1. Introduction

Antifouling paints (AFPs) are used on vessels to prevent biofouling, which can decrease vessel fuel efficiency and facilitate the spread of aquatic invasive species. AFPs frequently contain a metal active ingredient. Due to its broad spectrum antifouling capabilities, copper (Cu), in the form of copper oxide, copper hydroxide, or copper thiocyanate, is the primary biocide used in AFPs. In July 2018, 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 AFPs. The regulation sets a release rate cap of 9.5 µg/cm²/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 is initiating a long-term monitoring study of marinas in California to determine concentrations of DCu in those marina waters and, therefore, evaluate the results of the regulation and other mitigation actions. The objective of this protocol is to discuss the background, objectives, personnel, study plan, and timeline of the described monitoring study.

DCu is a water quality concern because it can leach from the paints into marina waters and potentially result in toxicity to non-target 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). The California Toxics Rule (CTR), which has set acute (4.8 µg/L) and chronic (3.1 µg/L) water quality standards for DCu, aims to protect those species.

Recreational vessel marinas 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. Several studies in the 1990s and 2000s focused on measuring concentrations of metals in Southern California. The resultant data led to several marinas being placed on the Clean Water Act’s 303(d) list for impaired waters. Total maximum daily load allocations and associated implementation plans were developed for three of those marinas, Shelter Island...
Yacht Basin in San Diego, Marina del Rey in Los Angeles, and Newport Bay in Orange County (still currently in draft form), (between 2006–present).\(^7\)\(^9\)

In 2006, CDPR’s Surface Water Protection Program (SWPP) conducted a monitoring study to determine the extent of DCu pollution across California.\(^10\) The study measured DCu in 22 marinas, which represented freshwater, and brackish- and salt-water marinas in Northern, Central, and Southern California. Sizes of marinas ranged from 400 to 5000 boats. Median marina DCu concentrations ranged from 0.5 µg/L (Folsom Marina) to 13.6 µg/L (Marina del Rey).\(^10\) 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. Other concurrent monitoring studies 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.\(^11\)

Researchers have also observed a concentration gradient in marinas with higher concentrations near the back and decreasing concentrations towards the mouth, which typically has a lower density of boats and increased flushing capacity.\(^4\)\(^,\)\(^12\) All of these studies concluded that the high DCu concentrations were due to leaching from Cu-AFPs.\(^4\)\(^,\)\(^6\)\(^,\)\(^10\)\(^-\)\(^13\)

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, and salinity.\(^4\)\(^\)\(^,\)\(^14\) 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.\(^10\) In addition, each water sample was evaluated using the Biotic Ligand Model (BLM), which is a metal bioavailability model that predicts toxicity concentrations 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.

In response to the CTR exceedances and associated toxicity, 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 by 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.\(^15\) SWPP scientists used water chemistry parameter inputs and 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 chosen to result in DCu concentrations in marinas with ≤1270 vessels that would be in continuous compliance with the chronic CTR, which accounts for >95% of marinas in California. Reductions, however, are expected to occur in all marinas in California regardless of size. Monitoring is necessary to evaluate the effect of the release rate cap regulation, along with implementation of other mitigation recommendations including management of in-water hull cleaning, in reducing DCu concentrations in California marinas.

2. **Objectives**

The objectives of this study are to:

- Determine concentrations of DCu in California marinas over several years.
- Determine the variation in DCu concentrations based on size and region of selected marinas.
- Determine potential toxicity of marina samples based on measured water chemistry parameters using the saltwater biotic ligand model.

3. **Personnel**

This study will be conducted by staff from the Environmental Monitoring Branch, Surface Water Protection Program, under the general direction of Dr. Jennifer Teerlink, Senior Environmental Scientist (Supervisor). Key personnel are listed below:

- **Project Leader:** Aniela Burant, Ph.D.
- **Field Coordinator:** KayLynn Newhart
- **Reviewing Scientist:** Xuyang Zhang, Ph.D.
- **Statistician:** Dan Wang, Ph.D.
- **Analytical Chemistry:** Environmental Chemistry Laboratory, Department of Toxic Substances Control

Questions concerning this monitoring project should be directed to Aniela Burant, Environmental Scientist, at (916) 445-2799 or by email at Aniela.Burant@cdpr.ca.gov.

