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Extent and Magnitude of Copper Contamination in Marinas of the San Diego Region, California

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ABSTRACT

Marinas are areas of special water quality concern because of the potential for pollutant accumulation within their protected waters. Perhaps the largest contaminant source to marinas is antifouling paints that leach copper to prevent the growth of encrusting organisms on vessel bottoms. Despite the potential environmental risk in marinas, particularly in San Diego, California, where as many as 17,000 recreational vessels are berthed, very little monitoring of marinas has been conducted. The objective of this study was two-fold: 1) Determine the extent and magnitude of dissolved copper concentrations in marinas throughout the San Diego region, and 2) Determine if elevated copper concentrations in marinas of the San Diego region are resulting in adverse biological impacts. A probabilistic study design was used to sample water-column copper concentrations and toxicity (using *Mytilus galloprovincialis*) at 30 stations. Results indicated that exceedance of state water quality objectives was widespread (86% of marina area), but that toxicity was much less prevalent (21% of marina area). Toxicity identification evaluations (TIEs) conducted at the most toxic sites indicated that toxicity was largely due to trace metals, most likely copper. Toxicity was reduced using TIE treatments that chelated trace metals such as cation exchange column, ethylenediaminetetraacetic acid (EDTA), sodium thiosulfate (STS). Moreover, increasing dissolved copper concentrations correlated with increasing toxicity and these copper concentrations were high enough to account for virtually all of the observed toxicity.

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INTRODUCTION

Marinas are areas of special water quality concern because of the potential for pollutant accumulation. There are several potential contaminant sources to enclosed harbors that can decrease water quality, including vessel antifouling coatings, shipyard or boatyard discharges, runoff from adjoining urban and industrial areas, motor exhaust, and hazardous material spills, among others. Exacerbating the concern over water quality is that marinas are, by definition, areas that require calm waters for navigation and berthing. Therefore, pollutant inputs might not sufficiently mix and disperse, but rather accumulate to environmentally hazardous levels in marinas.

Perhaps the largest contaminant source to marinas is vessel antifouling paints. Antifouling paints are designed to slowly release biocides in order to prevent the growth of encrusting organisms and algae that will corrode fittings, decrease speed, and increase fuel consumption (WHOI 1952). Copper is currently among the most commonly used biocides in recreational vessel antifouling paints (Valkirs 2003). Schiff et al. (2004) demonstrated that these paints, which may contain between 20% and 76% copper content (as cuprous oxide), leach approximately 4.0 $\mu g/cm^2$/day or roughly 25 g/month for a typical 9 m power boat.

The problem of copper inputs is likely to be aggravated in marinas with very dense berthing. Marinas in the San Diego region of California berth more than 17,000 recreational vessels, yet very little monitoring of marinas for copper has been conducted. The data that has been collected indicate that water quality problems may exist. Water column surveys from San Diego Bay indicated that some of the greatest concentrations of dissolved copper were found near enclosed yacht basins (Zirino et al. 1998). Sediment chemistry monitoring has indicated that the greatest concentrations occurred in marinas compared to other port/harbor areas (Noblet et al. 2002). Only two directed surveys of copper concentrations in marinas have been conducted in the San Diego region. The first examined dissolved copper concentrations across several yacht basins, but was conducted more than 10 years ago (McPherson and Peters 1995). The second focused on only a single yacht basin, but resulted in a total maximum daily load for copper (SDRWQCB 2005).

This study attempts to answer two primary questions: 1) What is the extent and magnitude of dissolved copper concentrations in marinas throughout the San Diego region? and 2) Are elevated copper concentrations in marinas of the San Diego region resulting in adverse biological impacts? The goal of the first question is to ascertain if copper contamination in marinas is a large-scale regionwide (or greater) management problem, or if it is an isolated issue best managed at the local level. The context of extent and magnitude is predicated upon the use of water quality thresholds. Answering the second question is important because water quality thresholds may or may not be entirely predictive of potential environmental impact. Therefore, it is important to validate that observed “high” concentrations, if encountered, result in adverse biological impacts and to confirm that these impacts are the result of copper rather than one of the other potential contaminants found in marinas. The potential for biological impacts in this study will be assessed using toxicity tests followed by toxicity identification evaluations.

METHODS

There are four main publicly accessible embayments in the San Diego region; Dana Point Harbor, Oceanside Harbor, Mission Bay, and San Diego Bay. Within these four harbors, there are 12 yacht basins. A randomized sampling design was used to assess the extent and magnitude of copper concentrations and toxicity for this study. Samples were allocated randomly within these yacht basins, ensuring that at least one sampling site occurred within each embayment. This design allows for an unbiased estimate of average concentrations or toxic effect, as well as the percent area (in two dimensions) or percent volume (in three dimensions) that exceeds thresholds of concern cumulatively across all yacht basins. However, it provides very little information on the status of any single yacht basin. Therefore, this study will describe conditions across all yacht basins in total and, for the most part, refrain from making conclusions regarding individual harbors.

