic flushing regimes at these sites may serve to explain this deviation.

Since hard fouling is not a major issue in freshwater, boats in freshwater areas do not need to rely as heavily on copper AFPs to protect their hulls. Therefore, freshwater marinas, particularly those that are in landlocked water bodies, tend to have very few boats with hulls painted with AFPs. Also, marinas in freshwater tend to be smaller (contain less slips for mooring) especially when compared to their saltwater counterparts. Moreover, boats in freshwater marinas may not spend as much time in the water due to trailering practices and the relative ease of dry storage. Considering these potential loading factors, we expected to see the lowest copper concentrations in freshwater marinas. The two lake marinas in our study—Tahoe Keys and Folsom Lake—exhibited the two lowest median DCu concentrations by far among all the marinas.

In our study, when all the marina DCu data were separated by water types and compared, DCu concentrations in salt and brackish water marinas were statistically higher than DCu concentrations in freshwater marinas. This finding is consistent with our observations of AFP use and water types since AFP use appears to be more prevalent among boats that are moored in salt and brackish waters.

It is important to note, however, that boats that are moored in some freshwater marinas may occasionally spend time in salt or brackish water during their use. So, in some cases, AFPs are employed on these boats. Some of the boats observed at Sacramento and Village West marinas had AFPs on their hulls. The use of AFPs there is likely a reflection of the periodic operation of these boats in the adjacent saline waters of S.F. Bay and beyond. This may explain why these two freshwater marinas exhibited moderate marina median DCu concentrations and why concentrations of DCu and TCu were also distinctly higher inside of these two marinas compared to their LRSs.

There are likely other noteworthy sources of copper that exist within the marina environment. In the end, until an exhaustive source identification and copper mass loading study in the marina environment can be done, it will be difficult to precisely allocate loading from all the various marina sources. Such a study may perhaps identify

additional sources. In 2007, MEC Environmental initiated a monitoring study of various marina-associated pollutants (including metals) in a protected water area prior to the construction and operation of a marina facility (R. Schottle, personal communication, 2007). The findings from this study should provide a clearer picture on the effects of boat-associated pollutants on existing background conditions.

At this time, considering (1) the study results for DCu and TCu, (2) the available scientific literature, (3) field observations and anecdotal evidence (including responses from the marina survey), (4) the consideration of other likely sources of copper in the marina environment, and (5) the predominant use of copper AFPs compared to other types of AFPs in California, it is likely that boat AFPs are the most significant source of copper in salt and brackish water marinas, particularly during periods of dry weather.

The level of AFP contribution will vary from marina to marina due to site-specific factors. However, it is likely that contributions of AFPs to the marina's water column load of copper is highest in (1) saltwater marinas where AFP use is high, (2) larger marinas where there is a high number of AFP-painted vessels, and (3) locations where contributions from non-AFP marina sources are relatively low. In particular, the concentrations of copper in the LRSs of many of the marina areas suggest that the background load of copper must always be considered when marina concentrations of copper are evaluated, as these loads could represent a sizable portion of what is observed in the marina.

Marina Sources of Zinc

Antifouling Paints

Zinc is a common marina pollutant found at elevated concentrations in marina waters and sediments (Singhasemanon, 2004). Some AFPs contain and leach zinc. The sole zinc biocide, contained in AFPs sold and use in California, is zinc pyrithione (ZnPt₂ or trade name Zinc Omadine®). This chemical is used as a booster biocide, which supplements the antifouling effects of a product's primary biocide to be effective on a wider range of fouling pests. Thus, ZnPt₂ usually makes up a lower percentage of an AFP product than the primary active ingredient. There are 25 AFP products (including several manufacturing-use products) that contain ZnPt₂ currently registered with DPR for use in California.

Zinc oxide is also a non-biocidal component in AFPs; however, the water quality implications of this relatively water-insoluble compound have not been well studied. Therefore, at this time, it is difficult to estimate or evaluate the contribution of zinc oxide from leaching or underwater hull cleaning activities to the overall marina water column or sediment zinc load. Future evaluations of zinc in marinas should involve the determination of contributions of zinc oxide from AFP use.

Wood Preservatives

One wood preservative, ACZA, contains zinc. However, only the marina at Santa Barbara Harbor reported ACZA use on some of its above-water structures. Therefore, the very limited use of zinc-based wood preservative makes them an unlikely major source of zinc to the marina environment.

