Department of Pesticide Regulation
Environmental Monitoring Branch
Surface Water Protection Program
1001 I Street
Sacramento, CA 95812

Study 319 Report: Monitoring of Dissolved Copper in California Coastal Waterbodies, 2022

Pedro Lima and Xuyang Zhang
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1. INTRODUCTION

Copper antifouling paints (AFPs) are used to prevent biofouling on aquatic vessels and to improve the performance and fuel efficiency of their vessels. Due to its broad-spectrum antifouling properties, copper (Cu), in the form of copper oxide (CuO), copper hydroxide (CuH_2O_2), or copper thiocyanate ($C_2CuN_2S_2$), is the primary biocide used in AFPs. The use of AFPs has contributed to concentrations of dissolved copper (DCu) that exceed water quality criteria in many saltwater marinas in California (Burant et al., 2019a; Singhasemanon et al., 2009).

DCu is a water quality concern because Cu leaches from the paints into water and can result in toxicity to non-target aquatic organisms. Species of concern are mussels, such as the blue (*Mytilus edulis*) and Mediterranean mussels (*Mytilus galloprovincialis*), and the red abalone (*Haliotis rufescens*) (Elias, 2016). The California Toxics Rule (CTR) aims to protect those species by setting an acute (4.8 µg/L) and chronic (3.1 µg/L) water quality criteria for DCu (EPA, 2000).

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 (Bosse et al., 2014). Several studies in the 1990s and 2000s focused on measuring concentrations of metals in Southern California (Schiff et al., 2004; Young et al., 1979). The resultant data led to several marinas being placed on the Clean Water Act's 303(d) list for impaired waters. In response, the Regional Water Quality Control Boards (RWQCB) developed and implemented water quality management plans, in the form of a total maximum daily load (TMDL) allocation for three of those waterbodies in southern California, including Shelter Island Yacht Basin in San Diego,

Marina del Rey in Los Angeles, and Newport Bay in Orange County (Board, 2005; RWQCB, 2015; RWQCB, 2022).

In 2006, the California Department of Pesticide Regulation (DPR)'s Surface Water Protection Program (SWPP) conducted a monitoring study to determine the extent of DCu pollution across California (Singhasemanon et al., 2009). The study measured DCu in 22 marinas, which include freshwater, brackish- and salt-water marinas in California. The number of vessels in marinas ranged from 400 to 5000 boats. Median 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). 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.

Toxicity of DCu in natural waters is dependent on site-specific water chemistry parameters. DCu is bioavailable in the forms of freely dissolved or inorganically complexed. The speciation of DCu, and therefore the toxicity of DCu, in aquatic systems is influenced by temperature, pH, dissolved organic carbon (DOC), and salinity (Bosse et al., 2014; Thomas and Brooks, 2010). A subset of samples in the 2006 DPR Study were tested for toxicity, specifically on mussel embryo development for *Mytilus galloprovincialis*, and 17% of those samples had associated toxicity (Singhasemanon et al., 2009). One associated sample had a DCu concentration of 1.7 µg/L from Marina Bay Yacht Harbor in Richmond, which is below the acute toxicity threshold. 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.

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 (Schiff et al., 2007). Subsequent monitoring studies have shown similar results (AMEC Environment & Infrastructure, 2013; AMEC Environment & Infrastructure, 2017; Amec Foster Wheeler Environment and Infrastructure, 2018; Bosse et al., 2014; Candelaria, 2007; Weston Solutions, 2016; Wood Environment and Infrastructure Solutions, 2018). Researchers have also observed a concentration gradient within 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 (Bosse et al., 2014; Neira et al., 2009). These studies concluded that the high DCu concentrations were potentially due to leaching from Cu AFPs (Board, 2005; Bosse et al., 2014; Burant et al., 2019b; Neira et al., 2009; Neira et al., 2011; RWQCB, 2015; RWQCB, 2022; Schiff et al., 2007; Schiff et al., 2004; Singhasemanon et al., 2009; Young et al., 1979).