Sampling and Analysis

Thirty sites were selected throughout the San Diego region (Table 1). Samples were collected from marinas in Dana Point Harbor, Oceanside Harbor, and Mission Bay on August 15, 2005, and from marinas in San Diego Bay on August 29, 2005. Samples for chemical analysis were collected at three depths (0.5 m below the surface, at mid-depth, and near the bottom) using a Niskin sampler. The samples were immediately filtered to 0.45 µm (Life Sciences GN-6 filters) into precleaned I-Chem 300 high density polyethylene bottles and acidified to pH <2 with nitric acid (Omni trace ultra). Samples for toxicity were collected only at the surface (ca. 0.5 m) and transferred to 1-L cubitainers without acid or other preservatives. All samples were maintained on ice for transport to the respective analytical laboratories.

Dissolved copper concentrations were analyzed using inductively-coupled plasma mass spectrometry (ICPMS) following United States Environmental Protection Agency (EPA) Method 200.8. All batches of 20 or fewer samples were accompanied using quality assurance/quality control samples. Negative controls never exceeded the method detection limit (0.16 µg/L). All matrix spikes were within 25% of nominal values. All laboratory duplicates and matrix spike duplicates were within 30% of the original sample.

All toxicity tests were conducted using the mussel *Mytilus galloprovincialis* using the EPA method for Short Term Chronic Toxicity Tests (US EPA 1995). This short-term chronic test challenges the ability of the mussel embryo to develop normally after fertilized eggs were exposed to samples for 48 hr. Mussels were obtained from Carlsbad Aquafarms, (Carlsbad, CA). 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 conducted as positive control. After 48 h, the embryos were preserved and examined using a microscope to assess the percentage of normal development. Toxic effects are expressed as normal development relative to control development.

Six of the most toxic samples were selected for Phase I Toxicity Identification Evaluation (TIE) procedures (EPA 1996). These procedures were used to help identify the class of the contaminant(s) that are likely causing the observed toxicity. Each TIE treatment was designed to selectively remove or neutralize classes of compounds and their associated toxicity. Treated samples were then re-tested to observe if differences in normal embryo development resulted.

Table 1. Sampling site information. NAD83 datum.

Location	Station ID	Latitude	Longitude	Station Depth (m)
Dana Point Harbor	D1	33.4601	-117.7007	4.2
Dana Point Harbor	D2	33.4604	-117.6953	4.0
Dana Point Harbor	D3	33.4601	-117.6980	4.8
Dana Point Harbor	D4	33.4585	-117.6934	4.8
Dana Point Harbor	D5	33.4608	-117.6971	4.4
Oceanside Harbor	O1	33.2058	-117.3915	5.0
Oceanside Harbor	O2	33.2100	-117.3961	4.8
Mission Bay	M1	32.7637	-117.2043	7.8
Mission Bay	M2	32.7666	-117.2355	4.4
Mission Bay	M3	32.7776	-117.2489	3.7
San Diego Bay	S1	32.7201	-117.2202	3.8
San Diego Bay	S2	32.7195	-117.2224	4.4
San Diego Bay	S3	32.7217	-117.2233	3.8
San Diego Bay	S4	32.7159	-117.2281	4.6
San Diego Bay	S5	32.7145	-117.2323	5.9
San Diego Bay	S6	32.7266	-117.2084	4.4
San Diego Bay	S7	32.6252	-117.1044	3.2
San Diego Bay	S8	32.7207	-117.2266	3.8
San Diego Bay	S9	32.6291	-117.1345	3.8
San Diego Bay	S10	32.7191	-117.2271	4.3
San Diego Bay	S11	32.7176	-117.2337	3.0
San Diego Bay	S12	32.6246	-117.1052	3.9
San Diego Bay	S13	32.6240	-117.1022	3.7
San Diego Bay	S14	32.6213	-117.1012	3.7
San Diego Bay	S15	32.7153	-117.2331	3.4
San Diego Bay	S16	32.7262	-117.2071	4.5
San Diego Bay	S17	32.7166	-117.2295	5.9
San Diego Bay	S18	32.7275	-117.2003	5.0
San Diego Bay	S19	32.7113	-117.1733	6.0
San Diego Bay	S20	32.7159	-117.2326	3.7

Seven TIE treatments were conducted during this study including centrifugation (particle removal), C18 column (non-polar organics removal), cation exchange column (metals chelation), two concentrations of ethylenediaminetetraacetic acid (EDTA) (metals chelation), sodium thiosulfate (STS) (reduces oxidants and chelates some metals), and no treatment (TIE baseline sample). A control sample was included with each type of treatment to verify the toxicity of each manipulation. Samples for each treatment were tested at 50% (diluted with seawater) and 100% sample strength.