Sacrificial Anodes

Zinc is also used in saltwater areas as sacrificial anodes that are attached to boat hulls and other metal surfaces that come into contact with saltwater. Zinc anodes protect less-corrodible metals (e.g., copper) from decay while sacrificing themselves in the process resulting in a continual release of zinc ions into the surrounding water.

Aluminum-based anodes are preferred for anodic protection in brackish waters, and magnesium-based anodes in freshwater. In our study, DZn concentrations tend to be high in saltwater marinas, particularly the larger marinas along the Central and South Coast. Brackish and freshwater marinas tend to exhibit lower DZn concentrations. This difference in DZn concentrations among water types (saltwater > fresh and brackish water) was statistically significant. Therefore, the magnitude of DZn concentrations in the study marinas is consistent with the general use pattern of zinc anodes. Bird et al. (1996) and Matthiessen et al. (1999) established that sacrificial zinc anodes are the major source on zinc in the marina environment. Moreover, both studies found that emissions from sacrificial anodes

are so great that they appear to be a major influence on zinc levels in the larger water body in which marinas are a part of.

At this time, considering (1) the study results for DZn, (2) the available scientific literature, (3) field observations and anecdotal evidence (including responses from the marina survey), (4) the consideration of other likely sources of zinc in the marina environment, and (5) the limited use of zinc AFPs in California, it is likely that sacrificial anodes are the most significant source of zinc in saltwater marinas during periods of dry weather. In California's saltwater marinas, the contribution of AFPs to the marina zinc load is likely to be smaller than the contribution from ubiquitous zinc anodes. For fresh and brackish water marinas, the significance of zinc anodes to the marina load of zinc is likely to be smaller due to boaters' reliance on non-zinc sacrificial anodes. Regardless of the relative ranking of the sources of zinc in marinas across different water types, the current zinc load from the combined applications and sources of zinc in the marina environment is not significant enough to result in a water column concentration that exceeds water quality standards.

Toxicity/Toxicant Identification Evaluation

Toxicity tests were conducted to assess the potential adverse impacts of the water samples to pre-selected test organisms and toxic endpoints. Toxicity tests are common tools that are used by agencies, including those that regulate water quality (i.e., RWQCBs), to determine if biological impairments exist.

Eight of the 47 water samples were toxic to copper-sensitive mussel embryo development bioassays. Seven of these eight toxic samples were collected from MdR. The DCu concentrations in these seven samples ranged from 11.5–18.4 µg/L. These concentrations are within the range of documented EC₅₀ values from similar toxicity tests as compiled and discussed in Arnold et al. (2005b). Thus, these toxicity results were within the expected concentration range. The toxicity that was observed in the sample that came from MBYH, however, was more surprising. The DCu concentration in the MBYH sample in question was only 1.7 µg/L; however, statistically significant toxicity (albeit relatively low) was observed. It is possible that a false positive or type I error occurred in the analysis of this sample.

Two of the toxic samples from MdR were selected for TIE tests. The tests determined that a trace metal (most likely copper) was the likely cause of toxicity in these samples. Considering the TIE results and the high DCu concentrations of the all the samples taken at MdR, persistent toxicity to *M. galloprovincialis* may exist in the waters of MdR. The regular exceedances of the CTR acute copper standard at this location also strongly suggest that there may be a significant risk to aquatic organisms at MdR. If biological and ecological impacts from copper are to be studied, MdR would be an excellent candidate location based on the frequent occurrences and high magnitude of DCu and TCu concentrations observed there. DCu concentrations documented at MdR are even higher than the concentrations documented at SIYB in San Diego Bay (SDRWQCB, 2005).

Although toxicity samples were also collected from Pittsburg, Benicia, Vallejo, Loch Lomond, Berkeley, San Francisco, South Beach Harbor, Downtown Shoreline, and Alamos Bay marinas, none of the samples taken from these locations exhibited any statistically significant toxicity. The five highest DCu concentrations outside of the MBYH and MdR samples were 8.9, 7.7, 7.4, 5.3, and 5.3 µg/L. Thus, DCu concentrations as high as 8.9 µg/L did not induce a response in the copper sensitive toxicity test. Although the water chemistry of each sample, particularly those factors that regulate the bioavailability of copper, must be taken into consideration (e.g., DOC, pH), it is remarkable to see that DCu concentrations that are close to two times higher than the CTR saltwater acute standard were not toxic in the copper-sensitive *M. galloprovincialis* test. This observation confirms the protective nature and intent of the CTR standards that were originally derived from U.S. EPA's aquatic life criteria development process.