In response to DCu concentrations that exceeded CTR criteria in saltwater marinas, the DPR implemented a regulation in July 2018 placing a copper release rate (or *leach rate*, used in this document interchangeably) cap on AFPs (DPR, 2018). The regulation sets a maximum allowable copper leach rate of 9.5 µg/cm^2/day for paints used on recreational vessels to reduce the

concentrations of DCu and the potential for aquatic toxicity associated with DCu in marinas. Manufacturers of AFPs were required to reformulate their products such that the copper leach rates were below 9.5 µg/cm^2/day. The leach rate cap selected also requires the use of best management practice cleaning methods to achieve the CTR chronic criterion.

To monitor the impact of the leach rate cap regulation, in 2019, DPR initiated a new long-term monitoring study of eight coastal and marine waterbodies (Burant, 2019; Lima and Smith, 2022). The first year of monitoring detected DCu in 100% of the waterbodies. All DCu concentrations within the waterbodies were higher than their respective associated local reference site (LRS) concentrations. In Central and Southern California, 84% of the waterbody samples exceeded the CTR chronic criterion and 61% exceeded the CTR acute criterion. There was only one exceedance of the San Francisco Bay Regional Water Quality Control Board chronic site-specific objective (6.0 µg/L) for *Mytilus* species (Richard Looker; Amendment, 2007).

To continue the monitoring effort, DPR conducted another year of monitoring in the same eight waterbodies in 2022. The aim of this report is to present the results from the 2022 monitoring study. The long-term objectives of this study are to (1) determine the concentrations of DCu in selected, representative waterbodies; and, (2) determine the temporal and spatial trends in DCu across and within waterbodies. 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 DPR 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 freshwater criterion = 9 µg/L) (Singhasemanon et al., 2009).

Waterbodies were selected from Southern California to San Francisco Bay, with a greater emphasis on selecting waterbodies from Southern California (Table 1). This is because water bodies in Southern California tend to have higher DCu concentrations due to higher water temperatures and consequently increased fouling (Appendix 1, Table 1), (Minchin and Gollasch, 2003). 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 µg/L and 9.4 µg/L, respectively for *Mytilus* species (Richard Looker; Amendment, 2007). 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 vessel berths were prioritized for monitoring as reported in Burant et al. (2019b). Three waterbodies, Shelter Island Yacht Basin, Marina del Rey, and Newport Bay, that have an associated Cu TMDL were included (Board, 2005; RWQCB, 2015; RWQCB, 2022). The final 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 the 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***	***Surface Area (km^2)***	***Water Depth (m)***	***Mouth Width (m)***
Coyote Point Marina	North	San Mateo	4 (1)	565	0.11	4.36	247
Berkeley Marina	North	Berkeley	9 (1)	1,052	0.23	5.5	305
Santa Barbara Harbor	Central	Santa Barbara	9 (1)	1,143	0.23	6.0	193
Channel Islands Harbor	Central	Oxnard	15 (2)	2,150	0.67	3.66	74
Marina del Rey	South	Los Angeles	15 (2)	4,326	1.63	5.5	129
Redondo Beach Marinas	South	Redondo Beach	11 (1)	1,335	0.20	3.1	91
Newport Bay	South	Newport Beach	15 (2)	5,000	5.52	3.66	305
Shelter Island Yacht Basin	South	San Diego	9 (1)	2,133	0.93	6.0	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. Wherever possible, we tried to spread sampling among various locations including those near the slip where the vessels were berthed and the main channel that is a bit farther away from the vessels. 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 DPR sampling (seven points were sampled by the Port of San Diego). In addition to the 2019 study parameters (Burant et al., 2019b) seven sites were added at the Channel Islands Harbor. Maps of sampling locations in each waterbody are found in Appendix 1: Figures 1–8.

Each waterbody had at least one associated LRS that was used to determine background concentrations of DCu. The 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." (EPA, 1996). Sampling occurred with two battery-operated peristaltic pumps (one for DCu sampling and one for TSS/DOC sampling), polyethylene tubing, and pre-cleaned polyethylene sampling bottles (EPA, 1996). The pump was cleaned in between waterbodies using reverse osmosis (RO) 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, an Aqua Troll 400 multi-parameter water quality Sonde (In Situ Inc., Fort Collins, CO) 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 as "sonde hands" conducting Sonde measurements and record-keeping (EPA, 1996). 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 (EPA, 1997). 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. All DCu samples were double-bagged and placed on ice (~4ºC) for transport. Although DCu in acidified water has a holding time of six months, all samples were extracted and analyzed before then. Other site-specific observations (e.g., proximity to commercial vessels, possible underwater hull-cleaning operations, weather conditions) were recorded during sampling.