EDTA was added to a concentration of 30 and 60 mg/L to each test sample. STS was added to a concentration of 50 mg/L with no significant control response. The EDTA and sodium thiosulfate treatments were given at least one hour to interact with the sample prior to the start of toxicity testing. Samples were centrifuged for 30 min at 3000xG to remove particle-borne contaminants. In addition, samples were centrifuged to remove particles prior to being passed through the cation exchange (Supelco Supelclean LC-WCX SPE) or C18 (Varian Mega Bond Elut solid phase extraction) columns. Eluates of both the C18 and cation exchange columns were tested for chemistry as well as toxicity.

Data Analysis

Dissolved copper concentration data were analyzed in three fashions. First, the spatial extent and magnitude of dissolved copper was examined by creating a thematic map of surface water concentrations. Second, summary statistics including area weighted mean dissolved copper concentrations were examined by depth for spatial gradients. Finally, the relative percent area and volume in marinas that exceeded water quality thresholds was estimated. In this case, the most appropriate threshold is chronic water quality criterion of 3.1 µg/L (SWRCB 2000).

Toxicity data were analyzed in four fashions. First, the spatial extent and magnitude of toxicity was examined by creating a thematic map of surface water concentrations. Second, summary statistics including area weighted mean response levels were calculated. Third, the relative percent area in marinas that were toxic was estimated. Toxicity was defined as significantly different (using t-tests) and < 80% of normal development relative to controls. Finally, TIE data were evaluated to determine the potential constituent(s) responsible for the observed toxicity. TIE interpretation included examining treatment effectiveness, correlation with sample concentrations, and predicted toxicity based on copper levels found in each sample.

RESULTS

Dissolved copper contamination was widespread in the marinas of the San Diego region (Figure 1). Concentrations in the surface water samples ranged from nondetectable to 21.0 µg/L and averaged 7 µg/L (Table 2). All the study areas had elevated copper concentrations with the greatest concentrations observed in Dana Point Harbor. The lowest concentrations were generally found in Oceanside Harbor. There was a depth related gradient in copper concentrations (Table 2). Dissolved copper was significantly higher in surface than bottom waters ($p = 0.01$, ANOVA).

Dissolved copper concentrations exceeded water quality thresholds in approximately 86% of the marina surface water area (Table 2). The amount of area differed by depth; 83 % of the area exceeded water quality thresholds in mid-depth waters compared to 61% of the area in bottom waters. Integrating by depth, approximately 75% of the volume in marinas of the San Diego region exceeded water quality thresholds for dissolved copper.

Toxicity to mussel embryos was less pervasive than copper contamination (Figure 2). Toxicity was only found in samples from Dana Point Harbor and San Diego Bay (Shelter Island Yacht Basin). Normal development in surface waters ranged from 0-104% of the control response and averaged 79% normal development. In contrast to dissolved copper concentrations, only 21% of the area in marinas of the San Diego region were deemed toxic.

Despite varying levels of baseline toxicity, a similar pattern of TIE treatment effectiveness was observed among all of the samples evaluated. The cation exchange column, STS, and C18 treatments were effective at reducing toxicity in all samples evaluated (Figure 3). In only one sample was toxicity not completely removed. This sample exhibited strong baseline toxicity (0% normal development). The cation exchange was the most effective treatment in this sample followed by C18 and STS (45% and 43% normal development, respectively).

The cation exchange column was a very effective treatment for chelating trace metals. Concentrations of copper were substantially reduced following this treatment (Table 3). Copper concentrations were reduced by an average 76% following the cation exchange column treatment. No concentration exceeded 3.6 µg/L.

The C18 treatments are typically associated with removal of organic constituents. However, C18 columns were also observed to sequester trace metals including copper (Table 3). While not as effective as cation exchange resins, copper concentrations in the C18 eluate were reduced by an average 45% compared to the untreated sample. No concentration exceeded 10.1 µg/L.

