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Study 319 Report: Monitoring of Dissolved Copper in California Coastal Waterbodies

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1.0 Introduction

The use of copper antifouling paints (Cu-AFPs) on waterborne vessels to prevent biofouling has contributed to concentrations of dissolved copper (DCu) that exceed water quality criteria in many saltwater marinas in California.[1] AFPs are used to prevent biofouling on waterborne vessels[1] and commonly contain one or multiple metal active ingredients. Due to its broad-spectrum antifouling properties, copper (Cu), in the form of copper oxide, copper hydroxide, or copper thiocyanate, is the primary biocide used in AFPs. In response to DCu concentrations that exceeded California Toxics Rule (CTR) criteria in saltwater marinas, the California Department of Pesticide Regulation (CDPR) promulgated a regulation placing a copper release rate (or leach rate, used in this document interchangeably) cap on Cu-AFPs. The regulation, implemented beginning in July 2018, sets a release rate cap of 9.5 µg/cm^2/day for paints used on recreational vessels to reduce the concentrations of dissolved copper (DCu) and the potential for aquatic toxicity associated with DCu in marinas. CDPR initiated a new long-term monitoring study of eight coastal and marine waterbodies, such as marinas and boat basins, in California to determine concentrations of DCu in those waters. The aim of this report is to present the background, objectives, methods, and discussion of the results from the first year of the monitoring study. Future work will also be discussed. Some of the waterbodies of interest contain multiple marinas and moorings, therefore waterbodies will be used as an all-encompassing term to represent these areas.

DCu is a water quality concern because Cu leaches from the paints into water, and potentially can result in toxicity to non-target aquatic organisms. Species of concern are mussels, such as the blue and Mediterranean mussels, (*Mytilus edulis* and *Mytilus galloprovincialis*, respectively) and the red abalone (*Haliotis rufescens*).[2] The California Toxics Rule (CTR), which has set acute (4.8 µg/L) and chronic (3.1 µg/L) water quality criteria for DCu, aims to protect those species.[3]

Recreational vessel marinas and boat basins are particularly susceptible to pollution from DCu and other antifouling active ingredients. These marinas have high concentrations of vessels, which spend long periods moored in marinas. Marinas are designed to protect vessels from hydrodynamic action, which

results in poor flushing of water in and out of the marina.[4] Several studies in the 1990s and 2000s focused on measuring concentrations of metals in Southern California.[5, 6] The resultant data led to several marinas being placed on the Clean Water Act's 303(d) list for impaired waters. In response, the appropriate Regional Water Quality Control Board develops and implements a water quality management plan, in this case in the form of a total maximum daily load (TMDL) allocation. Cu TMDLs and associated implementation plans were developed for three of those waterbodies in southern California, between 2006–present, including Shelter Island Yacht Basin in San Diego, Marina del Rey in Los Angeles, and Newport Bay in Orange County (still currently in draft form).[7-9]

In 2006, CDPR's Surface Water Protection Program (SWPP) conducted a monitoring study to determine the extent of DCu pollution across California.[1] The study measured DCu in 22 marinas, which include freshwater, and brackish- and salt-water marinas in Northern, Central, and Southern California. The number of vessels in marinas ranged from 400 to 5000 boats. Median marina DCu concentrations (with standard deviations) ranged from 0.5±0.15 µg/L (Folsom Marina) to 13.6±3.9 µg/L (Marina del Rey).[1] The study found that 51% of the samples were in exceedance of the CTR chronic water quality criterion and 33% were in exceedance of the CTR acute water quality criterion. A study by the Southern California Coastal Water Research Project showed similar results with four Southern California marinas having DCu concentrations ranging from non-detect to 21 µg/L, with a mean of 7.0 µg/L.[10] Subsequent monitoring studies have shown similar results.[4, 11-16] Researchers have also observed a concentration gradient in marinas with higher concentrations near the back of the marina and decreasing concentrations towards the mouth, which typically has a lower density of boats and increased flushing capacity.[4, 17] All of these studies concluded that the high DCu concentrations were due to leaching from Cu AFPs.[1, 4-10, 17, 18]

Toxicity of DCu in natural waters is dependent on site-specific water chemistry parameters. DCu is bioavailable in the freely dissolved form or if it is inorganically complexed. The speciation of DCu, and therefore the toxicity of DCu, in aquatic systems is dependent on temperature, pH, dissolved organic carbon (DOC), and salinity.[4, 19] A subset of samples in the 2006 CDPR Study were tested for toxicity, specifically on mussel embryo development for *M. galloprovincialis,* and 17% of those samples had associated toxicity.[1] One associated sample had a DCu concentration of 1.7 µg/L from Marina Bay Yacht Harbor in Richmond. The rest of the samples with associated toxicity all came from Marina del Rey and had DCu concentrations ranging from 11.5 – 18.4 µg/L. In addition, each water sample was evaluated using the Biotic Ligand Model (BLM), which is a metal bioavailability model that predicts toxicity concentration thresholds based on site-specific water chemistry criteria, including temperature, pH, dissolved organic

carbon, and salinity. There are two forms of this model, the freshwater BLM and the saltwater BLM. Results from the freshwater BLM and the saltwater BLM predicted that about 13% and 18% of the samples, respectively, would result in toxicity; almost matching the available toxicity monitoring data for the same samples with associated observed toxicity data.