2.4 Sampling Timeframe

This study is focused on measuring DCu concentrations during the summer months (June to August). This corresponds to the dry season in California, when the copper input from other sources (e.g., urban runoff) is at a minimum (Burant, 2019). However, due to the impact of the COVID-19 pandemic, availability of SWPP and marina personnel was limited, which extended the study throughout fall 2022. Berkeley, Coyote Point, Marina del Rey, Newport Bay, and

Redondo Beach marinas were all sampled during the fall months (September to November). Specifically, Coyote Point Marina had a multi-month dredging project, consisting of a planned sediment removal that takes place every five years with an objective of increasing the marina safety for boat navigation.

The sampling timeframe did not extend through the storm season (typically November to March). However, it is worth noting there weren't any storm events that occurred during the November 2022 sampling period. Storm events introduce confounding hydrologic factors, such as flushing, dilution, mixing, and sediment resuspension (Singhasemanon et al., 2009). Wet weather months (December to March) were excluded as the main objective of this study is to quantify DCu concentrations from AFPs.

2.5 Dissolved Copper Analysis

Analysis for DCu in seawater was conducted by scientists at the DTSC-ECL. All 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.

Dissolved copper in seawater was measured directly by the ICP-MS/MS. After the internal standard (Germanium, single element) was mixed with 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 the matrix spikes was within the control limits (75–125%) (Appendix 4, Table 1).

2.6 Secondary Constituent Analysis

Analysis of total suspended solids (TSS) was completed by the SWPP staff. The TSS were analyzed according to Ensminger (2013). Measurements of pH, temperature, salinity, total dissolved solids, conductivity, and dissolved oxygen were completed *in situ* during each

sampling event (Edgerton, 2020) with the Aqua Troll Sonde (Appendix 1, Table 2). Holding times for DOC in water (30 days) were exceeded as a consequence of equipment malfunction. Consequently, predictive toxicity modeling was not performed on all samples.

2.7 Modeling Methods

The 2022 monitoring results were combined with the 2019 data for statistical analysis. 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 1-2). Pearson's correlation coefficients 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=117) and testing set (n=48). 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 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) with the exception of Newport Bay Site #1 (-3%, see Appendix 1, Table 1). The DCu concentrations within the waterbodies ranged from 48% (Newport Bay Site #4) to

2,547% (Marina del Rey Site #4) higher than their associated LRS concentration(s). This confirms previous studies that found that Copper AFPs on vessel hulls are the likely source of DCu in marinas and boat basins (Board, 2005; Bosse et al., 2014; Burant et al., 2019b; Neira et al., 2009; Neira et al., 2011; RWQCB, 2015; RWQCB, 2022; Schiff et al., 2004; Singhasemanon et al., 2009; Young et al., 1979).

Higher DCu median values were detected in the water bodies in Southern California: 10.31 µg/L at Shelter Island Yacht Basin, 9.02 µg/L at Marina del Rey, and 7.48 µg/L at Redondo Beach (Figure 2, Table 2). Higher DCu concentrations in Southern California were also detected during the previous studies (Burant et al., 2019b; Singhasemanon et al., 2009). Such observations might be related to lower water temperatures at the Northern and Central California marinas (Appendix 1, Table 1), resulting in less fouling and AFP use when compared to Southern marinas.