EDTA also chelates trace metals, but demonstrated mixed success for marina samples (Figure 3). The mixed success was largely due to EDTA induced toxicity. EDTA controls, where EDTA was mixed with laboratory dilution water to a concentration of 60 mg/L, resulted in 4% normal development relative to laboratory dilution water alone. Interestingly, EDTA associated toxicity decreased after EDTA addition to marina samples. Normal development increased in five of six samples at the 60 mg/L EDTA additions. The improved performance of marina samples was attributed to copper sequestering EDTA. This observation was further supported by 30 mg/L EDTA additions. EDTA treatment controls at 30 mg/L performed much better than the 60 mg/L treatment controls; normal development in 30 mg/L controls averaged 67% normal development. As a result, 30 mg/L EDTA additions to marina samples consistently removed toxicity including complete toxicity removal in three of four samples tested at this concentration.

Centrifugation had little to no effect on toxicity (Figure 3). No change in toxicity was observed in three of the six samples treated. Marginally decreased toxicity was observed in the remaining three samples. Therefore, toxicity was largely not attributed to particulates.

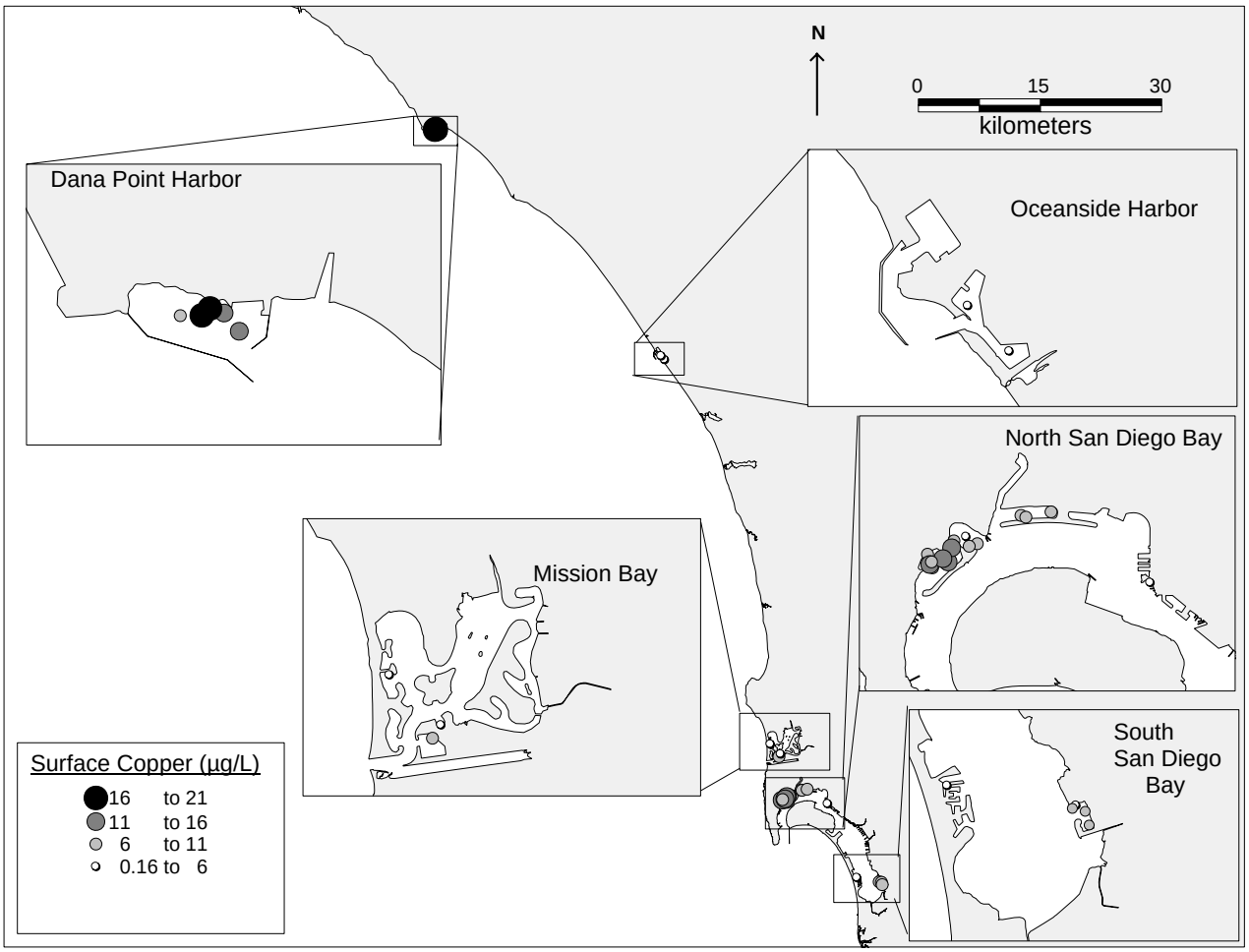

Figure 1. Copper concentrations in marinas of the San Diego region.