In response to the CTR exceedances and associated toxicity in CDPR's 2006 study, CDPR responded with a series of regulatory actions that resulted in a Cu release rate cap for AFPs. This release rate cap regulation was developed using the Marine Antifoulant Model to Predict Environmental Concentrations (MAM-PEC). This model is a two-dimensional hydrodynamic fate and transport model that is used to predict environmental concentrations of AFPs in harbors and marinas.[20] SWPP scientists used 15 variables, including water chemistry parameters and physical characteristics of waterbodies, along with a water quality goal of 3.1 µg/L (i.e., the CTR chronic criterion) in MAM-PEC to determine maximum allowable leach rates for different modeling scenarios. The modeling scenarios were representative of different marinas with varying physical and chemical properties including size, number of boat slips, tidal range, background DCu, and other water chemistry parameters. The leach rate cap used in the regulation was based on the modeling scenario and subsequent DCu concentrations in marinas with ≤1270 vessels will would be in continuous compliance with the chronic CTR. The leach rate cap selected also requires the use of best management practice cleaning methods, such as the use of a soft carpet, to achieve the CTR chronic criterion. This bin size of marina includes >95% of marinas in California. Reductions, however, are expected to occur in all marinas and boat basins in California regardless of size.

The implementation of the release rate cap led SWPP to initiate an ambient monitoring program for DCu in marine waterbodies. The long-term objectives of this study are to (1) determine the concentrations of DCu in selected, representative waterbodies; (2) determine the temporal and spatial trends in DCu across and within waterbodies; and (3) determine the potential toxicity of waterbodies based on measured water chemistry parameters using the saltwater biotic ligand model. The data analysis reported here is the first step in evaluating long-term trends in DCu concentrations. Comparisons of previous sampling efforts will be discussed and the differences between this study and previous sampling efforts will be properly contextualized.

2.0 Methods and Materials

2.1 Waterbody Selection

Waterbodies were selected while considering many factors; the most important of which were region, size of waterbody, Cu TMDL implementation, and willingness of marina owner/operator to assist CDPR with sampling. Only saltwater locations were included. Previous studies showed that all freshwater

and brackish water marina samples were below the freshwater CTR values for DCu (acute freshwater criterion = 13 µg/L and chronic saltwater criterion = 9 µg/L).[1]

Waterbodies were selected from Southern California to San Francisco Bay, with a greater emphasis on selecting waterbodies from Southern California (Table 1). Water temperatures are higher in Southern California (Appendix 1, Table 1), which can result in increased fouling.[21] This creates a greater need for AFPs, more frequent cleaning, and potentially could result in higher DCu concentrations. In addition, the San Francisco Bay Regional Water Quality Control Board has implemented site-specific objectives for DCu. The chronic and acute site-specific objectives range from 6.0–6.9 µg/L and 9.4–10.8 µg/L, respectively for *Mytilus* species.[22] Impairment to San Francisco Bay only occurs if the site-specific objective concentrations are exceeded.

A range of waterbody sizes, in terms of number of vessels and surface area, were considered. Waterbodies that had a higher number of boat slips were prioritized for monitoring. Zhang and Singhasemanon (2014) created five marina scenarios as part of the MAM-PEC modeling (Table 1); with the outputs from the modeling suggesting that the leach rate cap plus mitigation recommendations would likely be effective for marinas with <1270 vessels. Although at least one waterbody from each scenario size was included in this study; seven of the eight waterbodies contain 1000 vessels or more (Table 1). Total surface area and estimated number of vessels can be found in Table 1. Three waterbodies, Shelter Island Yacht Basin, Marina del Rey, and Newport Bay, that have an associated Cu TMDL (or draft TMDL) were included.[7-9]

Finally, the most important aspect of waterbody selection was whether a marina owner/operator or waterbody manager was willing to cooperate on sample collection, as they needed to provide and drive the sampling vessel for SWPP scientists.

Table 1. Location, Size, Depth, Vessel Numbers, and Samples for Each Waterbody

Waterbody	Region	Location	No. of Samples per Waterbody*	No. of Vessel Berths	MAM-PEC Scenario	Surface Area (km²)	Water Depth (m)	Mouth Width (m)
Coyote Point Marina	North	San Mateo	4 (1)	565	1 (<733 vessels)	0.11	4.36	247
Berkeley Marina	North	Berkeley	9 (1)	1052	2 (<1270 vessels)	0.23	5.5	305
Santa Barbara Harbor	Central	Santa Barbara	9 (1)	1133	2 (<1270 vessels)	0.23	6	193
Channel Islands Harbor	Central	Oxnard	10 (1)	2150	4 (<2263 vessels)	0.67	3.66	74
Marina del Rey	South	Los Angeles	15 (2)	4754	5 (<4754 vessels)	1.63	5.5	129
Redondo Beach Marinas	South	Redondo Beach	11 (1)	1335	3 (<1833 vessels)	0.201	3.1	91
Newport Bay	South	Newport Beach	15 (2)	5000	5 (<4754 vessels)	5.52	3.66	305
Shelter Island Yacht Basin	South	San Diego	9 (1)	2133	4 (<2263 vessels)	0.93	6	200

* Parenthetical denotes the number of local reference sites in a waterbody

2.2 Sampling Site Locations

The number of sampling locations within each waterbody varied depending on size, but generally sampling sought to provide spatial representation of DCu concentrations. There were several site-specific limitations/considerations. Monitoring at Shelter Island Yacht Basin was conducted in coordination with the Port of San Diego, who had carried out their TMDL sampling the day before the CDPR sampling (six points were sampled by the Port of San Diego). Maps of sampling locations in each waterbody are found in Appendix 1: Figures 1–8.

