

Monitoring of Dissolved Copper in California Coastal Waterbodies



Aniela Burant, Ph.D.
Senior Environmental Scientist
Surface Water Protection Program
California Department of Pesticide Regulation

Outline

- Background on dissolved copper (DCu)
- Previous CDPR efforts
- Copper Antifouling Paint (Cu-AFP) Regulation
- CDPR Monitoring Study
 - Methods
 - Results
- Modeling
 - Spatial and Temporal Trends
- Limitations and Future Work

Copper and Water Quality

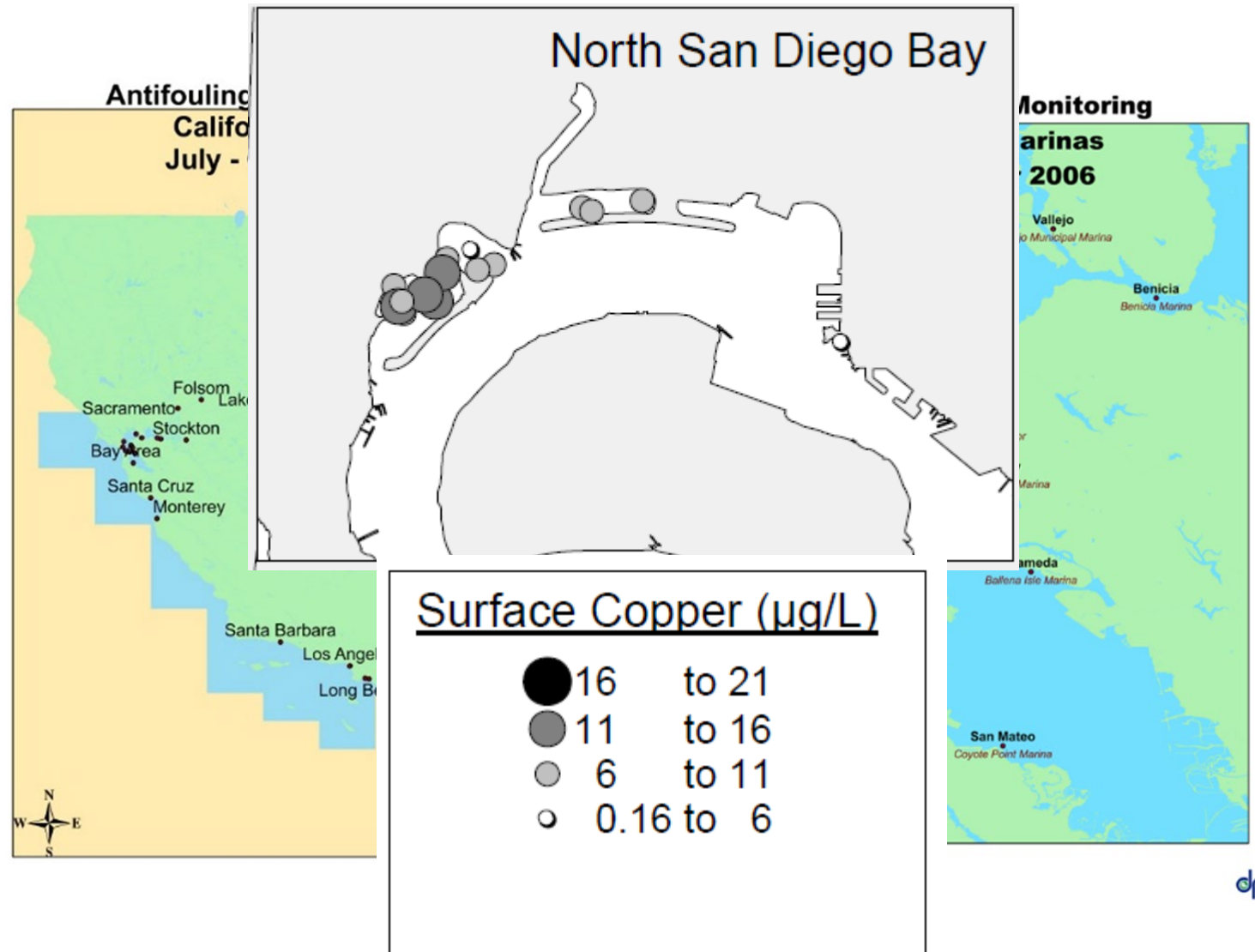
Background

- Copper (Cu^{2+}) is toxic to both target and non-target organisms
 - Only as labile or bioavailable copper
- Species of concern are mussels (blue and Mediterranean)
- California Toxics Rule (CTR) is an enforceable water quality standard
- Dissolved Copper:
 - Acute water quality criterion: $4.8 \mu\text{g/L}$ 
 - Chronic water quality criterion: $3.1 \mu\text{g/L}$ 