In this study, we specifically considered the toxicity of copper to a mussel species. However, recent studies suggest that low parts-per-billion concentrations of dissolved copper can negatively impact olfactory sensory neurons and predator avoidance behaviors of salmonids that are critical for their survival (McIntyre et al., 2007; Pyle and Mirza, 2007; McPherson et al., 2004). Therefore, elevated copper concentrations observed in many marinas in this study, even at levels that may not affect mussel species, could potentially be hazardous to salmonids. Future consideration of the aquatic impacts of copper must certainly evaluate this aspect of toxicity.

Predictive Copper Toxicity Models

Since it is impractical and expensive to conduct toxicity tests on all the study samples, predictive toxicity models offered an alternate way to generate information on potential biological impacts. The predictive toxicity models (i.e., the freshwater Biotic Ligand Model [BLM], saltwater BLM, and Dissolved Organic Carbon [DOC] model) employed in this study focused on the potential effects of copper on aquatic test organisms. These models are notable in that they all take into account site-specific water quality characteristics that affect the bioavailability of copper to affect aquatic organisms.

The freshwater BLM has already been adopted by U.S. EPA as the recommended approach to calculate the national ambient water quality criteria for copper (U.S. EPA, 2007). U.S. EPA is considering the applicability of the saltwater BLM as the basis for an update to its saltwater criteria. California's CTR standards were based on an older version of the federal criteria. Ultimately, U.S. EPA considers the current BLM-based approach to be more scientifically sound than the previous approach, which did not adequately integrate the impacts of bioavailability. Moreover, the revised criteria should replace the need for resource intensive site-specific adjustments for freshwater using the water effect ratio.

For our study, the freshwater BLM predicted that seven of 53 freshwater samples would exceed the 1-TU threshold. A closer evaluation of these results strongly suggested that only two of these seven toxicity predictions were reliable (see the Freshwater BLM Results Section). In comparison, DCu concentrations from all 53 samples evaluated by the model never exceeded the CTR freshwater CCC (chronic) and CMC (acute) standards. Thus, the freshwater BLM predicted that some risk (albeit low) to aquatic life exists due to the exposure to copper, while existing standards suggested that aquatic organisms are fully protected.

We also used a DOC-based model, as presented in Arnold et al. (2005) to evaluate the potential toxicity of salt and brackish water samples. Out of the 412 salt and brackish water samples evaluated, 86 (21%) contained high enough concentrations of DCu to equal or exceed the DOC-model predicted FCC and 54 of those also exceeded the FAC. Measured DCu concentrations tend to exceed CTR standards more frequently than DOC-model predicted toxicity thresholds. Occasionally, the opposite is true. This is most noticeable at San Francisco Marina, Santa Cruz Harbor, Monterey Harbor, and Santa Barbara Harbor. This phenomenon is most likely a reflection of the relatively low DOC concentrations that occur at these locations during our sampling events. Overall, the DOC model predicted water column toxicity well (89% success rate) when compared to actual toxicity test results from this study.

A draft saltwater BLM was recently completed for use on salt and brackish water samples. At this time, the model was only able to generate predicted EC₅₀ thresholds for *M. galloprovincialis* and *S. purpuratus*. It was not possible to generate CCC and CMC thresholds with which a more complete evaluation of risk to aquatic organisms could be made. However, the comparison of predicted acute TUs for *M. galloprovincialis* to actual toxicity results still allowed us to factor in the site-specific bioavailability of copper to determine if samples could be toxic to a copper-sensitive test organism and endpoint. Sixty seven of 373 samples (for which output could be calculated) or 18% of the samples contained a high enough concentration of DCu to reach or exceed the 1-TU threshold. Recall that since the acute CMC thresholds could not be calculated, a comparison of saltwater BLM results to CTR standards is not possible. Overall, the saltwater BLM predicted EC₅₀'s for *M. galloprovincialis* were in good agreement with actual toxicity (88% success rate). A comparison was not done for *S. purpuratus* since toxicity tests were not conducted on them.