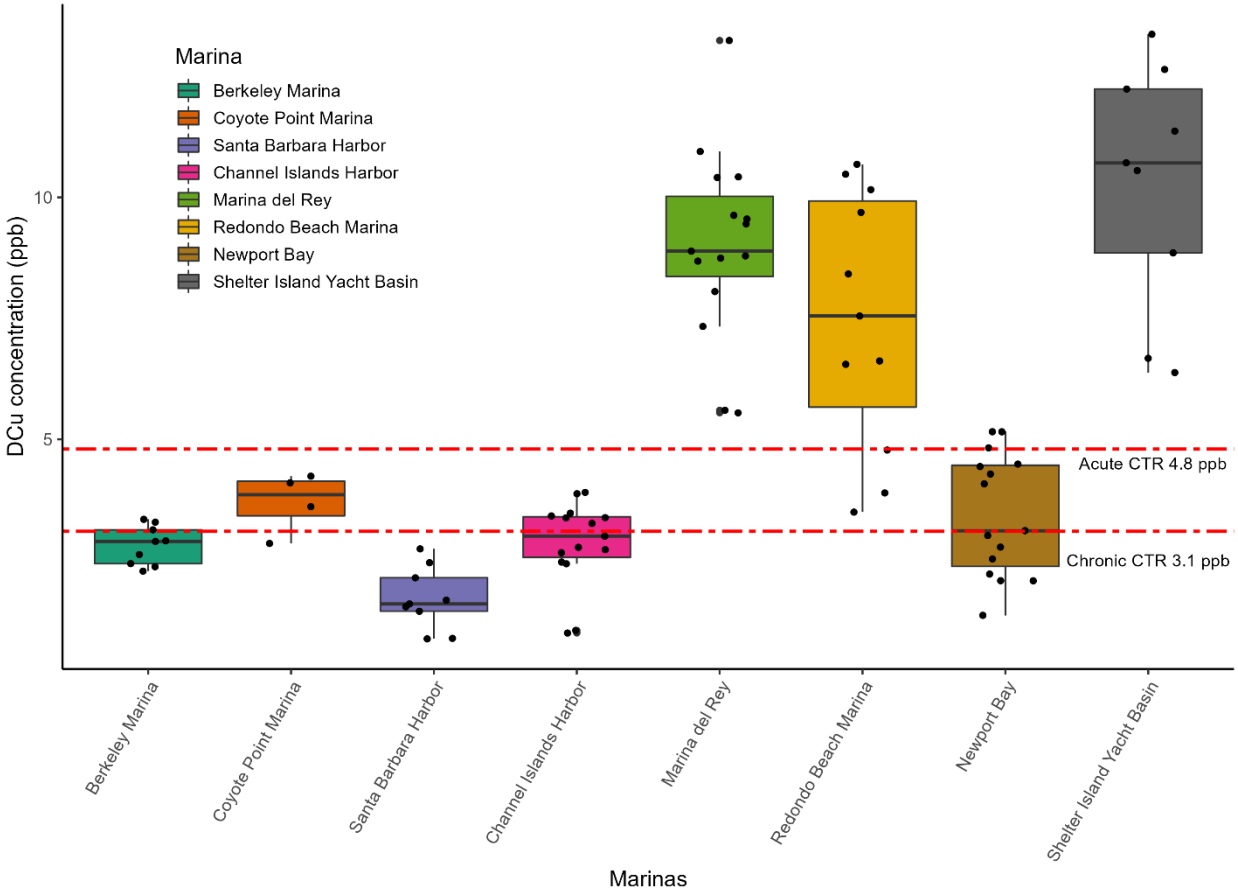

Figure 1. Ranges in 2022 DCu concentrations for each waterbody included in the study at the different California regions: Northern California (Berkeley and Coyote Point Marinas), Central California (Channel Islands Harbor and Santa Barbara), and Southern California (Redondo Beach, Marina del Rey, Newport Bay, and Shelter Island). The red lines represent the CTR acute criteria at 4.8 ppb, and CTR chronic criteria at 3.1 ppb.

For the Central and Southern California waterbodies, the measured concentrations were compared to the CTR criteria. Exceedance of the CTR chronic criterion (3.1 µg/L) and CTR

acute criterion (4.8 µg/L) was detected in 68% and 47% of the Central and Southern California waterbody samples, respectively. 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 (Richard Looker; Amendment, 2007). No samples exceeded the chronic or acute site-specific objective. 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. Dissolved copper 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*
Berkeley	2.81	2.81	0.41	1.21	0.0 [C]	0.0 [A]
Coyote Point	3.70	3.98	0.61	1.75	0.0 [C]	0.0 [A]
Santa Barbara [B]	1.71	1.61	0.63	ND	0.0	0.0
Channel Islands	2.85	2.95	0.87	ND, 3.13 [C]	46.7	0.0
Marina del Rey	9.02	9.06	1.96	ND, 2.19	100.0	100.0
Redondo Beach	7.48	7.55	2.58	0.53	100.0	72.7
Newport Bay	3.44	3.25	1.24	1.40, 1.99 [C]	53.3	20.0
Shelter Island	10.31	10.78	2.47	ND	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
[A] 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.
[B] Unexpected filtering system performance might have influenced data accuracy.
[C] Second reference point located at marina outlet (Appendix 1: Figures 1–8).