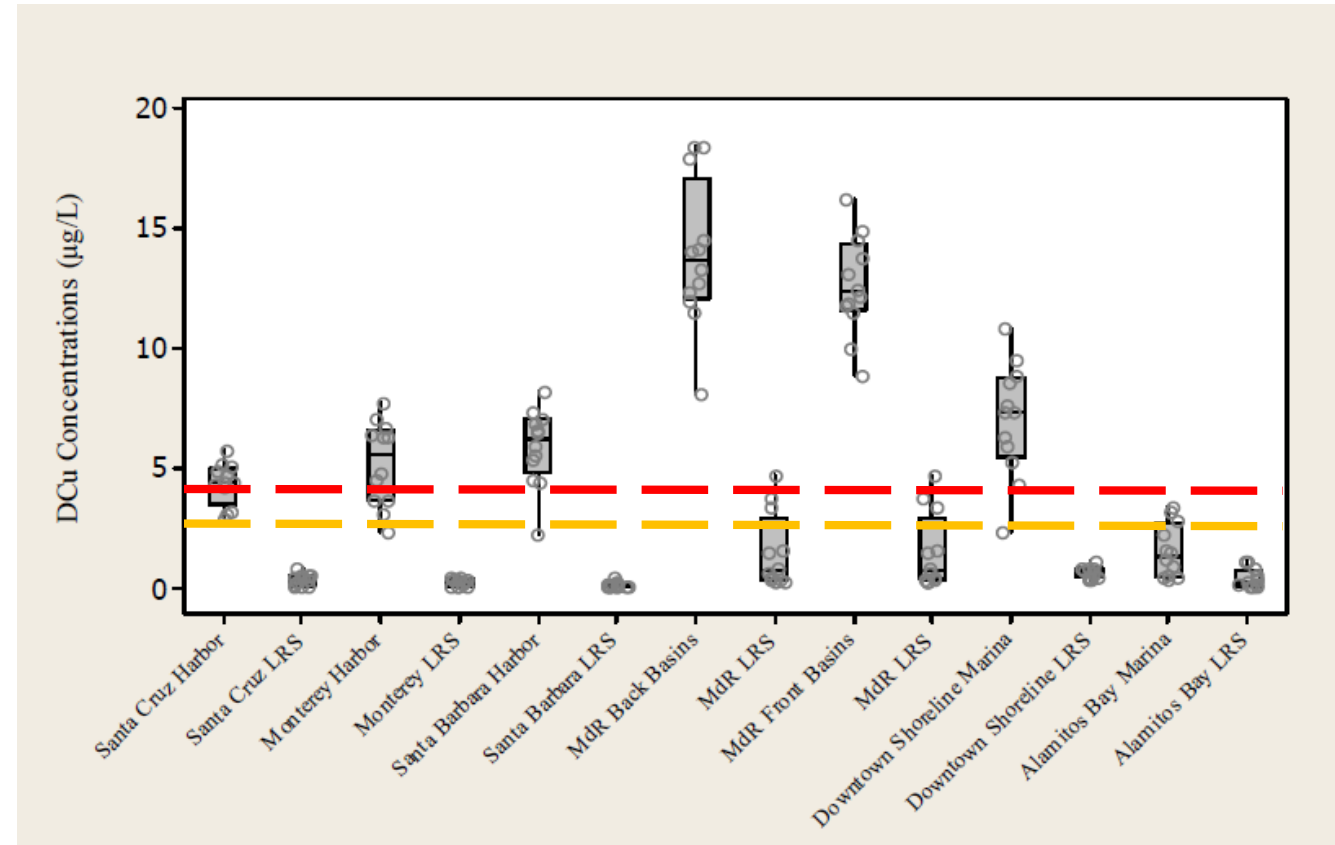
Marinas and Water Quality

- Recreational marinas susceptible to Cu pollution
 - High concentration of boats
 - Long periods of time in marinas
 - Poorly flushed
- 303(d) listing of impaired waters
- CDPR Monitoring Study