4. **Study Plan**

Dissolved copper is the primary constituent of interest. Secondary constituents of interest are water chemistry parameters such as temperature, pH, salinity, dissolved organic carbon (DOC), and total suspended solids (TSS). This sampling effort will be used to establish a network to determine long-term trends in DCu concentrations. The first set of samples in 2019 will be used to establish a pseudo-baseline concentration of DCu in the targeted marinas, and samples taken in subsequent years will be used to evaluate the effectiveness of the low leach rate regulation and other mitigation actions. DCu will also be measured outside of the marina at a local reference site to compare to the background levels at those sites.
There will be multiple samples taken in each marina; these will be taken at locations to assess the variability of DCu across the marina. In addition to quantitating DCu in each sample, measurements of water chemistry parameters will occur concurrently with each sample. Sampling of the water chemistry constituents will be used as input parameters in the BLM, which will be used to predict site-specific bioavailability of copper and the associated toxicity. Implementation of any in-water hull cleaning permitting requirements in each marina will be noted. Other mitigation actions, such as programs to convert to alternative biocides and/or boat lifts, will also be considered when assessing trends in DCu concentrations. Commercial, government, and military vessels are exempt from the Cu-AFP regulation. Therefore, field crews will make note of those vessels in the vicinity of the sampling sites. Sampling will occur in the summer months to avoid inputs from storm water runoff. Subsequent sampling efforts are planned on a biennial basis.

### 4.1. Assumptions and Limitations

This study is designed to determine DCu concentration in saltwater marinas. However, several assumptions and limitations must be considered to more generally address the sources of DCu in marinas and timing of the sampling.

We assume the main source of DCu in saltwater marinas is from AFPs. Specifically, the major pathway that introduces DCu into the water column is through passive leaching (including the resultant spike in passive leaching due to the refreshment of the surface of the antifouling paint from underwater hull cleaning). However, this study does not intend to quantify the relative contribution of passive leaching and underwater hull cleaning. Copper naturally occurs in ambient water, and there is site-specific variability for copper. We will use local reference sites to account for background concentrations. In addition, to focus on characterizing DCu associated with AFPs, sampling will occur in the dry season to eliminate the input of copper from stormwater runoff to marinas.

In July 2019, the Cu-AFP regulation will have been in effect for one year. The regulation restricts the first point of sale of AFPs in California; however, boatyards have two years (until June 2020) since the implementation of the regulation to sell or use noncompliant Cu-AFPs. In addition, many paints are on boats for several years and boatyard capacity for turnover is limited. Although it would have been preferable to take pre-regulation samples to set a recent baseline for DCu in marina, taking samples in summer 2019 will be a suitable alternative. Use of antifouling paints is not reported to CDPR’s Pesticide Use Reporting database; however, CDPR’s sales database can be used to track the sales of the lower leach rate paints that contain a biocide. The BLM can be used, in lieu of toxicity tests, to predict toxicological effects at specific sites, and give insight to where future toxicity testing should occur.

### 4.2. Site Selection
This study is designed to provide a baseline from which to evaluate the efficacy of the new Cu-AFP regulation and other mitigation actions. Site selection for the study will consider findings from the previous CDPR monitoring and modeling efforts. Site selection will, therefore, have specific considerations for region, water type, and size. The original CDPR monitoring study was designed to be representative of different water types and regions in California. That study found that larger saltwater marinas in Central and Southern California had higher concentrations of DCu than Northern California marinas. Central and Southern California marinas will be the focus of this study.