3.2 Difference between 2022 and 2019 monitoring results

Historical monitoring data for sampling sites are found in Appendix 3, Table 1. The monitoring results for the California Coastal marinas in 2019 are summarized in the annual project report (Burant et al., 2019b). All samples had DCu concentrations above the reporting limit of 0.5 µg/L (Figure 2). In 2019, 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), while 2022 results exceeded the CTR chronic and acute criterion in 68% and 47%, respectively.

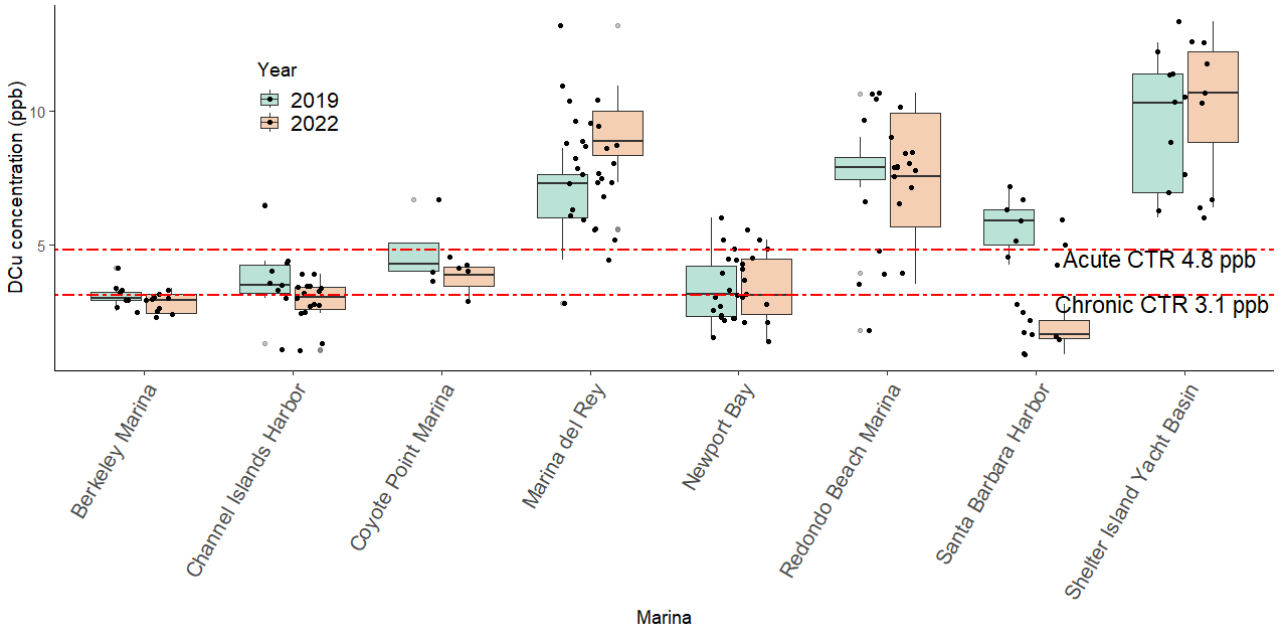

Figure 2. 2019 and 2022 ranges in DCu concentrations for each waterbody included in the study. The green boxplots represent 2019 DCu concentrations range, and the orange boxplots represents 2022 DCu concentrations range. The red lines represent the CTR acute criteria at 4.8 ppb, and the CTR chronic criteria at 3.1 ppb.