Previous CDPR Efforts

- DCu and associated toxicity exceeding water quality standards in many California marinas
- Toxicant Identification Evaluation Tests showed DCu was the likely cause of toxicity



--- = Acute Water Quality Criterion, 4.8 µg/L

--- = Chronic Water Quality Criterion, 3.1 µg/L

LRS = Local Reference Site; OUT of the marina

Previous CDPR Efforts

- AB 425: CDPR needs to determine a leach rate cap and make mitigation recommendations
- Marine Antifoulant Model to Predict Environmental Concentrations (MAM-PEC)
- CTR chronic criterion of 3.1 $\mu\text{g}/\text{L}$ dissolved copper is the goal
- What leach rate will be sufficient to achieve that concentration or lower in California marinas?



Copper AFP Regulation

3 CCR § 6190: No copper-based antifouling paint/coating shall be registered over a **leach rate** of $9.5 \mu\text{g}/\text{cm}^2/\text{day}$

- Any currently registered paint above that leach rate was cancelled.
- For recreational boats only
- July 2018



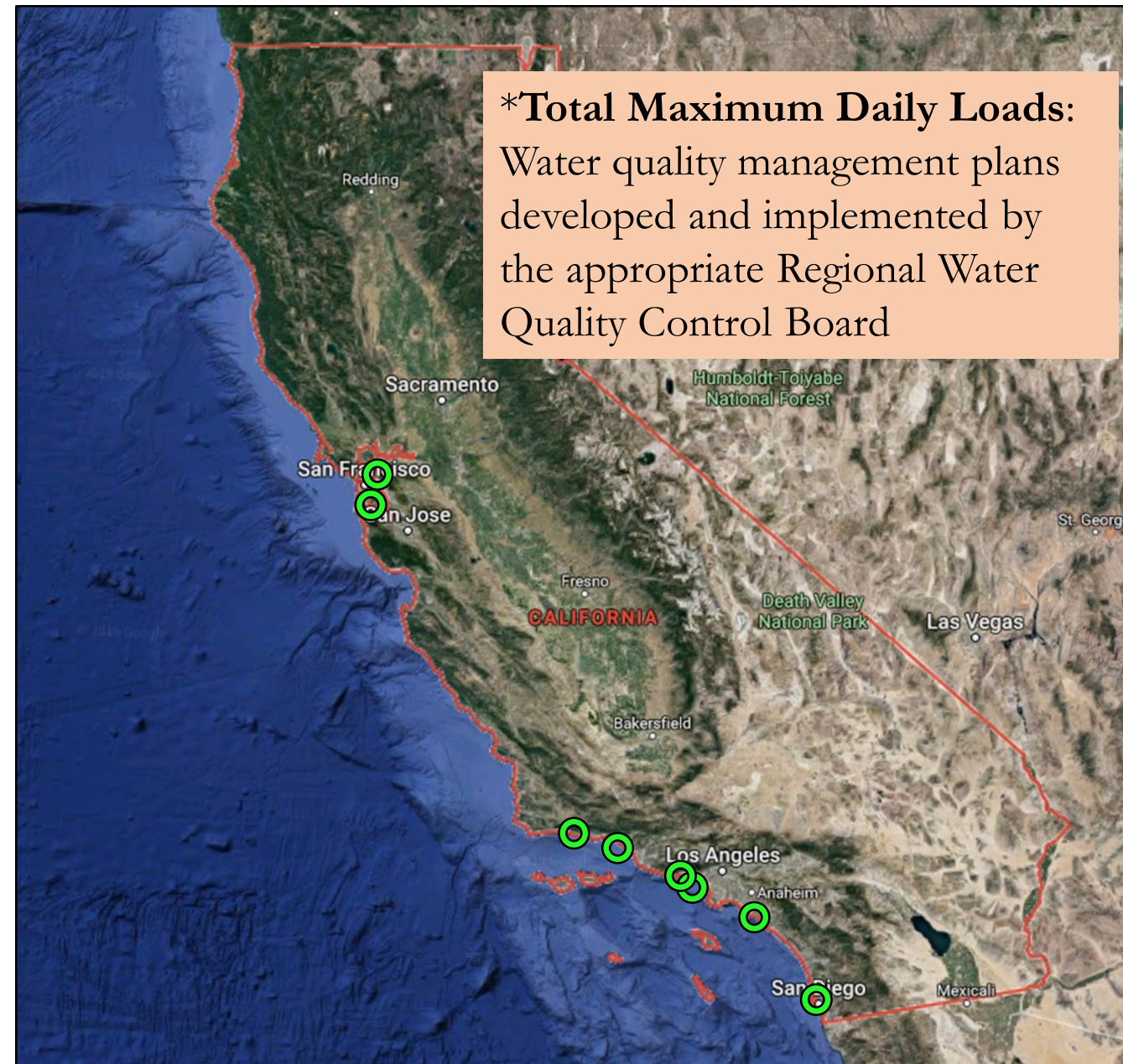
Study Objectives

- Determine the concentrations of DCu in selected, representative waterbodies
- Determine the temporal and spatial trends in DCu across and within waterbodies
- Determine the potential toxicity of samples based on measured water chemistry parameters using the saltwater biotic ligand model.



Waterbody Selection

- Region
 - Site Specific Objectives in San Francisco Bay
 - Higher water temperatures in Southern California
- Size
 - Coyote Point Marina < 1000 vessels
 - Berkeley, Santa Barbara, and Redondo Beach < 2000 vessels
 - Channel Islands, Newport Bay*, Marina del Rey*, and Shelter Island Yacht Basin* > 2000 vessels
- Cooperation of marina owner/operator