Each waterbody had at least one associated local reference site (LRS) that was used to determine background concentrations of DCu. LRS, which are labeled "L" on each waterbody map (Appendix 1, Figures 1–8), were typically open ocean samples, unless deemed unsafe by the boat operator. If deemed unsafe, LRS samples were taken as close to the open ocean as possible.

2.3 Sampling Methodology

DCu samples were collected in accordance with U.S. EPA Method 1669, "Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels."[23] Briefly, sampling occurred with a battery-operated peristaltic pump, polyethylene tubing, and pre-cleaned polyethylene sampling bottles.[23] The pump was cleaned in between waterbodies using DI water and ~5 minutes of native water rinsing. For each DCu sample, a corresponding sample for total suspended solids (TSS) and dissolved organic carbon (DOC) analysis was also taken. A field duplicate and matrix spike sample were taken for each waterbody. At each sampling location, including each LRS, a YSI EXOI Multiparameter Sonde meter (Sonde) was used to measure the temperature, salinity, and pH of the water.

Sampling required three SWPP field staff. One served as "clean hands," one served as "dirty hands", and the third conducted Sonde measurements and record-keeping.[23] Clean hands touched only what directly touched the sample, including sampling tubes and bottles. Dirty hands could touch everything else, such as the pump and coolers for transport. The staff members designated as clean and dirty hands must work in conjunction. Samples were taken at least two meters from the sampling vessel and one meter below the water's surface to ensure no interference from the hull paint on the vessel. Samples were filtered using an in-line 0.45 µm filter. The sample filtrate was collected into pre-labeled, pre-cleaned 500 mL polyethylene plastic bottles. The sample filtrate was acidified using ultra-high purity nitric acid by staff members at the Department of Toxic Substances Control – Environmental Chemistry Laboratory (DTSC-ECL) before analysis.[24] After preservation, the samples were stored for a minimum of 48 hours to allow for the copper to re-dissolve from the container into solution. Samples for TSS/DOC were not filtered or acidified. DCu samples were double-bagged and placed on ice (~4ºC) for transport. DCu in acidified water has a holding time of six months; all samples were extracted and analyzed before then. Other site-specific activities (e.g., proximity to commercial vessels, possible underwater hull-cleaning operations, weather conditions) were recorded during sampling.

For Coyote Point Marina, the sampling methodology deviated. Whole water samples were filtered in SWPP's West Sacramento Laboratory. It was discovered that deionized water that was used for cleaning at SWPP's West Sacramento Laboratory contained moderate levels of dissolved copper (DCu range = 65–71 µg/L, Appendix 4, Table 1). Therefore, it should be noted that the Coyote Point Marina samples may contain an artefact from that contamination.

2.4 Sampling Timeframe

This study is focused on exclusively measuring DCu concentrations during the summer months. This corresponds to the dry season in California, when the copper input from other sources (for example, urban runoff) was at a minimum. Storm events also introduce confounding hydrologic factors, such as flushing, dilution, mixing, and sediment resuspension.[1] Wet weather months were excluded as the main objective of this study is to quantify DCu concentrations from Cu-AFPs.

DOC is also variable depending on the season. DOC is the main factor controlling the bioavailability (and the toxicity) of DCu. Therefore, the predictive toxicity modeling presented here is only representative of the time and date of sampling.

2.5 Dissolved Copper Analysis

Analysis for DCu in seawater was conducted by scientists at the DTSC-ECL. DCu was measured by inductively coupled plasma-mass spectrometry triple quadrupole instrument (ICP-MS/MS). The ICP-MS/MS was used in High Matrix Introduction mode, which was enabled due to the high salt content of the sample matrix.

DCu in seawater was measured directly by the ICP-MS/MS. After the internal standard (Germanium, single element) was added to the sample, the sample was introduced to the instrument. A nebulizer converts the introduced liquid to an aerosol mist. From there, the copper in the sample is ionized by the hot argon plasma gas before passing into the mass spectrometer. The triple quadrupole mass spectrometer has two mass filters, Q1 quadrupole and Q2 quadrupole, with an octupole reaction system between them. The Q1 quadrupole filters for copper at a mass-to-charge ratio of 63 and 65 m/z. The octupole reaction system, operated in helium mode, removes polyatomic interferences, such as $ArNa^+$ (argon and sodium). After further selection by Q2 quadrupole, the analyte reaches the electron multiplier detector. Quantitation is assessed through Agilent Mass Hunter software.

This method has a limit of quantification of 0.5 µg/L. Extreme caution was used at the DTSC-ECL in the processing of these samples to ensure no contamination occurred. A method control and laboratory control sample/duplicate were analyzed daily as a check for contamination. The laboratory split all the samples. A sample (analytical) duplicate and matrix spike/duplicate were analyzed for each sample to ensure the method's robustness. All replicates were within quality control limits (relative percent difference ≤ 20%) and all but one matrix spike was within the control limits (75–125%) (Appendix 4, Table 1). For the sampling sites where field duplicates were measured, the DCu concentration reported is an average of the field and analytical duplicates.