4.2.1. Saltwater Marinas

This study will focus exclusively on saltwater marinas. The previous study showed that freshwater and brackish water marinas exhibited relatively low to medium DCu concentrations. These marinas are typically smaller than saltwater marinas; the largest fresh water or brackish water marina in the previous CDPR study contained 800 vessel slips. In addition, vessels in these marinas are not as susceptible to fouling as in saltwater marinas and, anecdotally, there is lower use of Cu-AFPs at these sites. In addition, saltwater CTR criteria are also lower than the generic CTR freshwater criteria values (acute criterion = 13 µg/L, chronic criterion = 9 µg/L).

4.2.2. Region

Marinas in this study will be more heavily located in Central and Southern California. Previous studies have shown that Central and Southern California marinas tend to have higher concentrations of DCu than those in Northern California, specifically San Francisco Bay marinas. Marinas in Northern California tend to also be smaller than those in Central and Southern California, with the largest marina in Northern California holding ~1100 vessels (Berkeley Marina). San Francisco Bay also has several site specific objectives (SSOs) for DCu. The chronic SSOs range from 6.0–6.9 µg/L and the acute SSOs range from 9.4–10.8 µg/L for Mytilus species; Clean Water Act regulatory action implemented by the San Francisco Bay Regional Water Quality Control Board occurs only if these concentrations are exceeded.

4.2.3. Marina Sizes

CDPR’s leach rate regulation was determined with the aid of MAM-PEC modeling. Five marina scenarios were modeled to determine the leach rate (Table 1). The final regulation was designed to achieve continuous compliance of the CTR of marinas with <1270 vessels, and almost all marinas in California are that size or smaller. Marinas will be selected with total slip numbers that are in all five scenarios in order to determine if there is a difference in relative DCu reductions among the groups.

Table 1. Marina Scenarios in MAM-PEC Modeling
### 4.2.4. Other criteria

Selected marinas will be evaluated using aerial photos and maps to determine possible sampling locations. Marinas that have relatively poor flushing are preferred (i.e., the worst-case scenario). Additional criteria include, in order of importance:  

1. The marina owner/operator is willing to collaborate on sample collection including providing a boat for sampling.
2. The marina contains slip areas that are sufficiently isolated from adjacent or surrounding sources (e.g., boatyards, industrial discharges).
3. Historical and current activities (e.g., dredging, construction) in the marina area will not interfere with the interpretation of results.

After all these considerations, eight marinas or harbors were chosen to be included in this study (Table 2). It should be noted that there are three marinas on this list that have associated total maximum daily loads: Shelter Island Yacht Basin, Marina del Rey, and to-be determined marina in Newport Bay.

<table>
<thead>
<tr>
<th>Marina Scenario</th>
<th>Number of Vessels</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scenario #1</td>
<td>733</td>
</tr>
<tr>
<td>Scenario #2</td>
<td>1270</td>
</tr>
<tr>
<td>Scenario #3</td>
<td>1833</td>
</tr>
<tr>
<td>Scenario #4</td>
<td>2263</td>
</tr>
<tr>
<td>Scenario #5</td>
<td>4754</td>
</tr>
</tbody>
</table>

#### Table 2. Marinas and Harbors Included in the Study

<table>
<thead>
<tr>
<th>Marina</th>
<th>Region</th>
<th>City</th>
<th>Marina Scenario</th>
</tr>
</thead>
<tbody>
<tr>
<td>Berkeley Marina</td>
<td>Northern</td>
<td>Berkeley</td>
<td>2</td>
</tr>
<tr>
<td>Coyote Point Marina</td>
<td>Northern</td>
<td>San Mateo</td>
<td>1</td>
</tr>
<tr>
<td>Santa Barbara Harbor</td>
<td>Central</td>
<td>Santa Barbara</td>
<td>2</td>
</tr>
<tr>
<td>Channel Islands Harbor</td>
<td>Central</td>
<td>Ventura</td>
<td>3</td>
</tr>
<tr>
<td>King Harbor Marina</td>
<td>Southern</td>
<td>Redondo Beach</td>
<td>2</td>
</tr>
<tr>
<td>Marina del Rey</td>
<td>Southern</td>
<td>Los Angeles</td>
<td>5</td>
</tr>
<tr>
<td>Newport Bay*</td>
<td>Southern</td>
<td>Newport Beach</td>
<td>N/A</td>
</tr>
<tr>
<td>Shelter Island Yacht Basin</td>
<td>Southern</td>
<td>San Diego</td>
<td>4</td>
</tr>
</tbody>
</table>

