



**Department of Pesticide Regulation  
Environmental Monitoring Branch  
Surface Water Protection Program  
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## **STUDY 319: Monitoring of Dissolved Copper in California Coastal Marinas**

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### **1. Introduction**

Antifouling paints (AFPs) are used on vessels to prevent biofouling (e.g., accumulation of plants, algae, small animals), which can decrease vessel fuel efficiency and facilitate the spread of aquatic invasive species.<sup>1</sup> Frequently, AFPs 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) announced a regulation placing a copper release rate (or leach rate, used in this document interchangeably) cap on AFPs. The regulation sets a maximum allowable copper leach rate of 9.5  $\mu\text{g}/\text{cm}^2/\text{day}$  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. The CDPR is conducting 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 intention of this protocol is to discuss the background, objectives, personnel, study plan, and timeline of the described monitoring study.

Dissolved copper is a water quality concern because it can leach from the AFPs into marina waters and potentially result in toxicity to non-target organisms. Species of concern include the blue (*Mytilus edulis*) and Mediterranean mussels (*Mytilus galloprovincialis*), and the red abalone (*Haliotis rufescens*).<sup>2</sup> The California Toxics Rule (CTR) aims to protect these species by setting an acute (4.8  $\mu\text{g}/\text{L}$ ) and chronic (3.1  $\mu\text{g}/\text{L}$ ) water quality standard for DCu.<sup>3</sup>

Recreational vessel marinas are particularly susceptible to pollution from AFP's because they tend to have high concentrations of vessels that 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.<sup>4</sup>

Several studies in the 1990s and 2000s focused on measuring concentrations of metals in Southern California.<sup>5,6</sup> 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 (TMDL) allocations and associated implementation plans were developed between 2006 and 2022 for three of those marinas: Shelter Island Yacht Basin in San Diego (2005), Marina del Rey in Los Angeles (2015), and Newport Bay in Orange County (2022).<sup>7-9</sup>

In 2006, CDPR's Surface Water Protection Program (SWPP) conducted a monitoring study to determine the extent of DCu pollution across California.<sup>10</sup> The study measured DCu in 22 marinas, which represented freshwater, brackish- and salt-water marinas in Northern, Central, and Southern California. These marinas ranged in size from 400 to 5,000 boats. Median marina DCu concentrations ranged from 0.5 µg/L (Folsom Marina) to 13.6 µg/L (Marina del Rey).<sup>10</sup> The CDPR study found that 51% of the samples exceeded the CTR chronic water quality criterion and 33% exceeded the CTR acute water quality criterion. Other concurrent monitoring studies showed similar results with measured DCu concentrations in four Southern California marinas ranging from non-detect to 21 µg/L (mean: 7.0 µg/L).<sup>11</sup> In marinas with a concentration gradient (i.e., higher concentrations near the back and decreasing concentrations towards the mouth), there is typically a lower density of boats and increased flushing capacity.<sup>4,12</sup> Results of the CDPR and outside agency research indicated that the high DCu concentrations were due to leaching from Cu-AFPs.<sup>4-6, 10-13</sup>

Toxicity of DCu in natural waters is dependent on site-specific water chemistry parameters. The 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.<sup>4, 14</sup> A subset of samples in the 2006 CDPR Study were used for toxicity testing on mussel embryo development for *M. galloprovincialis*; 17% of those samples exhibited statistically significant toxicity.<sup>10</sup> 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 from the monitoring data.

In response to the CTR exceedances and associated toxicity, CDPR responded with a series of regulatory actions that resulted in a maximum allowable copper leach rate (i.e., 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 is a two-dimensional hydrodynamic fate and transport

model used to predict environmental concentrations of AFPs in harbors and marinas.<sup>15</sup> The SWPP scientists used water chemistry parameter inputs (e.g., DOC, salinity) and a water quality goal of 3.1 µg/L (i.e., the CTR chronic criterion) in MAM-PEC to determine the maximum allowable leach rates for different modeling scenarios. The modeling scenarios are intended to be 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 set in the regulation was chosen to result in DCu concentrations in marinas with ≤1,270 vessels that would be in continuous compliance with the chronic CTR, which accounts for >95% of marinas in California. Reductions in copper concentration, however, are expected to occur in all marinas in California regardless of size. Therefore, ongoing monitoring is necessary to evaluate the effect of the CDPR 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:

- Measure concentrations of DCu in California marinas over several years.
- Determine the variation in DCu concentrations based on size and region of selected marinas.
- Calculate 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. Anson Main, Environmental Program Manager I. Key personnel are listed below:

Project Leaders: Pedro Lima, Ph.D.  
Rio Lininger  
Reviewing Scientist: Xuyang Zhang, Ph.D.  
Analytical Chemistry: Analytical Chemistry Branch, Department of Toxic Substances Control

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## 4. Study Plan

In this monitoring study, DCu is the primary chemical of interest. Secondary measurements 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 collected in 2019, established a baseline

concentration of DCu in the targeted marinas, and monitoring in subsequent years will be used to evaluate the effectiveness of the low leach rate regulation and other mitigation actions. The DCu will also be measured outside of each marina at a local reference site to compare DCu measured in marinas to the background DCu levels at those sites. To assess the variability of the DCu in marina waters, there will be multiple samples collected at several locations at each focal marina. In addition to determining DCu in each sample, measurements of water chemistry parameters will occur concurrently. The water chemistry measurements will be used as input parameters in the BLM, which will be used to predict site-specific bioavailability of copper and its 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 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, the SWPP staff will make note of those vessels in the vicinity of the sampling sites. Sampling will occur in the summer months to avoid inputs to marinas from storm water runoff. Sampling efforts will be conducted on an annual basis with half of the marinas being sampled in even years and the other half in odd years. This sampling season, corresponding to 2023, will consist of an odd year plan. Even and odd groupings were chosen based on marina size and location in order to represent both large and small and central and southern marinas in each year.

<b>Even Year Sampling</b>	<b>Odd Year Sampling</b>	<b>Marina Location</b>
Coyote Point Marina	Berkeley Marina	Central California
Channel Islands Harbor	Santa Barbara Harbor	Central California
King Harbor	Marina del Rey	Southern California
Shelter Island Yacht Basin	Newport Bay	Southern California

#### **4.1. Assumptions and Limitations**

Study 319 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 that 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 AFP 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.

The CDPR Cu-AFP regulation restricts the first point of sale of AFPs in California. Boatyards had two years after the implementation of the regulation in 2018 (until June 2020) to sell or use noncompliant Cu-AFPs. Additionally, many AFPs are on boats for several years and boatyard capacity for turnover is limited. The study conducted in 2019 was intended to provide baseline data for DCu in marinas as the use of paints in compliance with the 2018 regulation are implemented. We intend to use data collected in this study and subsequent years to evaluate changes to marina surface water concentrations. In lieu of toxicity tests, the BLM can be used 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 evaluate the efficacy of the 2018 Cu-AFP regulation and other mitigation actions. Site selection for the study considered findings from previous CDPR monitoring and modeling efforts.<sup>10, 23</sup> Site selection has specific considerations for region, water type, accessibility, and size. The original CDPR monitoring study conducted in 2006 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.<sup>10</sup> Therefore, Central and Southern California marinas are the focus of this study with eight marinas or harbors included in this study. Sampling sites remain the same as those selected in 2019 and 2022.<sup>23</sup>

### **4.2.1. Saltwater Marinas**

Study 319 will focus exclusively on saltwater marinas. The 2006 CDPR study showed that freshwater and brackish water marinas exhibited relatively low to medium DCu concentrations compared to marinas situated in saltwater.<sup>10</sup> 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 freshwater/brackish marinas are not as susceptible to fouling as in saltwater marinas and, anecdotally, there is lower use of Cu-AFPs at these sites.<sup>10</sup> In addition, saltwater CTR criteria (acute criterion = 4.8 µg/L, chronic criterion = 3.1 µg/L) are also lower than the generic CTR freshwater criteria values (acute criterion = 13 µg/L, chronic criterion = 9 µg/L).