2.6 Secondary Constituent Analysis

Analysis of TSS/DOC was completed by SWPP staff. DOC in water was analyzed using a TOC-V CSH/CNS analyzer (Shimadzu Corporation, Kyoto, Japan), according to Ensminger (2013).[25] Holding times for DOC in water were exceeded for Redondo Beach Marinas, Shelter Island Yacht Basin, Channel Islands Harbor, and Santa Barbara Harbor. These data are not included in this report and predictive toxicity modeling was not performed on those samples. Total suspended solids were analyzed according to Ensminger (2016).[26] Measurements of pH, temperature, salinity, total dissolved solids, conductivity, and dissolved oxygen were completed *in situ* using the Sonde.

2.7 Saltwater Biotic Ligand Model

The Biotic Ligand Model Research Version 3.41.2.45 was employed to predict site-specific toxicity based on the measured water quality data. A biotic ligand is the binding site on the organism that is linked to the toxic effects on that organism.[27] The model assumes that toxicity is associated with the amount of freely dissolved Cu available to bind to the biotic ligand.[28] The amount of the metal available to bind to the biotic ligand depends on the factors that control the speciation of that metal in water (i.e., DOC, pH, temperature, and salinity).

The research version of the BLM (Biotic Ligand Model Research Version 3.41.2.45)[29] was selected because it allows for prediction of an adjusted LC_{50} or EC_{50} value based on the site-specific conditions for selected aquatic organisms. These are the concentrations at which toxicity due to DCu is expected to occur for this sampling point and time in the waterbody of interest. The research version of the BLM allows for the user to choose the organism of interest. In this study, *Mytilus galloprovincialis* (Mediterranean mussel) was selected for predicted toxicity measurements. *Mytilus galloprovincialis* is the standard organism by which DCu toxicity tests are performed.[1, 15, 30, 31]

Toxic units were calculated using the measured DCu concentration and the predicted EC_{50} for each site. One toxic unit is equal to a concentration where there is a 50% effect for a specific endpoint (in this case, the endpoint is mortality). Since EC_{50}s change based on the specific water chemistry parameters, toxic units are a way to normalize data to compare toxicity across datasets.

2.8 Modeling Methods

A multi-parameter model was developed to determine the factors that contribute to DCu levels in marine waterbodies. A set of 18 explanatory variables were considered for modeling. These explanatory variables fell into three major categories: water chemistry parameters (such as dissolved oxygen and salinity), sampling site location parameters (such as latitude and distance from sampling site to mouth), and waterbody properties (such as surface area and annual mean water temperature).

Least absolute shrinkage and selection operator (LASSO) regression was used for model development and selection. This process identifies which explanatory variables are most strongly associated with the response variable (i.e., DCu concentration). Statistically unimportant explanatory variable (i.e., variables with no correlation with DCu concentrations) coefficients are reduced to zero (and therefore removed from the model). LASSO uses a tuning parameter called lambda (λ) to control the amount of shrinkage in the model selection process. Shrinkage helps to avoid overfitting the model. If λ is set to zero, this results in an ordinary least squares regression (or no removal of explanatory variables). As λ increases, more explanatory variable coefficients are set to zero. The value of λ was chosen using cross-validation.

The explanatory variables may be correlated with each other, so correlation coefficients (Pearson's r) were calculated between each explanatory variable, as well as p-values set to a significance of 0.05 (Appendix 2, Tables 2-3). This will provide information on collinearity between explanatory variables and will provide context to the results.

Model fitting was conducted using R statistical software. Data were partitioned into a training set (n=58) and testing set (n=24). The training set was used to fit the model and the testing set was used to evaluate model performance. Model performance was evaluated by comparing the root mean square error (RMSE) and adjusted-R^2 of the model. The adjusted-R^2 considers the number of explanatory variables and will increase if the addition of a new explanatory variable improves the model by more than would be considered by chance.

3.0 Results and Discussion

3.1 Dissolved Copper Results

All samples within the waterbody had DCu concentrations above the reporting limit of 0.5 µg/L (Table 2, *Figure 1*). All sampling sites within waterbodies had higher DCu concentrations than their respective LRS (Appendix 1, Table 1). The DCu concentrations within the waterbodies ranged from 30% (Berkeley Marina Site #7, see Appendix 1, Table 1) to 2030% (Redondo Beach Marinas Site #7, see Appendix 1, Table 1) higher than their associated LRS concentration(s). This confirms previous studies that found that Cu-AFPs on vessel hulls are the source of DCu in marinas and boat basins.[1, 4-9, 17, 18]