*CDPR will sample at multiple locations in Newport Harbor

#### 4.3. Local Reference Sites

Local reference sites (LRS) will be sampled to determine the background concentrations of DCu. Water chemistry parameters will also be measured to inform the saltwater BLM for local reference sites. LRS should be measured right outside of the marina. The marina managers/operators will aid CDPR staff in selecting an LRS. The following are necessary considerations when selecting an LRS:  

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1. The site was located outside the influence of marina activities and potential sources of AFPs, but adjacent to the marina area and within the same body of water.

2. The site was sufficiently isolated from potentially confounding inputs (e.g., boatyards, industrial discharges, and various historical contamination).

3. Recent and current activities (e.g., dredging, construction) in the immediate area would not significantly interfere with the interpretation of results.

4. There was suitable and safe access to the site.

4.4. Sampling Method

Water samples will be collected by boat from multiple points within each of the marinas in order to determine the presence of a gradient in the marina (Appendix A). Potential sampling locations within the marina will be identified via aerial photos and maps. The marinas will be stratified according to the surface area of the marina, which will be determined via measurement with Google maps. Samples will be taken in the middle of fairways, adjacent to the mid-points of docks. Samples will be taken at least two meters from the sampling vessel to ensure no interference from the hull paint on the vessel. There will be at least one corresponding LRS sample, field duplicate, and matrix spike per marina. A field blank will be collected by running deionized water through the sampling equipment at each marina. At each sampling location, including each LRS, a YSI EXOI Multiparameter Sonde meter (or Sonde) will be used to measure the temperature, salinity, and pH of the water.

DCu samples will be collected in accordance with U.S. EPA Method 1669, “Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels.” As per this method, sampling will occur with a battery-operated peristaltic pump, polyethylene tubing, and pre-cleaned polyethylene sampling bottles. Deionized (DI) water will be used to clean sampling bottles and for generating field blanks.

Sampling will require three SWPP field staff. One will serve as “clean hands,” one will serve as “dirty hands,” and the third will conduct Sonde measurements and record-keeping. Clean hands will touch only what directly touches the sample, including sampling tubes and bottles. Dirty hands can 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 will be filtered using an in-line 0.45 µm filter. This filter will be replaced for each sample in each marina. The sample filtrate will be collected into U.S. EPA-certified, pre-labeled pre-cleaned 250 mL polyethylene plastic bottles. The sample filtrate will be acidified to a pH level of <2.0 with Optima® ultra-pure nitric acid. Samples for TSS/DOC will not be filtered or acidified. Samples will be immediately double-bagged and placed on ice (~4°C) for transport. The water samples can be stored for up to six months prior to metals analysis. Each sample will have an accompanying
CDPR chain-of-custody form. Other site-specific activities (i.e. active construction activities, possible underwater hull-cleaning operations, weather conditions) will be recorded during sampling.

4.5. Dissolved Copper Analysis

The water samples will be sent to the Department of Toxics Substances Control (DTSC) Environmental Chemistry Laboratory in Pasadena, CA. The samples will be analyzed according to EPA Method 1640: Determination of Trace Elements in Water by Pre-concentration and Inductively Coupled Plasma-Mass Spectrometry, with some modifications. Laboratory QA/QC will follow CDPR guidelines and will consist of laboratory blanks, matrix spikes, matrix spike duplicates, surrogate spikes, and blind spikes. The reporting limit will be ≤ 0.1 ppb.

Total Suspended Solids and Dissolved Organic Carbon Analysis

Analysis of TSS/DOC will be completed by CDPR Staff at its West Sacramento Laboratory. DOC in water will be analyzed using a TOC-V CSH/CNS analyzer (Shimadzu Corporation, Kyoto, Japan). Total suspended solids will be analyzed for total suspended solids according to Ensminger (2016). Measurements of pH, temperature, and salinity will be completed in the field using the Sonde.