To examine the differences in concentrations between 2022 and 2019 results, the Kruskal-Wallis test was also used to determine if there were significant differences in DCu concentrations between the two years in each of the marinas. Test results showed that DCu concentration for some marinas (Channel Island Harbor, Marina Del Rey, and Santa Barbara Harbor) changed significantly from 2019 to 2022: higher 2022 DCu concentrations at Marina Del Rey, and lower at Channel Islands Harbor and Santa Barbara Harbor. The DCu concentration in the remaining five marinas stay at similar levels from 2019 to 2022. Moving forward, DPR will continue to monitor DCu concentrations in these water bodies to determine long term trends.

3.2.1 Northern California Marinas

In the Northern California marinas studied, relative percentage difference (RPD) between the two years (2019 and 2022) ranged from -59.9% (Coyote Point Marina Site #1, see Appendix 3, Table 2) to 15.8% (Berkeley Site #7, see Appendix 3, Table 2). As previously mentioned, Coyote Point Marina had a multi-month dredging project in 2022, consisting in a planned sediment removal that takes place every five years with the objective of increasing the marina safety for boats navigation. In 2019, Coyote Point Marina 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 DCu (range between 65–71 µg/L). Therefore, it should be noted that the 2019 Coyote Point Marina samples may contain an artefact from that contamination (Burant et al., 2019b).

3.2.2 Central California Marinas

For Central California marinas, RPD between the two seasons (2019 and 2022) ranged from -139.8% (Santa Barbara Harbor Site #8, see Appendix 3, Table 2) to 9.4% (Channel Islands Harbor Site #9, see Appendix 3, Table 2). In particular, a larger DCu concentration discrepancy between years can be noted at the Santa Barbara Harbor. This may be associated with sample filtration or higher adoption of lower leach rate AFP products in this region. As previously mentioned, DCu samples were filtered using an in-line 0.45 µm filter, however, sampling field observations indicated an unsatisfactory performance of the filtering system, which may have influenced the accuracy of the DCu concentrations. Additionally, lower leach rates of the new copper AFP products may have influenced DCu range concentrations in 2022 and consequently a discrepancy with the 2019 data.

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 can contribute up to 62% higher load than no hull cleaning, while BMP cleaning tactics can contribute up to a 45% higher load than no cleaning (Earley et al., 2014). Therefore, implementation of BMP cleaning tactics will likely have a significant effect on DCu concentrations. A Clean Marina Program has been in place in Santa Barbara Harbor since 2004, but no significant changes in the hull cleaning practices have been observed between 2019 and 2022 (City of Santa Barbara, personal communication) (Adair and Engebreston, 2022). Staff from DPR will continue to monitor DCu concentrations in these water bodies.

3.2.3 Southern California Marinas

For Southern California marinas, RPD between the two sampling years (2019 and 2022) ranged from -55.7% (Redondo Beach Marinas Site #5, see Appendix 3, Table 2) to 66.7% (Marina del Rey Site #1, see Appendix 1, Table 2). Redondo Beach, and Marina del Rey higher DCu concentrations were observed near the back of the marina and decreasing concentrations towards the mouth, which typically has a lower density of boats and increased flushing capacity. Such observations validate findings by other researchers that also observed a concentration gradient in marinas (Bosse et al., 2014; Neira et al., 2009). At Newport Bay, the highest DCu concentrations are found in the west part in both marinas and channels, where the residence time of the water is the highest due to low flushing (City of Newport, personal communication) (Kappeler, 2019).

In 2022, for the Southern California waterbodies, 86% of waterbody samples exceeded the CTR chronic criterion (3.1 µg/L) and 70% exceeded the CTR acute criterion (4.8 µg/L). As previously discussed, higher water temperatures in Southern California can lead to increased fouling and AFP use potentially increasing DCu concentrations when compared to colder waters.

3.3 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 0.55 and an adjusted-R^2 of 0.76 (Figure 3).

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.

