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 in 2025 and 2026

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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 (Lewis, 1998). These paints often contain a metal-based 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. 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. Dissolved copper (DCu) impairment is a water quality concern because of the potential to result in toxicity to non-target organisms. Species of concern include the blue (*Mytilus edulis*) and Mediterranean mussels (*Mytilus galloprovincialis*), and the critically endangered red abalone (*Haliotis rufescens*) (Elias et. Al, 2016). The California Toxics Rule (CTR), established by the US EPA in 2000, aims to protect these species by setting an acute (4.8 µg/L) and chronic (3.1 µg/L) water quality standard for DCu (US EPA, 2000).

In 2006, DPR's Surface Water Protection Program (SWPP) conducted an investigative monitoring study to determine the extent of DCu pollution across California. The study measured DCu in 22 marinas, which represented freshwater, brackish- and salt-water marinas in Northern, Central, and Southern California. The DPR study found that saltwater waterbodies had higher concentrations of DCu than fresh or brackish waterbodies and that 51% of all samples exceeded the CTR chronic water quality criterion and 33% exceeded the CTR acute water quality criterion. In response to the CTR exceedances and associated toxicity, AB 425 passed in the California legislature requiring DPR to set a maximum allowable leach rate for AFP products and to produce a list of recommended mitigation methods to address copper pollution.

Using water chemistry parameters (e.g., DOC, salinity) and a water quality goal of 3.1 µg/L (i.e., the CTR chronic criterion), SWPP staff applied the Marine Antifoulant Model to Predict Environmental Concentrations (MAM-PEC) to determine a maximum leach rate of 9.5 $\mu g/cm^2/day$ for paints used on recreational vessels. This leach rate, effective July 1, 2018, was chosen to ensure continuous compliance with the chronic CTR for DCu. Reductions in copper concentration are expected to occur in all marinas in California regardless of size or location. Therefore, long-term monitoring is necessary to evaluate the effectiveness of the 2018 leach rate cap regulation in reducing DCu concentration and minimizing potential aquatic toxicity in California marinas. This protocol outlines the study's background, objectives, personnel, study plan, and timeline.

2. Objectives

The objectives of this study are to:

- Measure concentrations of DCu in California marinas.
- 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 (BLM).

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 Leader:	Rio Mecredy
Reviewing Scientists:	Xuyang Zhang, Ph.D. Pedro Lima, Ph.D.
Analytical Chemistry:	Analytical Chemistry Branch, Department of Toxic Substances Control

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4. Study Plan

The first set of samples collected in 2019 established baseline concentrations of DCu within the targeted marinas. Samples collected in subsequent years will be used to evaluate trends in DCu concentrations and to assess the effectiveness of the low leach rate regulation and other mitigation actions. The eight marinas established in previous years will continue to be sampled in 2025 and 2026. These marinas are divided into two groups, each containing sites from different regions and varying sizes (Table 1). Sampling will follow a biennial schedule. To avoid potential DCu inputs of storm runoff, sampling will take place in the driest months, July and August.

Water samples will be collected by boat from multiple points within each marina, harbor, or bay. To ensure no interference from the hull paint on the sampling vessel, water samples will be collected at least two meters out. Each sampling event will include at least one corresponding local reference site (LRS) sample and one field duplicate sample. At each sampling location, including each LRS, SWPP staff will measure temperature, salinity, and pH using an Aqua TROLL 400 multiparameter water quality sonde. Each sample will have an accompanying DPR chain-of-custody form. Other site-specific activities or variables (e.g., active construction activities, possible underwater hull-cleaning operations, weather conditions) will be recorded during sampling. In lieu of toxicity tests, the BLM will be used to predict toxicological effects at specific sites and give insight into where future toxicity testing should occur.

4.1. Assumptions and Limitations

Study 319 is designed to determine DCu concentrations in saltwater marinas. However, several assumptions and limitations must be considered to more generally address the many sources of DCu in marinas. 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. Although this is likely not the only source of Cu input into marinas, this study does not intend to quantify the relative contribution of underwater hull cleaning activities, seasonal runoff, or inputs from low leach rate exempt vessels. DPR staff will make note of any active hull cleaning occurring near sampling locations at the time of sampling as well as any boatyard or government vessels in the vicinity that could contribute to DCu loading and concentrations.

Additionally, the 2018 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. AFPs used on boat hulls only need to be repainted upwards of every 4 years. Therefore, if a boat was repainted in 2018 before July 1st it could have been in compliance despite using a pre-regulation paint up until 2022. The first year of this study was intended to provide baseline data for DCu in marinas before high leach rate paints were phased out. We intend to use data collected in this study and subsequent years to evaluate changes to marina surface water concentrations.