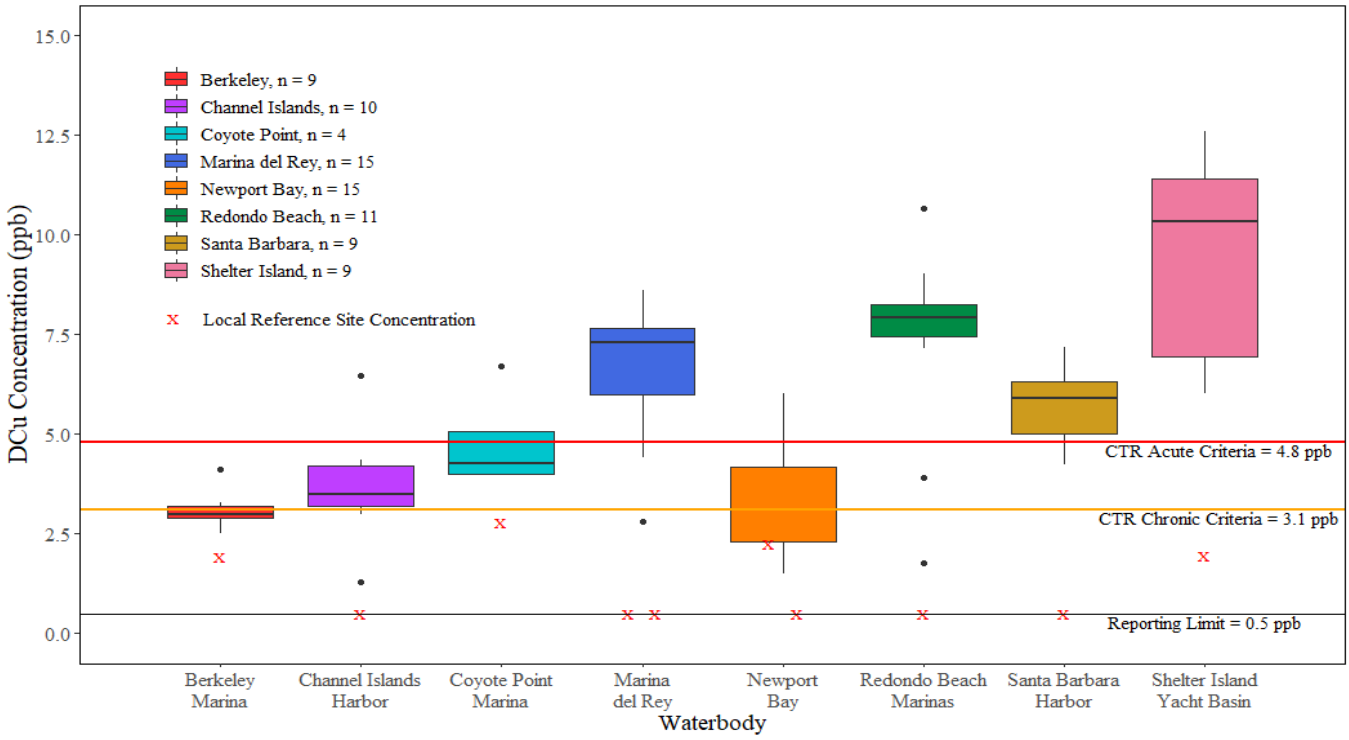

Figure 1. Ranges in DCu concentrations for each waterbody included in the study. The red line represents the CTR acute criteria at 4.8 ppb, the orange line represents the CTR chronic criteria at 3.1 ppb, and the black line represents the reporting limit at 0.5 ppb. Local reference site concentrations for their respective waterbodies are shown as red X. For the LRS concentrations that were reported as non-detects, the concentration is indicated at the reporting limit line.

For the Central and Southern California waterbodies, the measured concentrations were compared to the CTR criteria. For the Central and Southern California waterbodies, 84% of waterbody samples exceeded the CTR chronic criterion (3.1 µg/L) and 61% exceeded the CTR acute criterion (4.8 µg/L). For Northern California locations, Coyote Point Marina and Berkeley Marina, the measured concentrations were compared to the San Francisco Bay's DCu site-specific objectives. One sample in Coyote Point Marina exceeded the chronic site-specific objective and no samples exceeded the acute site-specific objective. However, this may be due to sampling artefact from background DCu concentrations at SWPP's West Sacramento Laboratory. Maps providing a spatial representation of DCu concentrations including exceedance of CTR criteria or site-specific objectives, are found in Appendix 1, *Figures 1–8*.

Table 2. Summary Statistics for Waterbodies in this Study

Waterbody	Median (µg/L)	Mean (µg/L)	Std Dev (µg/L)	Local Reference Site (µg/L)	% above Chronic CTR	% above Acute CTR
Newport Bay	3.12	3.40	1.33	ND, 2.27	53.3	20.0
Marina del Rey	7.29	6.64	1.57	ND, ND	93.3	86.7
Santa Barbara	5.89	5.65	1.00	ND	100.0	77.8
Berkeley	2.98	3.06	0.46	1.93	0.0^	0.0^
Redondo Beach	7.91	7.32	2.44	ND	90.9	81.8
Channel Islands	3.49	3.68	1.32	ND	80.0	10.0
Coyote Point*	4.26	4.80	1.29	2.78	25.0^	0.0^
Shelter Island	10.32	9.27	2.56	1.97	100.0	100.0

ND: Non-detect
Chronic CTR: Chronic California Toxics Rule Criterion for Dissolved Copper in Seawater, 3.1 µg/L
Acute CTR: Acute California Toxics Rule Criterion for Dissolved Copper in Seawater, 4.8 µg/L
^Compared to San Francisco Bay site-specific objectives, which for this part of San Francisco Bay are 6.0 µg/L and 9.4 µg/L chronic and acute toxicity, respectively.
*May contain sampling artefacts; these samples were filtered at DPR's West Sacramento Laboratory. The laboratory water at the laboratory had high DCu concentrations (~68 µg/L).