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

The model, in Equation 2, has 7 explanatory variables: surface area of the waterbody (X_{SA}), total suspended solids (X_{TSS}), dissolved oxygen (X_{DO}), water temperature at sampling (X_{SWT}), mean annual water temperature (X_{MAWT}), width of the waterbody mouth (X_{MW}), latitude (X_{Lat}), whether the sampling location is a main channel site or closer to fairways or mooring areas (C). 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.

$$\ln (DCu)_{predicted} = 1.5 - 0.29 \cdot X_{SA} + 0.01 \cdot X_{TSS} - 0.06 \cdot X_{DO} + 0.39 \cdot X_{SWT} + 0.07 \cdot X_{MAWT} + 0.09 \cdot X_{MW} - 0.1 \cdot C - 0.06 \cdot X_{Lat} \quad \text{Equation 2}$$

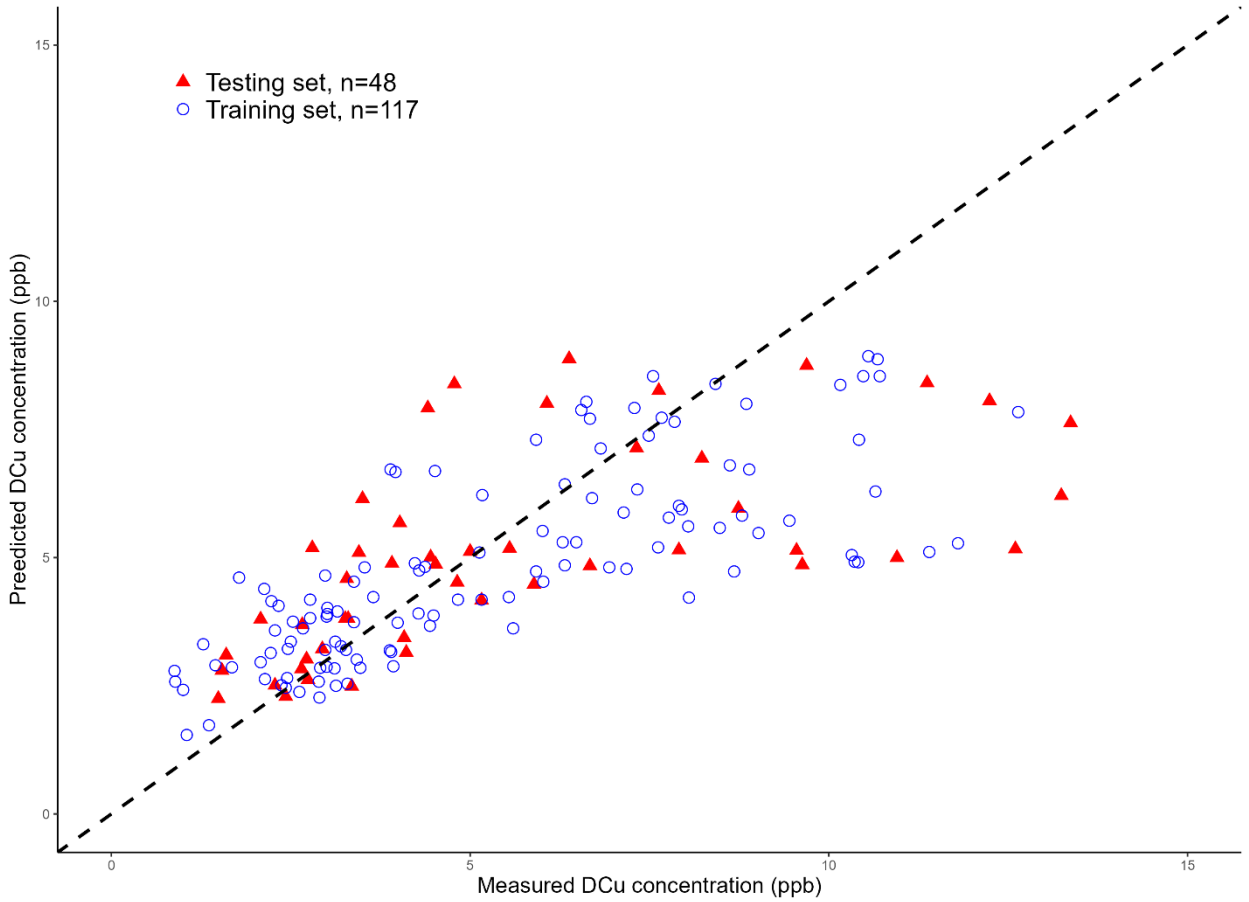

Figure 3. Predicted versus measured DCu concentrations (ppb) for the predictive DCu model. Red triangles represent the testing set and blue circles represent the training set. The dashed line represents a 1:1 fit. The closer points are to the 1:1 fit, the better the model is at predicting that value.