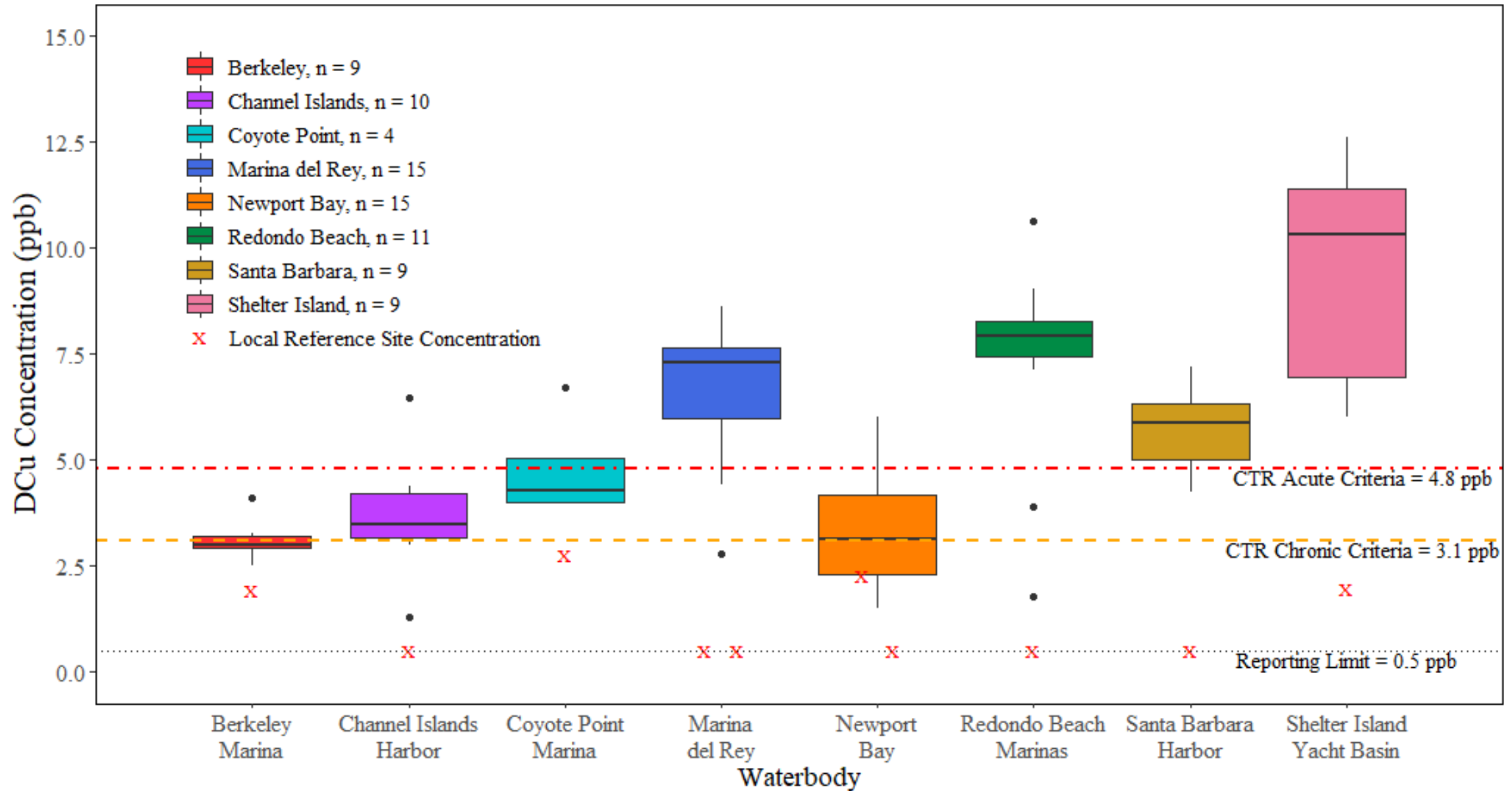


Sampling Site Selection

- Number of samples dependent on size of waterbody
- Standardized sampling process
- In-line filtering
- Local reference sites
- Secondary constituent data



Results and Discussion



Results and Discussion

- 100% detection frequency in the waterbodies
- Waterbody concentrations were 30% (Berkeley Marina) to **2030%** (Redondo Beach Marinas) higher than LRS sites
- CTR chronic criterion exceedance = **79%**
- CTR acute criterion exceedance = **52%**



Modeling – LASSO Regression

- LASSO Regression was used to determine a best fit model for predicting DCu concentrations
- Included 18 explanatory variables
- What variables contribute to DCu concentrations?

Spatial Trends

Modeling



Results of Modeling

- Best fit modeling resulted 7 explanatory variables included in the model
 - Regional spatial trends
 - Trends between the waterbodies
 - Spatial trends
 - Trends within the waterbodies
 - Waterbody characteristic trends
- $RMSE = 0.587, R_{adj}^2 = 0.919$