### **4.2.2. Region**

The majority of marinas in the state are 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 ~1,100 vessels (Berkeley Marina). San Francisco Bay also has several site-specific

objectives (SSOs) for DCu. The chronic SSOs range from 6.0 to 6.9 µg/L and the acute SSOs range from 9.4 to 10.8 µg/L for *Mytilus* species.<sup>16</sup> The 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

The CDPR 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 <1,270 vessels and almost all marinas in California are that size or smaller. Marinas were 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

Marina Scenario	Number of Vessels
1	733
2	1,270
3	1,833
4	2,263
5	4,754

Table 2. Marinas and Harbors Sampled in the Study

Marina	Region	City	Number of Vessels	Reference Sites	Sampling Sites
Berkeley Marina	Northern	Berkeley	1,052	1	9
Coyote Point Marina	Northern	San Mateo	565	1	4
Santa Barbara Harbor	Central	Santa Barbara	1,133	1	9
Channel Islands Harbor	Central	Ventura	2,150	2	15
King Harbor Marina	Southern	Redondo Beach	1,335	1	11
Marina del Rey	Southern	Los Angeles	4,754	2	15
Newport Harbor	Southern	Newport Beach	5,000	2	15
Shelter Island Yacht Basin	Southern	San Diego	2,132	1	9

#### 4.3. Local Reference Sites

Local reference sites (LRS) are located right outside of the marina and 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. The marina managers/operators will assist CDPR staff in selecting an LRS. The following factors were considered when selecting the LRS<sup>10, 23</sup>:

1. The site is 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 is 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 is 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 to determine the presence of a gradient in the marina (Appendix A). The marinas will be stratified according to the surface area of the marina, which will be determined via measurement from Google maps. Water samples will be collected in the middle of fairways, adjacent to the mid-points of docks. To ensure no interference from the hull paint on the vessel, water samples will be collected at least two meters from the sampling vessel. There will be at least one corresponding LRS sample, field duplicate, matrix spike and matrix spike duplicate 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, the SWPP staff will measure the temperature, salinity, and pH of the water using an Aqua TROLL 400 (In-Situ) multiparameter water quality sonde.

Dissolved copper 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.<sup>17</sup> Deionized (DI) water will be used to clean sampling bottles and for generating field blanks.

To ensure quality data collection, all field sampling events will require three SWPP field staff. One staff member will serve as “clean hands,” one will serve as “dirty hands”, and the third will conduct sonde measurements and record-keeping.<sup>17</sup> 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 0.7 µm filter that will be replaced every 5 to 6 samples. The sample filtrate will be collected into U.S. EPA-certified, pre-labeled pre-cleaned 250 mL polyethylene plastic bottles. Samples for TSS/DOC will not be filtered onsite. Samples will be immediately double-bagged and placed on ice (~4°C) for transport. To preserve sample integrity, 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 (e.g., 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 Toxic 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.<sup>18</sup> The reporting limit will be  $\leq 0.1$  ppb.

#### **4.6. Total Suspended Solids and Dissolved Organic Carbon Analysis**

Analysis of total suspended solids (TSS) and dissolved organic carbon (DOC) will be completed by CDPR Staff at its laboratory located in Rancho Cordova, CA. The DOC in water will be analyzed using a Vario TOC Cube TOC/TN Analyzer (Elementar Analysensysteme GmbH, Langenselbold, Germany).<sup>19</sup> Total suspended solids will be analyzed using a vacuum pump, Buchner filter funnel, and glass fiber microfilters according to methods developed by Ensminger (2016).<sup>20</sup> All other water quality parameters will be taken in the field at the time of sample collection.

#### **4.7. QA/QC**

The samples will be taken in accordance with US EPA Method 1669. The method recommends several QA/QC procedures, which will be employed in this study.<sup>17</sup> Equipment will be rigorously cleaned using reverse osmosis water between each marina sampling site. To ensure cleaning procedures are conducted properly, 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 (i.e., washing the sample bottle with sea water) will occur before sampling at each site within the marina. A field duplicate, matrix spike, and matrix spike duplicate will be collected at each field site.

#### **4.8. Data Analysis**

This protocol is describing 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. In order to statistically analyze the collected data, various parametric and non-parametric tests are expected to be employed. The exact statistical tests will be determined based on the detection frequency of the metals and normality of the data.



#### 4.9. 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.<sup>2</sup> A biotic ligand is the binding site on the organism that is linked to the toxic effects on that organism.<sup>21</sup> The model assumes that toxicity is associated with the amount of Cu bound to the biotic ligand.<sup>22</sup> 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 (e.g., DCu, DOC, pH, temperature, and salinity).