4.2. Waterbody Selection

The marinas, harbors, and bay included within this study remain the same as those included in previous sampling years to monitor long-term trends (Figure 1). Waterbody selection for the study considered region, water type, accessibility, and size. Findings from the 2006 DPR monitoring study indicate larger saltwater marinas in Central and Southern California being a primary concern for higher concentrations of DCu than Northern California marinas (Singhasemanon et al. 2009). This is likely due to colder northern water temperatures causing a slower rate of fouling and less frequent hull cleaning. Also, marinas in Northern California tend to be smaller than those in Central and Southern California, with the largest northern marina holding ~1100 vessels (Berkeley Marina) compared to the largest southern marinas holding ~5000 vessels (Marina del Rey and Newport Bay). Therefore, majority of the selected waterbodies are located in the southern part of the state. As sampling follows a biennial schedule, the waterbodies were split into two groups each including one northern, one central, and two southern locations (Table 1).

4.2.2. Sampling Site Selection

Sampling sites within the selected waterbodies were chosen to represent a variety of conditions within the marina (Figures 2 – 10, Appendix A). Considerations included distance to the mouth of the marina, channel type (i.e. larger open channels or fairways) and areas of low and high tidal flow exchange.

Table 1. Waterbody location, number of sites and schedule.

Marina	Region	Sample Year	City	Reference Sites	Sampling Sites
Berkeley Marina	Northern	2026	Berkeley	1	9

Marina	Region	Sample Year	City	Reference Sites	Sampling Sites
Coyote Point Marina	Northern	2025	San Mateo	1	4
Channel Islands Harbor	Central	2026	Ventura	2	15
Santa Barbara Harbor	Central	2025	Santa Barbara	1	9
King Harbor Marina	Southern	2026	Redondo Beach	1	11
Marina del Rey	Southern	2025	Los Angeles	2	15
Shelter Island Yacht Basin	Southern	2026	San Diego	1	9
Newport Bay	Southern	2025	Newport Beach	2	15

4.2.2. 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 assisted DPR staff in selecting an appropriate LRS depending on specific characteristics of the marina layout. Due to unpredictable conditions at the time of sampling, it is understood that boat operators will attempt to get as close to the predetermined LRS coordinates as safety allows. Any deviation from the original LRS site will be recorded by DPR staff. The following factors were considered when selecting the LRS:

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 carious 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.

During the 2024 sampling period, it was discovered that a reference site within Channel Islands Harbor could be receiving confounding inputs from a steam energy plant upstream from the marina inlet. Therefore, two sampling sites along the upper channel inlet will be added to the Channel Islands Harbor roster in order to test potential metal pollution inputs and overall viability as an LRS site.

5. Sampling Method

Dissolved copper samples will be collected in accordance with method 1669 (US EPA, 1996). Per this method, sampling will occur with a battery-operated peristaltic pump, vinyl tubing, and pre-cleaned polyethylene sampling bottles. Reverse Osmosis (RO) water will be used for generating field blanks and cleaning the exterior of the sampling bottles before shipment to the analytical lab.

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 (US EPA, 1996). 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 as per US EPA sampling method 1669. Samples will be filtered using a Polycap Capsule 0.2 μm filter that will be replaced every 6 to 8 samples or when the filter shows signs of heavy particulate build up. The sample filtrate will be collected into US 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 (~4ºC) for transport. To preserve sample integrity, the water samples can be stored for up to six months prior to metals analysis.

6. Data Collection

6.1. Dissolved Copper Analysis

Water samples will be sent to the Department of Toxics Substances Control (DTSC) Environmental Chemistry Laboratory in Pasadena, CA to be analyzed for DCu. The samples will be analyzed according to Method 1640 (US EPA, 1997) with some modifications. Laboratory QA/QC will follow DPR guidelines and will consist of laboratory blanks, matrix spikes, matrix spike duplicates, surrogate spikes, and blind spikes (Segawa 1995). The reporting limit for DCu is ≤ 0.1 ppb.

Additionally, other parameters such as tide height, water temperature, pH, salinity, DOC, and total suspended solids (TSS) will be collected. Monitoring studies have observed DCu concentrations varying significantly depending on tidal exchange status (Johnson 2007; RWQCB S. D. R. 2005). Therefore, in addition to tide height, the tides will be classified as flood while the tide is increasing, ebb when the tide is outgoing, and slack when there is little to no horizontal motion of the water.