Both annual mean water temperature (NOAA, 2023) 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 (Minchin and Gollasch, 2003). Increases in organismal growth, especially during the summer when this study took place, could result in increased cleaning frequency or more abrasive cleaning methods. Those cleaning actions will result in higher DCu concentrations (Earley et al., 2014).

Unlike the analysis with only 2019 data, mouth width of the waterbody was selected as opposed to distance to the mouth. However, these two variables are significantly correlated (Pearson's r = 0.34, P-value = 0.001). With some exceptions, generally DCu concentrations increase as a sampling location's distance to the mouth increases. This is likely due to difference in tidal exchange.

DCu concentrations are influenced by its sampling location, whether at a main channel site or located closer to vessels (e.g., fairways or mooring areas). This phenomenon is evident in Newport Bay (Appendix 1, Figure 7) where the highest DCu concentrations are found in the west

part of Newport Bay in both marinas and channels. However, this effect can be lessened if the sampling location is a main channel site for many of the waterbodies. Lower DCu concentrations occur at the sites and locations that are farther away from vessels where there is a better tidal exchange (AMEC Environment & Infrastructure, 2017; Bosse et al., 2014; Wood Environment and Infrastructure Solutions, 2018).

Latitude is negatively correlated with DCu concentrations (Pearson's r = -0.41, Appendix 2, Tables 2 and 3). 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 were found to have lower DCu concentrations (Singhasemanon et al., 2009). However, salinity was not chosen to be included in this model as salinity and latitude have relatively high collinearity (Pearson's r = -0.77, Appendix 2, Tables 2 and 3).

Dissolved copper concentrations were positively correlated to waterbody depth and negatively correlated with surface area. The mechanism behind this negative correlation between surface area and DCu is not clear. Surface area has a relatively high correlation with the number of vessels (Pearson's r = 0.9, Appendix 2, Tables 2 and 3). A higher number of vessels in a waterbody could potentially contribute to a higher load of DCu. However, water bodies with bigger surface area likely will have more mixing and dilution resulting in lower DCu. In addition, 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).

4.0 SUMMARY

This report presents results from the first and second year of a long-term monitoring study of DCu in California coastal waterbodies. Eight saltwater waterbodies of various sizes in 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, 68% of the waterbody samples exceeded the CTR chronic criterion (3.1 µg/L) and 47% exceeded the CTR acute criterion (4.8 µg/L). In the Northern California sites, no samples exceeded the San Francisco Bay chronic site-specific objective.

The results presented here were used to determine if there were significant differences in DCu concentrations between the 2019 and 2022 years in each of the marinas. Test results showed that DCu concentration for the Channel Island Harbor, Marina Del Rey, and Santa Barbara Harbor changed significantly from 2019 to 2022. The DCu concentration in other five marinas stay at similar levels from 2019 to 2022. Staff from DPR will continue to monitor DCu concentrations in these water bodies to establish long term trends in dissolved copper concentrations.

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 surface area of the waterbody, total suspended solids, dissolved oxygen, water temperature at sampling, mean annual water temperature, width of the waterbody mouth, latitude of sampling site, and whether the sampling site was a main channel site or located closer to vessels.

The water samples were not 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. DOC is the main factor controlling the bioavailability (and the toxicity) of DCu. In future studies, DPR plans to include the predictive toxicity modeling. The best fit predictive DCu concentration model will be updated with data from future sampling efforts.

Due to the DPR regulatory actions that resulted in a Cu release rate cap, all new AFPs should have leach rates lower than the maximum allowable copper leach rate of 9.5 $\mu g/cm^2/day$. Moving forward, SWPP staff will continue to monitor DCu and anticipate that a transition period is expected as users switch to lower leaching Cu-AFPs as boat owners renovate their property. The progress of implemented or recommended mitigations is unclear, as more years might be needed to evaluate the regulation and mitigation effects. In the interim, DPR will continue its copper monitoring efforts to further investigate these effects in the water bodies.

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