Water quality measurements collected from the sites are input into the model. The model then generates results – 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 *H. rufescens* (red abalone), the most sensitive species to DCu in the species sensitive distribution.<sup>22</sup> 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 such as 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. Therefore, the measured salinity will adjust the individual ion concentrations based on the assumed ratio.

#### 5. Timeline

Field Sampling: July–August 2023

Chemical Analysis: October 2023

Draft Report: March 2024

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## Appendix A

Expected sampling locations, based on criteria from the initial protocol (2019)<sup>23</sup>, are indicated on the map of each marina or harbor. This year (2023) sites are not expected to change; sites may be modified in the future. Boxes labeled “L” indicate local reference sites.



**Figure 1.** Sampling locations within Berkeley Marina.



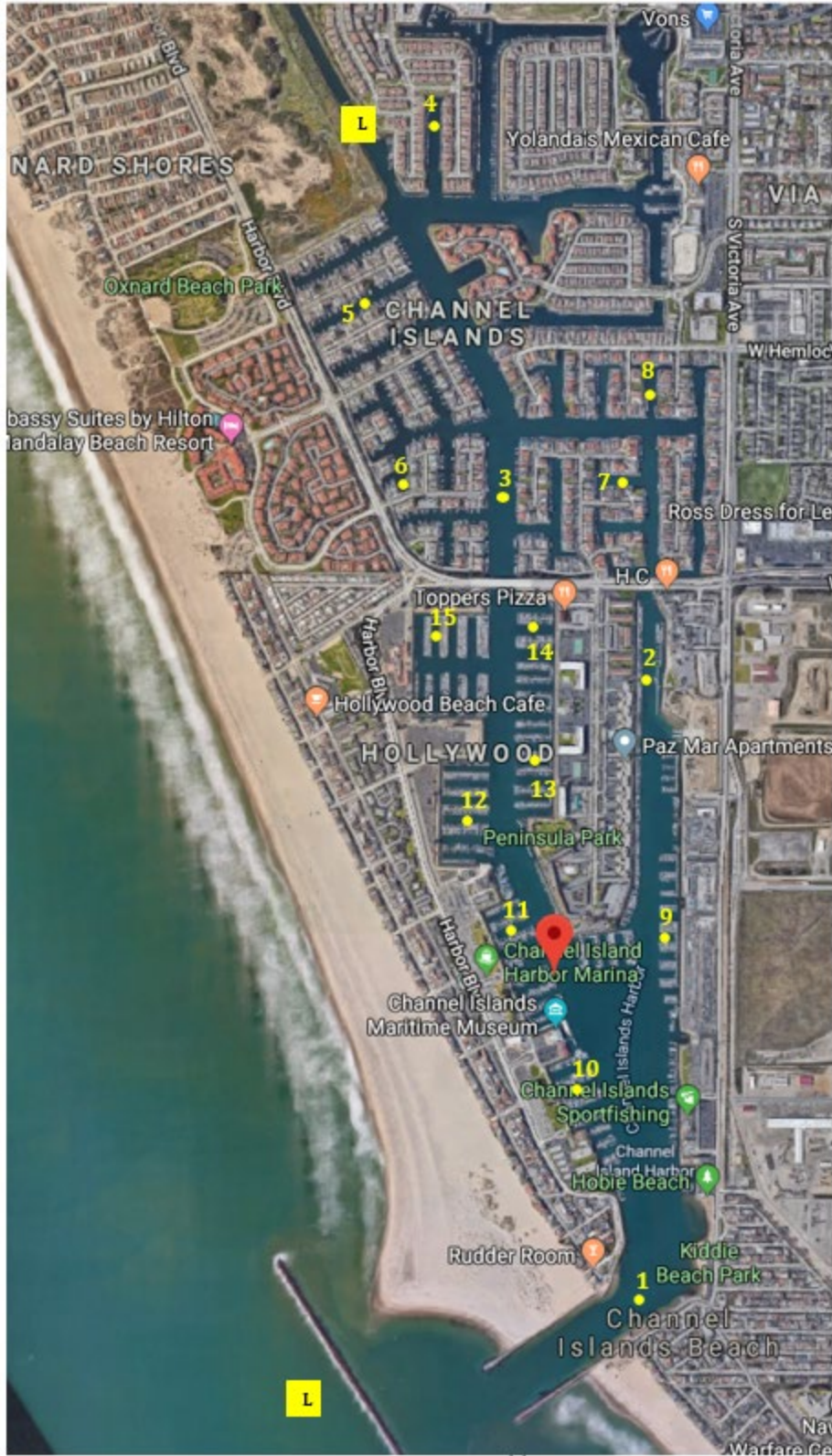
Figure 2. Sampling locations within Coyote Point Marina.