3.2 Water Chemistry Data

Salinity, pH, temperature, and DOC were needed as inputs for the saltwater BLM. Salinity, pH, and temperature were measured *in-situ*, along with dissolved oxygen concentration, conductivity, and total dissolved solids. Salinities in the San Francisco Bay marinas were lower than the Central and Southern California waterbodies. Water chemistry data for each site are reported in Appendix 1, Table 2.

3.3 Biotic Ligand Modeling Results

Site-specific EC_{50} values for *Mytilus galloprovincialis* were predicted for Coyote Point Marina, Berkeley Marina, Newport Bay, and Marina del Rey (Appendix 2, Table 1). Site-specific EC_{50} values were not predicted for Shelter Island Yacht Basin, Redondo Beach Marinas, Santa Barbara Harbor, and Channel Islands Harbor because holding times for DOC measurements were exceeded. DOC is necessary to calculate site-specific EC_{50} values. Predicted toxic units (TU) were calculated for a subset of sites using the corresponding the EC_{50} data. Marina del Rey was the only waterbody to have sampling sites with predicted TU greater than 1 (maximum TU = 1.06), with 4 out of 17 samples with a TU $\geq$1 (24% of samples). This corresponds to DCu concentrations between 7.32–8.62 µg/L (above the acute and chronic CTR criteria).

3.4 Multi-Parameter Predictive Dissolved Copper Model

LASSO regression was employed to develop a best-fit model for predicting DCu concentrations. This exercise was completed in order to determine correlation, not causation. Possible reasons for the correlations are explained in the following sections. The LASSO regression method was used to balance picking the simplest model from 18 potential explanatory variables while reducing the root mean square error (RMSE) of the model's predicted values. The testing set was used to validate the model. The predictive model has an RMSE of 0.587 and an adjusted-R^2 of 0.919 (*Figure 2*).

DCu values were log-transformed for modeling purposes. Exploratory variables were measured with different units, so Equation 1 was used to standardize the variables. In Equation 1, X_i is the explanatory variable of interest, X_{mean} is the mean of the explanatory variable of interest, X_{stddev} is the standard deviation of the explanatory variable of interest, and $X_{transformed}$ is the transformed variable, which will be used in the DCu predictive model. Appendix 2, Tables 4 and 5, lists the transformed variables for each data-point.

$$X_{transformed} = \frac{X_i - X_{mean}}{X_{StdDev}} \qquad \text{Equation 1}$$

The model, in Equation 2, has 7 explanatory variables: water temperature at sampling ($X_{Sampling\ Water\ Tempature}$), mean annual water temperature ($X_{Mean\ Annual\ Water\ Temperature}$), distance of sampling site to the waterbody mouth ($X_{Distance\ to\ Mouth}$), latitude ($X_{Latitude}$), whether the sampling location is a main channel site or closer to fairways or mooring areas (C), water depth ($X_{Water\ Depth}$), and surface area of the waterbody ($X_{Surface\ Area}$). The variable "C" is a non-transformed variable and is a binary of option of "1" for a main channel site or "0" for a site closer to vessels (mooring areas and fairways). Each explanatory variable's inclusion in the model can be explained by the supporting data and observations, including those in the literature.

$$\ln(DCu\ Concentration)_{predicted} = 1.66 + 0.04 \cdot X_{Sampling\ Water\ Tempature} + 0.06 \cdot X_{Mean\ Annual\ Water\ Temperature} + 0.01 \cdot X_{Distance\ to\ Mouth} - 0.43 \cdot C - 0.02 \cdot X_{Latitude} + 0.20 \cdot X_{Water\ Depth} - 0.17 \cdot X_{Surface\ Area} \qquad \text{Equation 2}$$