4.6. QA/QC

The samples will be taken in accordance to US EPA Method 1669. The method recommends several QA/QC procedures, which will be employed in this study. Equipment will be rigorously cleaned using DI water, detergent, and a nitric acid bath between each marina sampling site. To ensure proper cleaning procedures, an equipment blank will be taken after each cleaning procedure. Each marina will have a corresponding field blank to determine artifacts, if any, from the field sites. Native rinsing will occur before sampling at each site within the marina. A field duplicate and matrix spike will be collected at each field site.

4.7. Data Analysis

This protocol is describing the first round of sampling in what is expected to be a long-term monitoring study. As data are collected, different statistical analyses will be used to evaluate DCu in the targeted marinas. However, more data will be required to determine the long-term trends. Initially, samples will be compared to both their respective chronic and acute CTR values and the concentrations measured at the LRS. The area of the marina where the sample was taken, regional location, water temperature, and size of marina will also be compared to measured values of DCu. Various parametric and non-parametric tests are expected to be employed. The exact tests will be determined based on the detection frequency of the metals and normality of the data.
4.8 Biotic Ligand Modeling

In lieu of toxicity testing, the draft saltwater BLM will be employed to predict site-specific toxicity based on measured, site-specific water quality data. In 2016, the U.S. EPA released the Draft Estuarine/Marine Copper Aquatic Life Ambient Water Quality Criteria, which uses the saltwater BLM in the development of those criteria.\(^2\) A biotic ligand is the binding site on the organism that is linked to the toxic effects on that organism.\(^3\) The model assumes that toxicity is associated with the amount of Cu bound to the biotic ligand.\(^4\) 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., DCu, DOC, pH, temperature, and salinity).

The model generates results specific to those inputs – a final acute value, a criterion maximum concentration, and a criterion continuous concentration. These are the concentrations at which toxicity due to DCu is expected to occur for this particular water body. Both acute and chronic toxic units are generated. This version of the BLM takes into account the toxicity of DCu to Haliotis rufescens, or the red abalone, the most sensitive species to DCu in the species sensitive distribution.\(^5\) These values will be compared to the measured DCu concentrations to determine if there is likely to be measured toxicity present at the site.

Several inputs to the BLM will be measured in-situ using the Sonde; these include the pH, temperature, and salinity of the waterbody. The DOC will be measured in a separate analysis. The BLM also assumes that the cations and anions present in saltwater are present at a certain ratio. The measured salinity will adjust the individual ion concentrations based on the assumed ratio.

5. Timeline

Field Sampling: July–August 2019
Chemical Analysis: November 2019
Draft Report: March 2020

6. References

9. RWQCB, S. A. R., Draft Amendments to the Water Quality Control Plan - Santa Ana Region to incorporate the Newport Bay Copper (Cu) TMDLs, and non-TMDL Action Plants for Zinc (Zn), Mercury (Hg), Arsenic (As), and Chromium (Cr). In California Regional Water Quality Control Board, Santa Ana, CA: 2018.
16. Richard Looker; Amendment, P. B. P., Copper Site-Specific Objectives in San Francisco Bay. 2007.
Appendix A

Expected sampling locations are indicated on the map of each marina or harbor. Boxes labeled “L” indicate local reference sites.

Figure 1. Sampling locations within Berkeley Marina
Figure 2. Sampling locations within Coyote Point Marina
Figure 3. Sampling locations within Santa Barbara Harbor
Figure 4. Sampling locations within the King Harbor Marina
Figure 5. Sampling locations within the Channel Islands Harbor
Figure 6. Sampling locations within Marina del Rey
Figure 7. Sampling locations within Newport Harbor
Figure 8. Sampling locations within Shelter Island Yacht Basin. Orange markers are sites that will be sampled by the Port of San Diego on the same sampling trip.