6.2.Total Suspended Solids and Dissolved Organic Carbon Analysis

Analysis of TSS/DOC will be completed by DPR Staff at its laboratory located in Rancho Cordova, CA. The DOC in water will be analyzed using a Vari TOC Cube TOC/TNb Analyzer (Elementar Analysensysteme GmbH, Langenselbold, Germany). Total suspended solids will be analyzed using a vacuum pump, Buchner filter funnels, and glass microfiber 0.7-micron filters according to DPR Method 010.01 (Ensminger, 2016).

6.3. 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. Equipment will be rigorously cleaned using reverse osmosis water between each marina sampling event. 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 will be collected during each sampling event. In previous years matrix spike and matrix spike duplicate samples were collected and submitted for analysis by DTSC. This collection will discontinue for the 2025-2026 sampling sessions as DTSC performs matrix spike and matrix spike duplicate procedure for every sample submitted in Study 319.

6.4. Data Analysis

Various statistical analyses will be used to evaluate DCu concentrations in the targeted marinas. However, more data will be required to determine the long-term trends. Initially, samples were compared to their respective chronic and acute CTR values and the concentrations measured at the LRS. The regional location, water temperature, size of marina, and distribution of sampling sites within each waterbody will be compared to measured values of DCu. In order to statistically analyze the data, various parametric and non-parametric tests are expected to be employed. The choice of statistical methods will be determined based on the detection frequency and distribution of the data.

6.5. Biotic Ligand Modeling

The Biotic Ligand Model (BLM) is a tool utilized by the US EPA for closely predicting site-specific toxicity in freshwater and saltwater environments. A biotic ligand is the binding site on an organism, often gill surfaces, where metals can bind and cause toxic effects on that organism (Di Toro et al, 2001). The BLM assumes toxicity is associated with the amount of Cu bound to the biotic ligand. Furthermore, it assumes the amount of the metal available to bind to the biotic ligand depends on the water quality parameters that control the speciation of that metal in water including DCu concentration, dissolved organic carbon (DOC), pH, temperature, and salinity. It should be noted that the BLM interface estimates full ion chemistry from salinity under the assumption that estuarine water is essentially diluted sea water with negligible ionic inputs from the freshwater source. This assumption is not valid in some cases, namely when the estuarine water's salinity approaches that of freshwater.

Water quality measurements collected from each sampling site will be input into the model. The model then generates both acute and chronic toxic criteria – 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 have occurred at the time of sampling. The saltwater BLM takes into account the toxicity of DCu to *H. rufescens* (red abalone), the most sensitive species to DCu in the species sensitive distribution (US EPA, 2016). These values will be compared to the measured DCu concentrations to determine if toxicity is likely to present at the site.

7. Timeline

Field Sampling: July – August of 2025 and 2026
Chemical Analysis: July – December of 2025 and 2026
Draft Report: March 2027

8. References

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Appendix A

Expected sampling locations, based on criteria from the initial protocol (2019) are indicated on the map of each marina or harbor. This year sites are not expected to change other than the addition of two upper channel sites in Channel Islands Harbor; sites may be further modified in the future. Circles labeled with "LRS" indicate local reference sites.