Table 2. Summary statistics for copper concentrations and toxicity from marinas in the San Diego region. Non-detects were treated as equal to ½ MDL for all calculations. The units are µg/L for the metals data and % control for the toxicity data. NA = not applicable. The chronic water quality threshold for copper is 3.1 µg/L. The threshold for toxicity is < 80% normal development relative to control.

Parameter	Depth	N	Min	Max	Average (95% C.I.)	Percent Area Exceeding Threshold
Dissolved Cu	All Depths	90	<0.16	21.0	7.0 (6.0 – 7.9)	77%
	Surface	30	1.1	21.0	8.5 (6.8 – 10.3)	86%
	Mid-depth	30	0.6	19.0	7.3 (5.6 – 8.9)	83%
	Bottom	30	<0.16	17.8	5.1 (3.6 – 6.6)	61%
Normal embryo development	Surface	30	0.0	104.5	79.3 (66.6 – 92.0)	21%

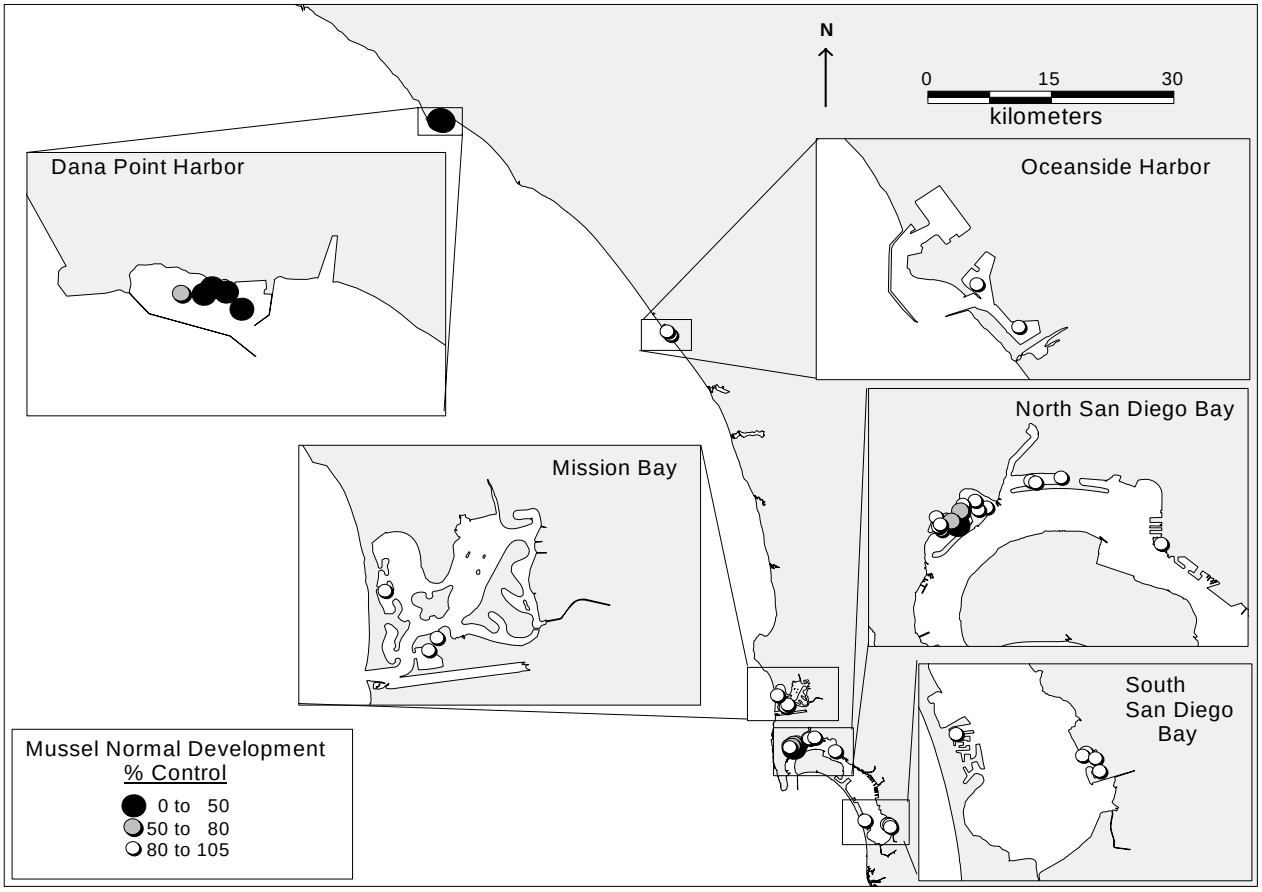

Figure 2. Mussel embryo development in marinas of the San Diego region.