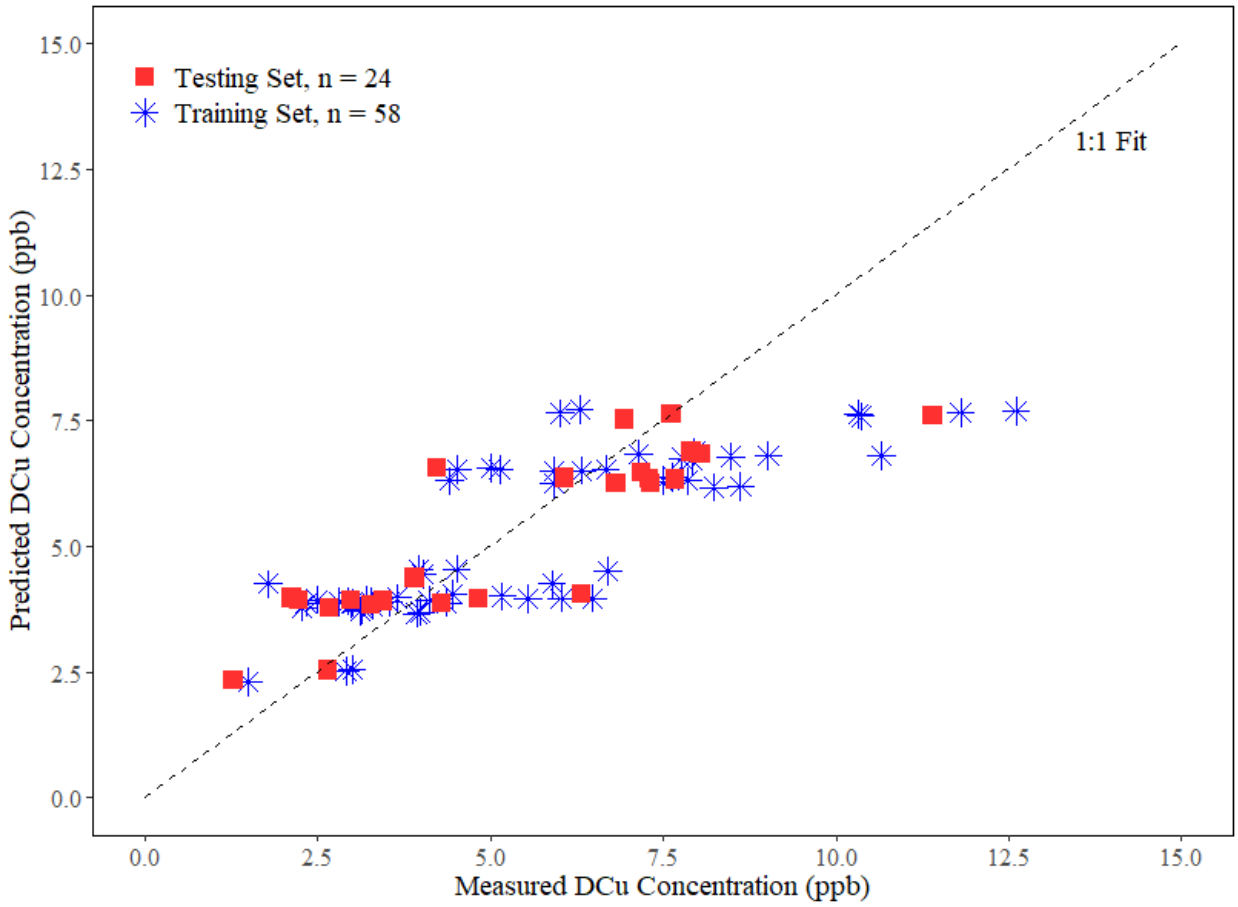

Figure 2. Predicted versus measured DCu concentrations (ppb) for the predictive DCu model. Red squares represent the testing set and blue starts represent the training set. The dashed line represents a 1:1 fit. The closer points are to the 1:1 fit, the better the model is at predicting that value.

Both annual mean water temperature[32] and water temperature at time of sampling had positive correlations with DCu concentrations. Higher water temperature likely leads to more organismal growth and subsequent fouling.[21] Increases in organismal growth, especially during the summer when this study took place, could result in increased cleaning frequency and/or more abrasive cleaning methods. Those cleaning actions will result in higher DCu concentrations.[33]

Distance of sampling location to mouth of the waterbody and whether a sampling location is a main channel site or located closer to vessels (e.g., fairways or mooring areas) will influence DCu concentrations. DCu concentrations increase as a sampling location's distance to the mouth increases. This is likely due to differences in tidal exchange. This phenomenon is evident in Newport Bay (Appendix 1, *Figure 7*). The highest DCu concentrations are found in the west part of Newport Bay in both marinas and channels, where the residence time of the water is the highest due to low flushing (City

of Newport, personal communication).[34] However, this effect can be lessened if the sampling location is a main channel site for many of the waterbodies. Better tidal exchange usually occurs at these sites and these locations are farther away from vessels, leading to lower DCu concentrations.[4, 14, 15]

Latitude has is negatively correlated with DCu concentrations. This was likely influenced by temperature- and salinity-driven regional differences. San Francisco Bay marinas have relatively lower DCu concentrations compared with the Central and Southern California waterbodies. The highest DCu concentrations of this study were measured at Shelter Island Yacht Basin, the southern-most waterbody. The San Francisco Bay marinas have lower salinities than the Central and Southern California waterbodies. Historically, waterbodies with lower salinities have lower DCu concentrations.[1] However, salinity was not chosen to be included in this model, probably because salinity and latitude have relatively high collinearity (Pearson's r = -0.87, Appendix 2, Tables 2 and 3).

Waterbody depth and surface area are positively and negatively correlated (respectively) with DCu concentrations. As water depth increases, DCu concentrations are projected to increase; while as waterbody surface area increases, DCu concentrations are projected to decrease. Surface area has a relatively high correlation with number of vessels (Pearson's r = 0.81, Appendix 2, Tables 2 and 3). A higher number of vessels in a waterbody could potentially contribute a higher load of DCu. However, the surface area variable may be influenced by the Newport Bay data, which has relatively lower DCu concentrations (Table 2) but is ~3.3x larger than the next largest waterbody (Marina del Rey) (Table 1).

3.5 Historical Monitoring Trends

Historical monitoring data from various sources were compiled to determine if there was a significant difference between historical monitoring data and data collected in this study. Sources of data included the 2006 CDPR study,[1] the Santa Ana Regional Water Quality Control Board,[16] the Los Angeles Regional Water Quality Control Board, City of Newport,[34] Marina del Rey Coordinated Integrated Monitoring Program,[11] and Southern California Coastal Water Research Project.[30] Only data that corresponded to the same sampling locations in this study were used. See Appendix 3, Table 1 for details of the differences between the sampling studies.