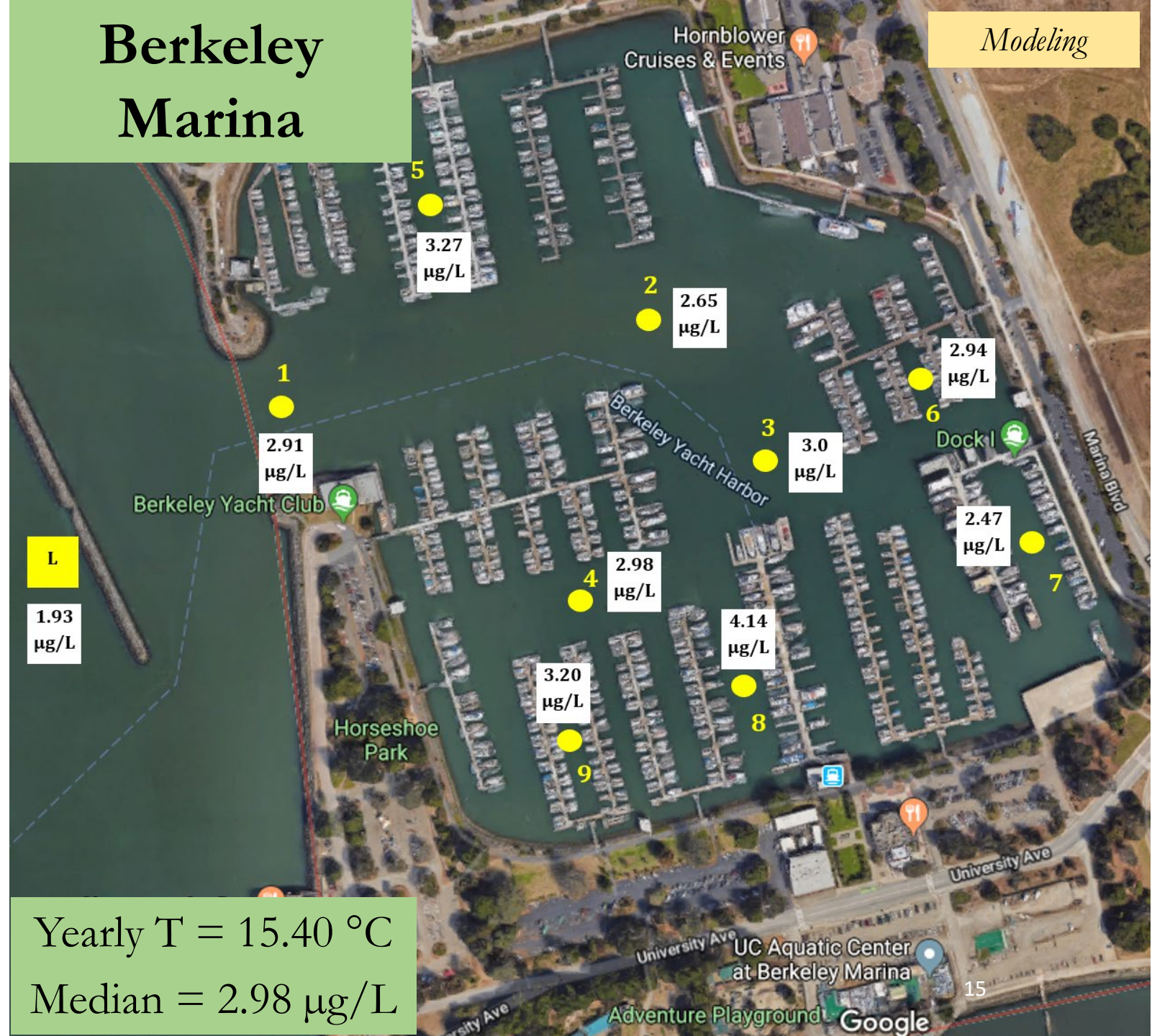


Regional Spatial Trends

- Latitude
- Yearly Average Temperature
- Temperature at Sampling



Berkeley Marina



Regional Spatial Trends

- Latitude



- Yearly Average Temperature

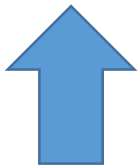


- Temperature at Sampling



Waterbody Spatial Trends