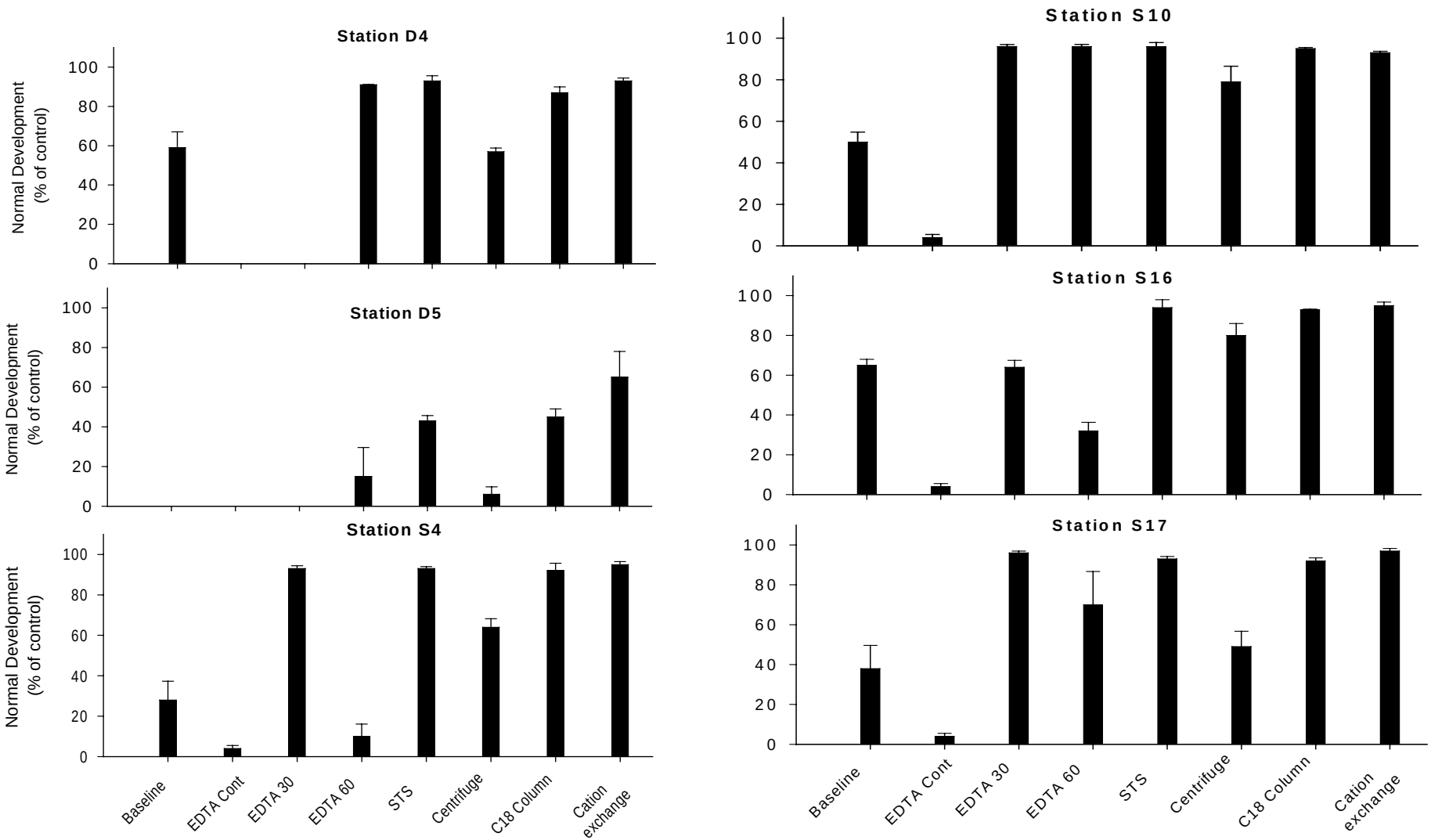

Figure 3. Effectiveness of TIE treatments.

Table 3. Concentrations of dissolved copper in untreated marina samples and samples treated with C18 and cation-exchange columns.

	Dissolved Copper (µg/L)		
Site	**Untreated**	**Post C18**	**Post Cation**
D4	12.0	7.5	2.9
D5	18.1	10.1	3.3
S4	12.7	6.8	3.1
S10	11.6	6.1	3.0
S16	10.4	5.6	2.6
S17	13.4	7.2	3.6

A strong relationship between the concentration of dissolved copper in marina samples and the degree of toxicity was observed (Figure 4). Normal embryo development was negatively correlated with the concentration of dissolved copper in the surface water samples ($r = -0.90$, $p < 0.01$). Moreover, the amount of toxicity measured in the field samples (mean normal embryo development = 70%) was similar to the amount of toxicity predicted from the regression analysis of the concurrent copper reference toxicant tests, and the concentrations of copper in the surface water samples (mean normal embryo development = 69%) (Figure 5).