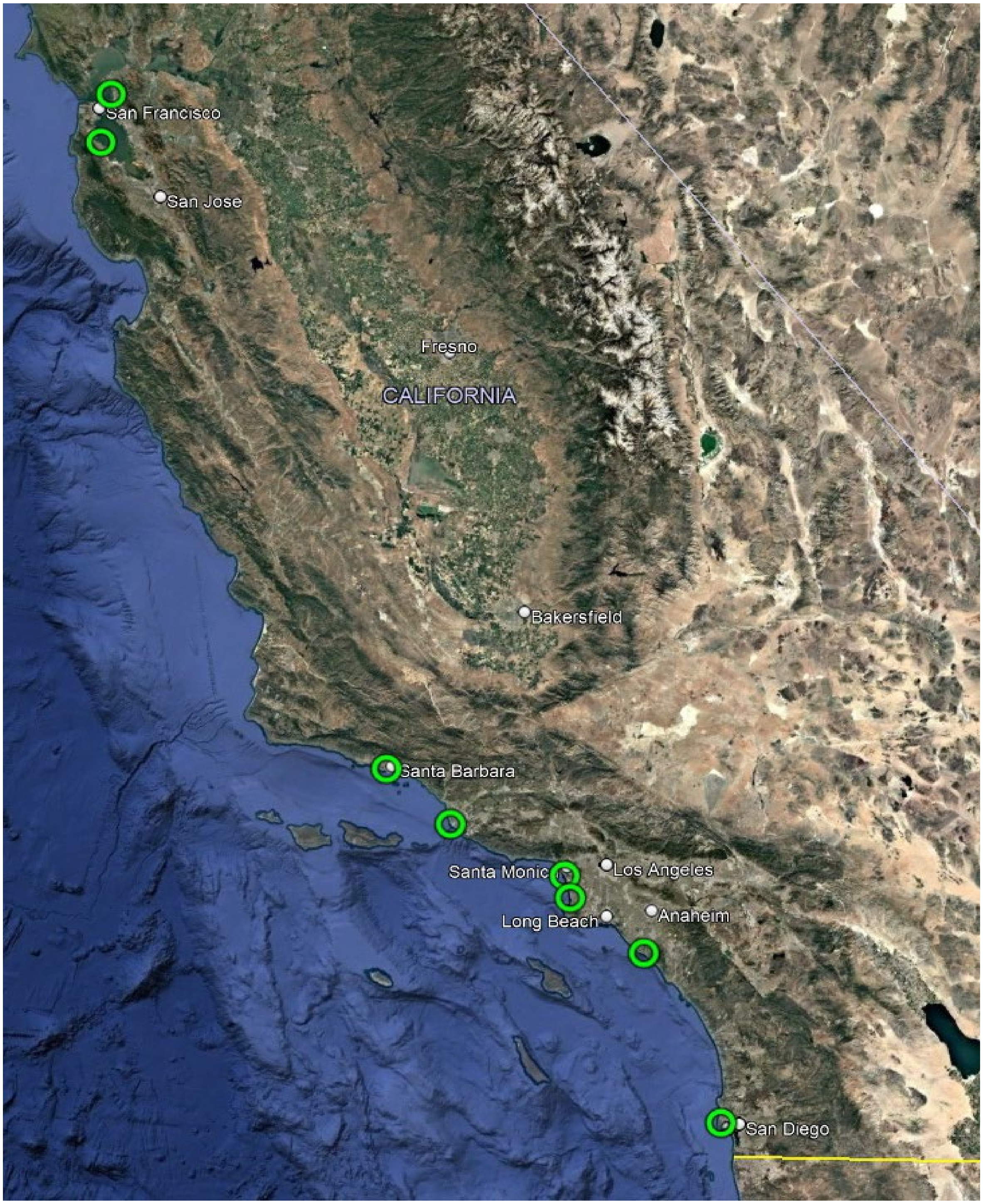

Figure 1. Distribution of waterbody locations.

Figure 2. Sampling locations within Berkeley Marina.

Figure 3. Sampling locations within Coyote Point Marina.

Figure 4. Sampling locations within Santa Barbara Harbor.

Figure 5. Sampling locations within the King Harbor Marina.

Figure 6. Sampling locations within the lower channel of Channel Islands Harbor.