- Main Channels
versus Fairways
- Distance to Mouth



Redondo Beach Marinas



Modeling

Median = 7.91 µg/L

Newport Bay

Modeling



Waterbody Characteristic Trends

- Water Depth



- Surface Area

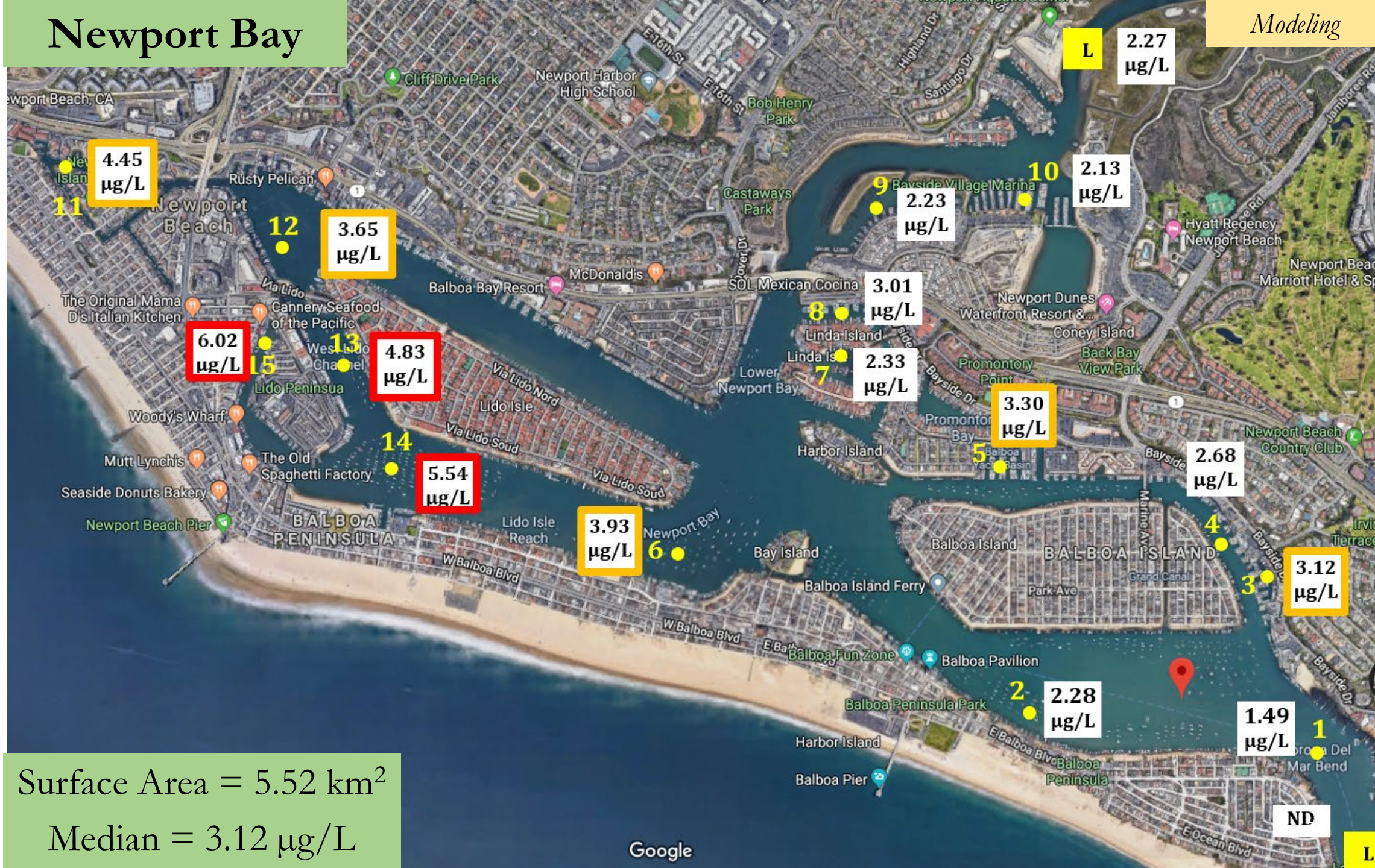


Newport Bay is $\sim 3.3\times$ larger
than next largest waterbody
(Marina del Rey)