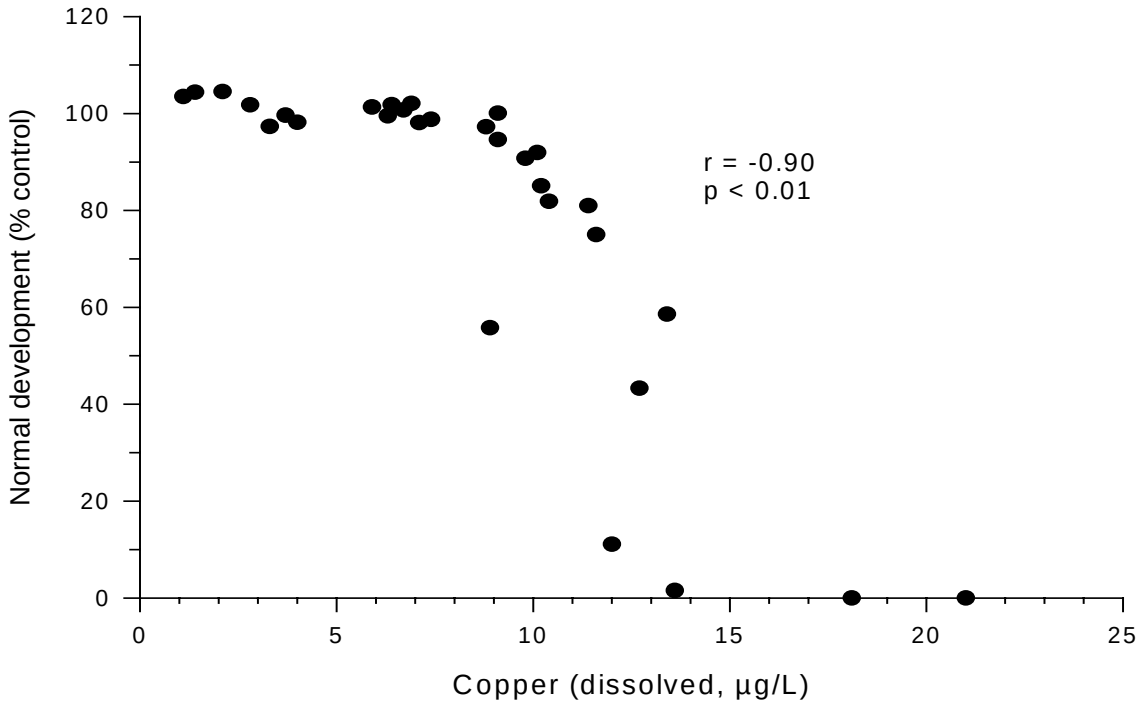

Figure 4. Relationship between mussel embryo development and surface water dissolved copper concentrations.

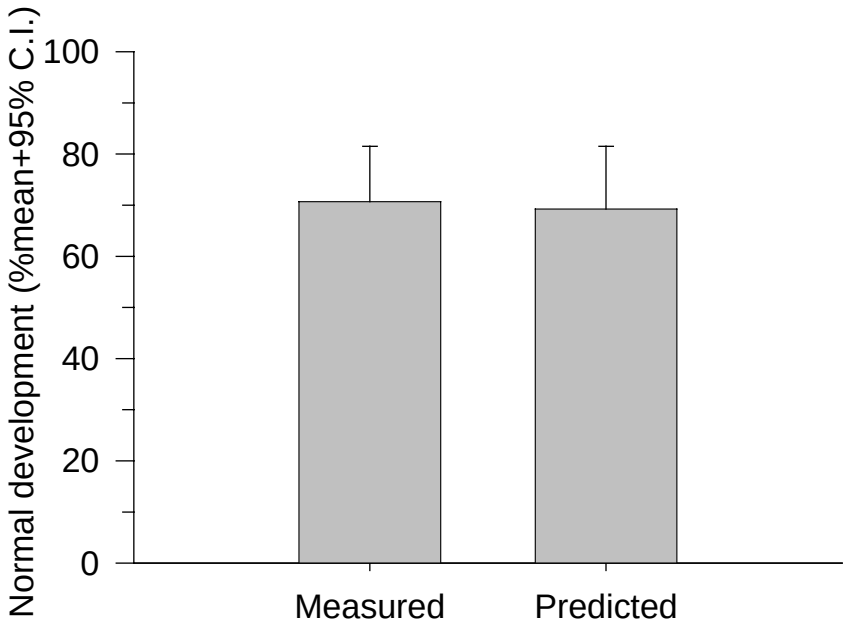

Figure 5. Comparison of average measured to average predicted normal mussel embryo development in the surface waters of San Diego area marinas. The predicted development was calculated from regression analysis of the concurrent copper reference toxicant tests, and the concentrations of copper in the surface water samples. N = 30.