**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.

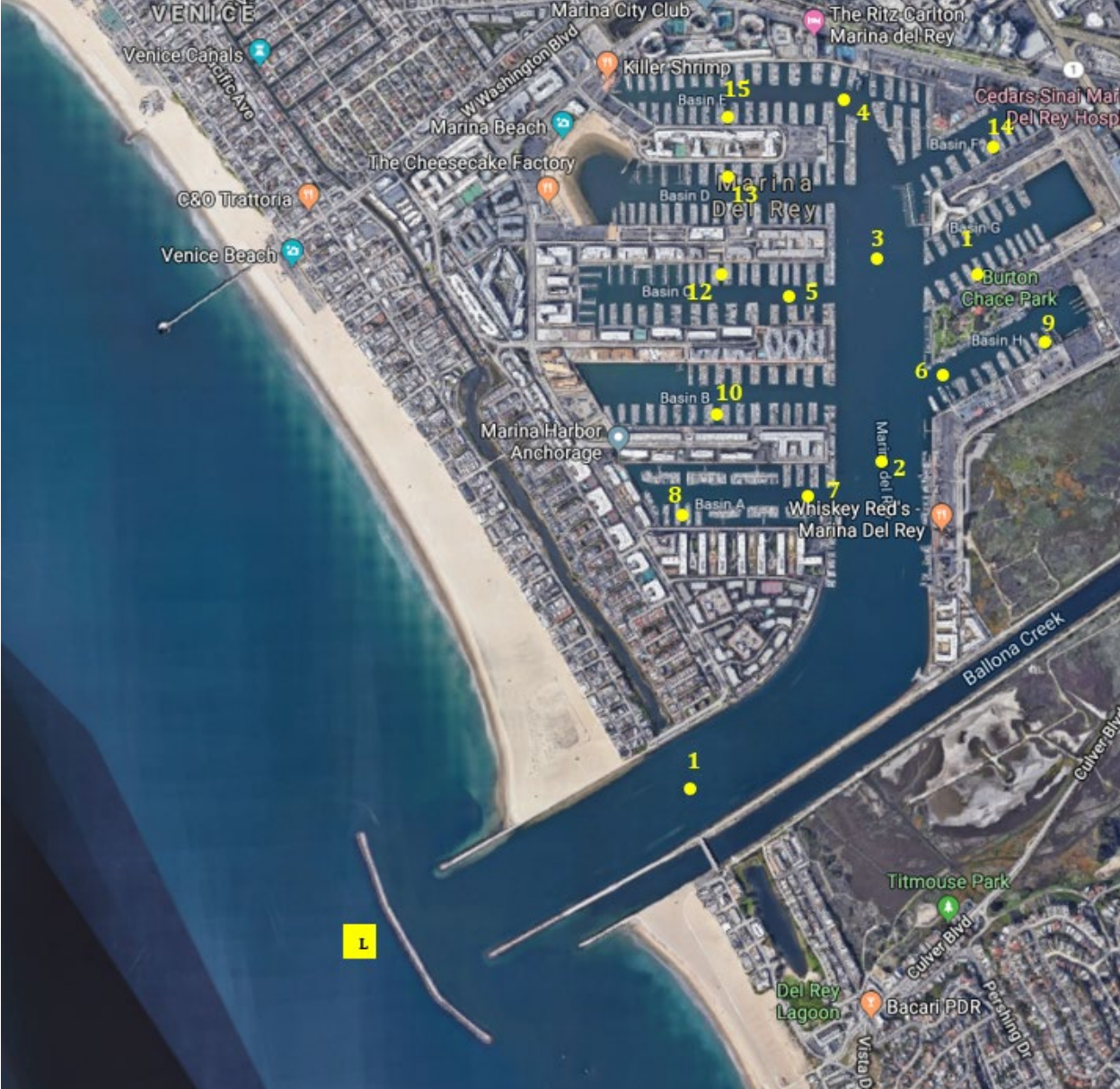


Figure 6. Sampling locations within Marina del Rey.





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.