Newport Bay

Modeling



Surface Area = 5.52 km²

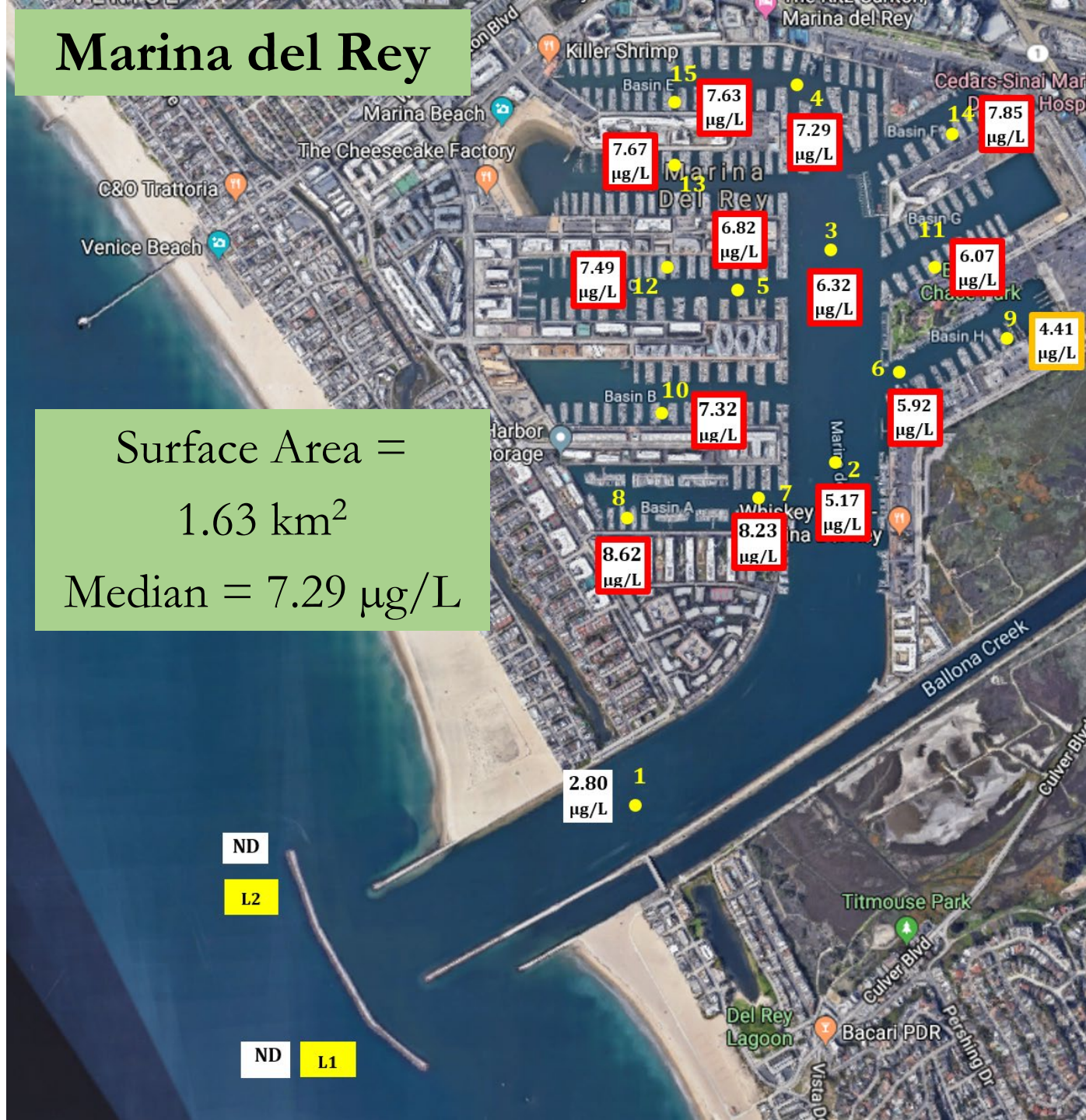
Median = 3.12 µg/L

Marina del Rey

Surface Area =

1.63 km²

Median = 7.29 µg/L



Biotic Ligand Modeling

Modeling

- Four sites: Coyote Point Marina, Berkeley Marina, Newport Bay, and Marina del Rey
- Measured DOC at every site
- Took T (°C), pH, and salinity *in-situ* measurements
- Inputs into a model to predict toxicity
 - Water chemistry controls speciation of copper



BLM Results

- EC_{50} for *Mytilus galloprovincialis* (Mediterranean mussel)
- Four samples at Marina del Rey had toxic units ≥ 1.0
 - $EC_{50} = 7.12 - 8.52 \mu\text{g/L}$
 - DCu concentrations = $7.32 - 8.62 \mu\text{g/L}$
- SCCWRP: Ambient toxicity rarely observed
- Need for additional samples at other waterbodies



Reference Point Concentrations

- Results presented here are considered a reference point to evaluate long-term trends
- Cu-AFPs are on vessels for years
- Boatyard capacity is limited



Limitations

Hull cleaning

- No distinction between spikes in passive leaching due to hull cleaning



Future Work

- Vertical concentration gradients
 - Spatial trends
 - DCu concentration are heterogeneous in the water column
- Tidal influence
 - Temporal trends
 - Tidal flushing affects DCu concentrations



Acknowledgments

- Mark Bettis of Coyote Point Marina (San Mateo County Parks)
- Stephen Bogner from Berkeley Marina
- John Kappeler from City of Newport
- Kelly Tait and Karen Holman from the Port of San Diego
- Jennifer Mongolo from Los Angeles Beaches and Harbor
- Gary Laolagi from City of Redondo Beach
- Mark Sandoval and Gary Hirtensteiner of Channel Islands Harbor (Ventura County)
- Karl Treiberg of Santa Barbara Harbor
- Scott Giatbaipoon of Department of Toxic Substances – Environmental Chemistry Laboratory
- Xuyang Zhang, KayLynn Newhart, Emily Edgerton, Sarah Albright, Jesse Ybarra, Jennifer Teerlink, and Nan Singhasemanon of California Department of Pesticide Regulation

Questions?

Contact:

Aniela Burant

Aniela.Burant@cdpr.ca.gov



Channel Islands Harbor

Median = 3.49 $\mu\text{g/L}$