DISCUSSION

This study found widespread copper contamination in the water column of San Diego area marinas. Approximately 86% of the surface water in the marinas exceeded the state water quality threshold for copper. Despite the widespread dissolved copper exceedance, toxicity was observed much less frequently. Abnormal embryo development was only observed in a subset of embayments constituting 21% of the San Diego marina area.

The discontinuity between water quality threshold exceedance and observed toxicity can be at least partially explained by the binding of free-copper ions in the filterable (0.45 µm) phase that was quantified during this study (Arnold et al. 2005). Other investigators have found that the free ion activity within San Diego Bay varies with measurements of colloidal and/or dissolved organic matter (Rivera-Duarte et al. 2005). Rosen et al. (2005) measured water column toxicity in outer San Diego Bay using *Mytilus,* which decreased with increased free copper ion activity and concomitant decreases in dissolved organic matter. Applying the bay-wide water effects ratios developed by Rosen et al. (2005) to our data, however, did not rectify the disparity between predicted water column toxicity based on the revised water quality threshold and the actual amount of measured toxicity.

Dissolved copper concentrations within marinas were influenced by proximity to sources and the potential for mixing and dilution. In this study, the areas with the highest dissolved copper concentrations tended to be associated with greatest vessel density and lowest water circulation. This is consistent with previous findings by others. For example, both Matthiessen et al. (1999) and Hall and Anderson (1999) found that marina and harbor areas in Europe had greater water column concentrations of dissolved copper than estuarine or open coastal areas. Similarly, Hall et al. (1992) found a gradient of dissolved copper with distance away from a marina in Chesapeake Bay, MD. Copper doses to thin films were always greater in marina than non-marina samples in Australia (Webb and Keough 2002). Dissolved copper concentrations increased with distance from the entrance of the Shelter Island Yacht Basin in 2000 (SDRWQCB 2005).

Trace metals, most likely copper, appeared to be the primary cause of toxicity. This idea was supported by two major findings. First, the most effective TIE treatments were those that focused on removal of trace metals. Cation-exchange resins were the most effective, but so were STS and EDTA. Second, there was a strong relationship between increasing concentrations of dissolved copper in the samples and the increasing amount of toxicity observed. Moreover, dissolved copper concentrations were high enough to induce toxicity based upon tests using spiked seawater. In fact, concentrations of dissolved copper were high enough to account for all of the measured toxicity.

While most of the evidence indicates trace metal related toxicity, other toxicants could not be discounted. For example, the C18 column treatments also reduced toxicity. While this may be an indication of toxicity associated with organic contaminants, a substantial reduction (50% on average) in dissolved trace metals from the C18 eluates was also observed, resulting in concentrations below the LC50 for copper. The binding of cationic metals in C18 columns has also been observed in previous experiments (Schiff et al. 2003). Elution of copper from the C18 column would have been a more definitive endpoint for our TIE assessment, but attempts to remove copper from the C18 column in our study were unsuccessful.

Dissolved copper concentrations in this study were similar to, or higher than, concentrations previously reported for marinas in the San Diego region. Dissolved copper concentrations in the

Shelter Island Yacht Basin (6.7 – 13.4 µg/L) were greater than those reported by Krett-Lane in 1980 (4.0 µg/L), by Valkirs et al. in 1994 (3 – 6.9 µg/L), or by McPherson and Peters in 1995 (<5 – 8), but were similar to the findings of Johnston in 1990 (8.9 and 11 µg/L). Dissolved copper concentrations in the nearby America's Cup Yacht Harbor in the current study (3.7 – 8.8 µg/L) were slightly lower than the values reported by McPherson and Peters (1995) (<5 – 11 µg/L), while concentrations in the Harbor Island West Basin from the current study (9.1 – 10.4 µg/L) were slightly greater than those reported by McPherson and Peters (5 – 7 µg/L). Finally, the concentration in Quivira Basin, Mission Bay, were comparable between the current study (6.4 µg/L) and measurements from 10 years ago by McPherson and Peters (1995) (<5 – 6 µg/L).

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