The Wilcoxon rank sum test was used to compare the historical and current DCu datasets due to the non-normality of the datasets. There was not a significant difference between the datasets (p-value = 0.257). This was not surprising, considering that the Cu-AFP regulation has only been in effect for a year at the time of sampling and existing product stockpiles with higher release rate paints are still on the markets. In addition, Cu-AFPs are on boats for multiple years and boatyard capacity for turnover is limited. Results presented here are considered a reference point to evaluate future trends. Reductions in

DCu concentrations are also dependent on the adoption and enforcement of the use of best management practice (BMP) hull cleaning technologies. Abrasive hull cleaning tactics contribute up to 62% higher load than no hull cleaning, while BMP cleaning tactics contribute up to a 45% higher load than no cleaning.[33] Therefore, implementation of BMP cleaning tactics will likely have a significant effect on DCu concentrations. CDPR will track waterbodies with BMP hull cleaning ordinances and consider the ordinances in the evaluation of DCu trends.

4.0 Future Work

The DCu results here do not account for several parameters that contribute to those trends in DCu concentrations. Specifically, the study design did not account for spatial variation within the water column or tidal flushing.

Previous studies of Shelter Island Yacht Basin show that spatial variation within the water column affects DCu concentrations.[4, 12, 14, 17] DCu concentrations from samples collected near the bottom of the basin were significantly lower than the near surface samples. The difference in DCu concentrations was most pronounced at the head of the basin (the head of the basin is the point furthest from the mouth of the marina) and closest to vessels. In contrast, the LRS samples had no vertical concentration gradient. The largest vertical concentration gradient, which was at the head of the marina, was likely due to both the presence of vessels and poor tidal flushing[4, 12, 17]

Tidal flushing also has an effect on DCu concentrations. At Shelter Island Yacht Basin, the effect of the tide was significant at the mouth and middle of the basin, but not at the head. The outgoing tide will flush copper out of the waterbody. There is low tidal flushing at the head of Shelter Island Yacht Basin and, therefore, higher DCu concentrations. The water column and tidal flushing studies have only been conducted at Shelter Island Yacht Basin; therefore, these results cannot be extrapolated to other waterbodies without further study. CDPR plans to investigate these factors in other waterbodies.

5.0 Summary

This study report presents results from the first year of a long-term monitoring study of DCu in California coastal waterbodies. Eight saltwater waterbodies of various sizes in Northern, Central, and Southern California were included in this study. Sampling sites within the waterbodies were selected to provide spatial representation of the waterbody, including the measurement of DCu at a LRS for each waterbody.

There was 100% detection frequency of DCu within the waterbodies. All DCu concentrations within the waterbodies were higher than their respective LRS concentrations. In Central and Southern California, 84% of the waterbody samples exceeded the CTR chronic criterion (3.1 µg/L) and 61%

exceeded the CTR acute criterion (4.8 µg/L). There was only one exceedance of the San Francisco Bay chronic site-specific objective; the exceedance occurred at Coyote Point Marina. There may be possible contamination that impacted this sampling result. Biotic ligand modeling was conducted to predict site-specific toxicity at four waterbodies. Four sites at Marina del Rey had predicted site-specific toxicity to the Mediterranean mussel (*Mytilus galloprovincialis*), with toxic units for those four sites ranging from 1–1.06.

LASSO regression modeling was used to develop a best-fit model to predict DCu concentrations. This modeling was used to analyze DCu spatial trends within and between the waterbodies. Seven explanatory variables were included in the best-fit model. These variables are latitude of sampling site, annual average water temperature, water temperature at sampling, distance from sampling point to waterbody mouth, depth of the waterbody, surface area of the waterbody, and whether the sampling site was a main channel site or located closer to vessels.

The results presented here are considered a reference point to evaluate long-term trends. There was no significant difference between historical monitoring data and this current dataset. SWPP plans to continue monitoring these waterbodies in the future. Predicted toxicity will be calculated using the saltwater biotic ligand model. The best-fit predictive DCu concentration model will be updated with data from future sampling efforts.

6.0 Acknowledgements

This project could not have been completed without the help of the harbormasters and other administrators from the various waterbodies of interest. In particular, we'd like to thank Mark Bettis of Coyote Point Marina, Stephen Bogner of Berkeley Marina, John Kappeler and Shane Burckle from the City of Newport Beach, Kelly Tait and Karen Holman from the Port of San Diego, Jennifer Mongolo, Maral Tashjian, and Michael Tripp from Los Angeles Beaches and Harbor, Gary Laolagi from the City of Redondo Beach, Mark Sandoval and Guy Hirtensteiner from Channel Islands Harbor, and Karl Trieberg of Santa Barbara Harbor.

We thank staff scientists, including Scott Giatpaiboon, Mario Vinoya, and Cesar Fernandez of the Department of Toxic Substances Control for providing dissolved copper in seawater analytical support under Contract #19-C0028.

Thank you to staff scientists Shana Rapoport from the Los Angeles Regional Water Quality Control Board and Linda Candeleria from the Santa Ana Regional Water Quality Control Board for useful discussions on copper antifouling paints and Marina del Rey and Newport Bay Cu TMDLs.

KayLynn Newhart, Emily Edgerton, Sarah Albright, Jesse Ybarra, and Jackie Maes of the California Department of Pesticide Regulation provided assistance in preparation and during these sampling trips.

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