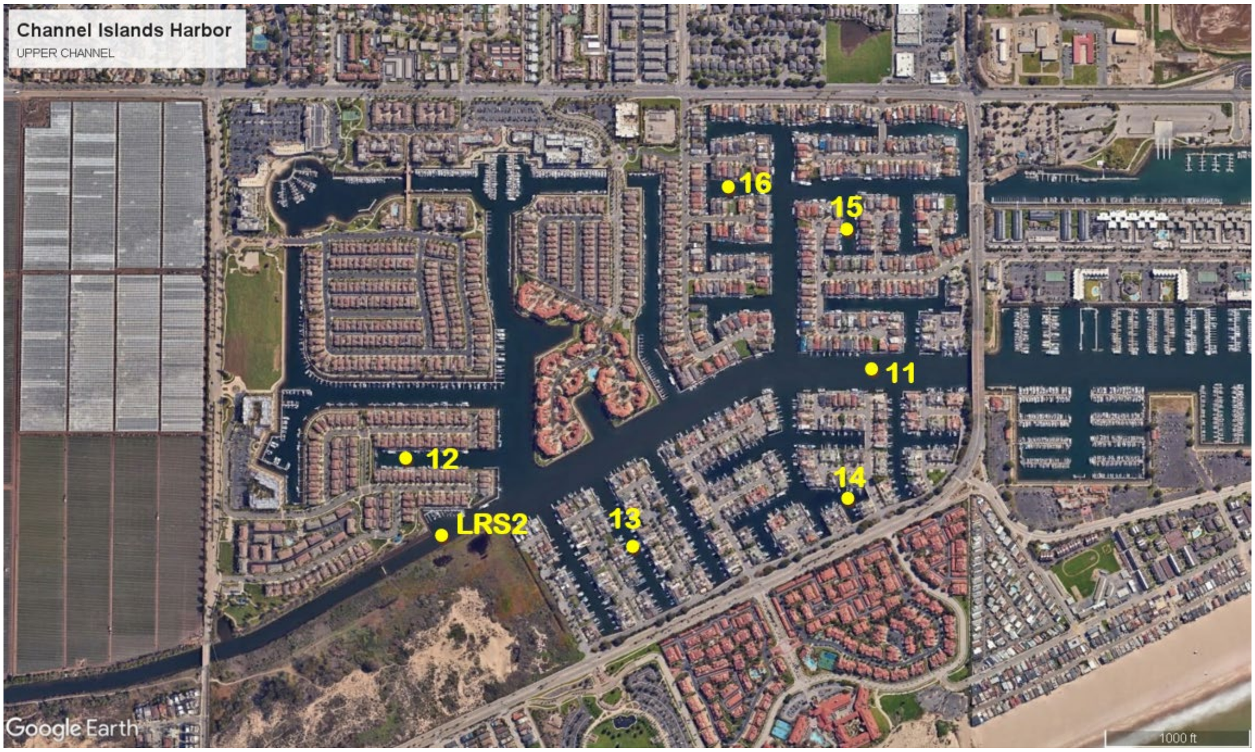

Figure 7. Sampling locations within the upper channel of Channel Islands Harbor.

Figure 8. Sampling locations within Marina del Rey.

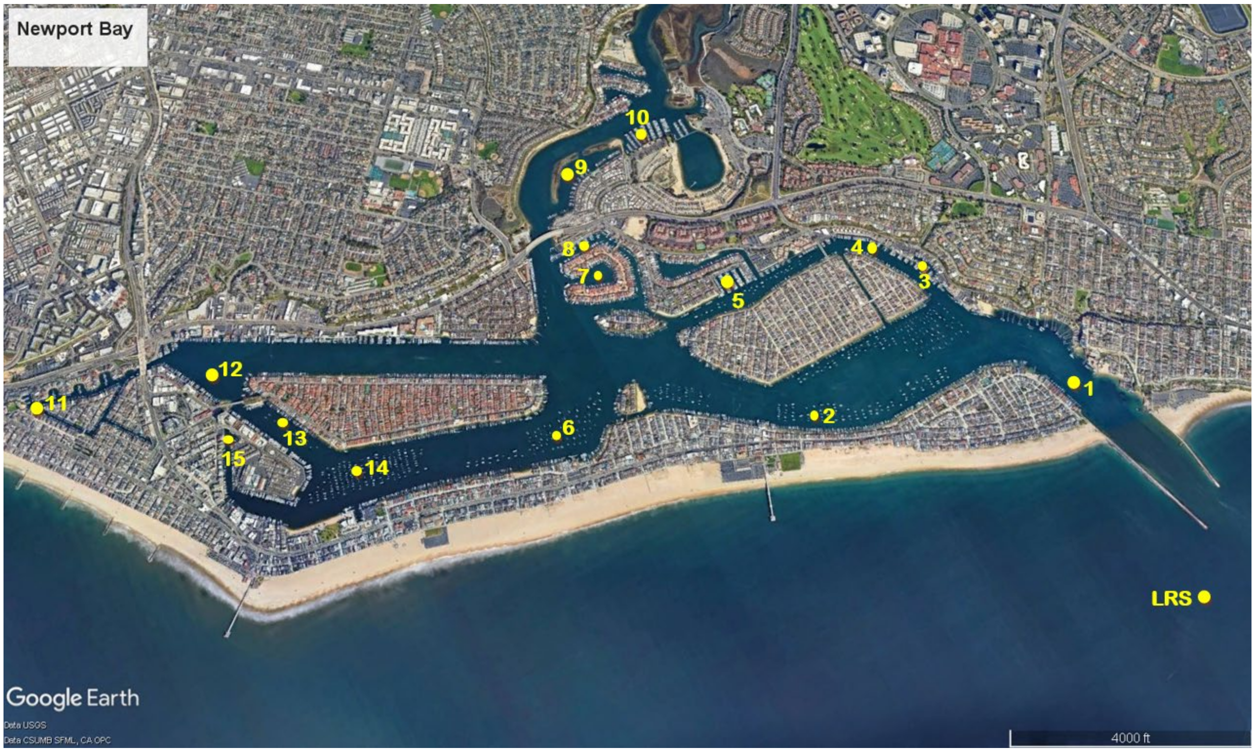

Figure 9. Sampling locations within Newport Harbor.

Figure 10. Sampling locations within Shelter Island Yacht Basin.