The fact that about 98% of all the samples for which toxicity was predicted were marina samples strongly suggests that the existing load of copper (representing the combined sources within a marina) in many of the study's marinas is high enough to pose a risk to copper-sensitive aquatic organisms. Risks for the LRSs, which were immediately adjacent to the marinas, appear to be much lower. Thus, the study of copper toxicity and impacts of copper to aquatic communities in marinas should be an important area for future research.

Scientific validation of these models with data from other studies has, thus far, been strong. Overall, agreement of model prediction to our toxicity results is also very good. Our comparison of the DOC model's and the saltwater BLM's predicted toxicity to actual toxicity results did show that these models tend to slightly over-predict toxicity. However, considering that the use of these models provide an inexpensive way to estimate toxicity and a more precise prediction of biological effects by accounting for bioavailability, these models appear to be reliable tools in the future evaluation of the potential ecological impacts from copper exposure.

V. Conclusions

The extensive monitoring of marina areas showed that California marinas have elevated concentrations of DCu, TCu, and DZn. Higher water column concentrations of these metals tend to occur in larger saltwater marinas such as those along the State's Central and South Coast. Lower concentrations were found in marinas that are located in freshwater lakes or in areas that are well-flushed.

Despite being frequently elevated compared to background levels, DCu and DZn concentrations in freshwater marinas were always below CTR freshwater standards for copper and zinc. Saltwater DZn concentrations were also always below CTR saltwater zinc standards. However, in many salt and brackish water marinas, DCu concentrations regularly exceed CTR water quality standards that have been established for the protection of aquatic life. Toxicity tests showed that marina water samples were sometimes disruptive to the normal development of mussel embryos. An evaluation of two of the toxic samples pointed to high concentrations of DCu as the most likely cause of the observed toxicity. Predictive toxicity models, which accounted for bioavailability, determined that many of the marina samples collected were likely to be toxic to copper-sensitive aquatic organisms.

Our source evaluation and the consideration of past research on metal sources in marinas suggest that for salt and brackish water marinas, AFPs are likely a major source of copper, particularly during periods of dry weather. The contribution of AFPs to the total marina copper load, however, will vary from marina to marina depending on the magnitude of each water body's background load and other marina sources. In brackish water marinas and many San Francisco Bay Area marinas where the background load of copper tends to be high, AFP use contributes less to the marina copper load than in Central and South Coast marinas where the background load tends to be low. Nonetheless, copper that is generated from leaching of AFPs and underwater hull cleaning of these paints clearly contribute to the exceedance of copper water quality standards.

Considering that water in 16 of the marinas in our study exceeded water quality standards for copper, it is possible that these areas will be placed on the CWA 303(d) impaired water bodies list. Moreover, recent studies of copper in Lower Newport Bay and along California's South Coast (Dana Point to the U.S./Mexico border) have shown that many of the marinas in these areas also exceeded the same standards. Therefore, it is possible that more than 40 California marinas could be placed on the CWA 303(d) list due to elevated DCu concentrations. Placement on this list could eventually result in TMDL development.

In recent years, there has been an increase in the registration of AFP products with ZnPt₂ as the primary active ingredient. If ZnPt₂ products gain a larger foothold on the AFP market (e.g., as a replacement for copper AFPs), contributions of zinc AFPs to the marina zinc load will increase and potentially lead to zinc-related toxicity. Future evaluations of ecological risks due to zinc AFP use should not rely solely on the comparison of water column or sediment concentrations of zinc to standards and guidelines, but also on the spatial and temporal distribution of the biocide ZnPt₂ and its trans-chelation product CuPt₂. CuPt₂ is more stable and more toxic to aquatic organisms than ZnPt₂. Conversion of ZnPt₂ to CuPt₂ tends to occur in natural water where copper concentrations are high like in some marinas.

At this time, U.S. EPA continues to refine its risk characterizations for antimicrobial uses of copper oxide and ZnPt₂. Once this characterization is complete, the Agency will evaluate its risk management options and announce its risk management decisions. U.S. EPA is also developing discharge permits for recreational and commercial vessels. Discharges from AFP use are currently included in these permits. Overall, these federal activities may potentially have a significant impact on how States, including California, regulate and use copper and zinc AFPs in the future.

VI. References

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