Monitoring for Indicators of Antifouling Paint Pollution in CA Marinas

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Antifouling Paint (AFP) Use

- AFPs are pesticide products
- Mode of action – leaching
- ~ 180 AFP products registered in CA
- > 90% utilizes copper-based biocides
  - Copper oxide, copper hydroxide, copper thiocyanate
- Booster biocides often co-formulated
  - Zinc pyrithione (a.k.a. omadine)
  - Irgarol 1051
  - Sea-Nine (DCOI)

AFP Use & Pollution in CA

- TBT monitoring 1980's
  - Adverse effects on snails & bivalves → EPA & DPR restrictions
- Massive shift to copper oxide
- Shelter Island Yacht Basin – San Diego
  - Copper TMDL (late 1990's)
  - Passive leaching & underwater hull cleaning
- DPR initiated broader investigation
- Copper AFP Sub-Workgroup (2004)
  - Gather existing data & identify gaps
- DPR Multi-Regional Study (2006)
  - DPR-SWRCB-EPA funded

Primary Study Objective

- Determine occurrence & magnitude of AFP biocides (i.e., Cu, Zn, and Irgarol/M1) in marina areas & determine if concentrations exceed water quality standards, criteria, guidelines, or other relevant benchmarks

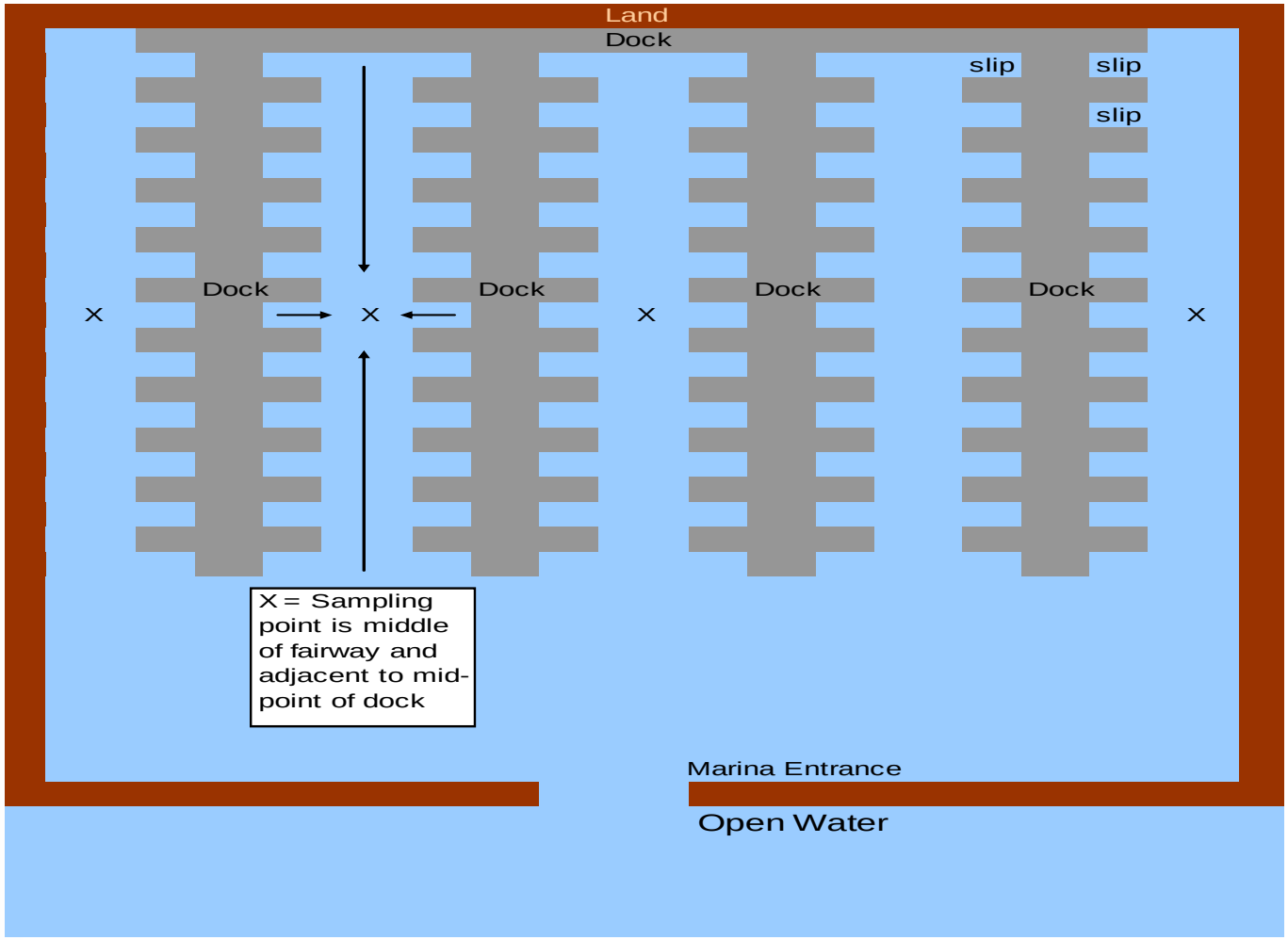
Secondary Objectives

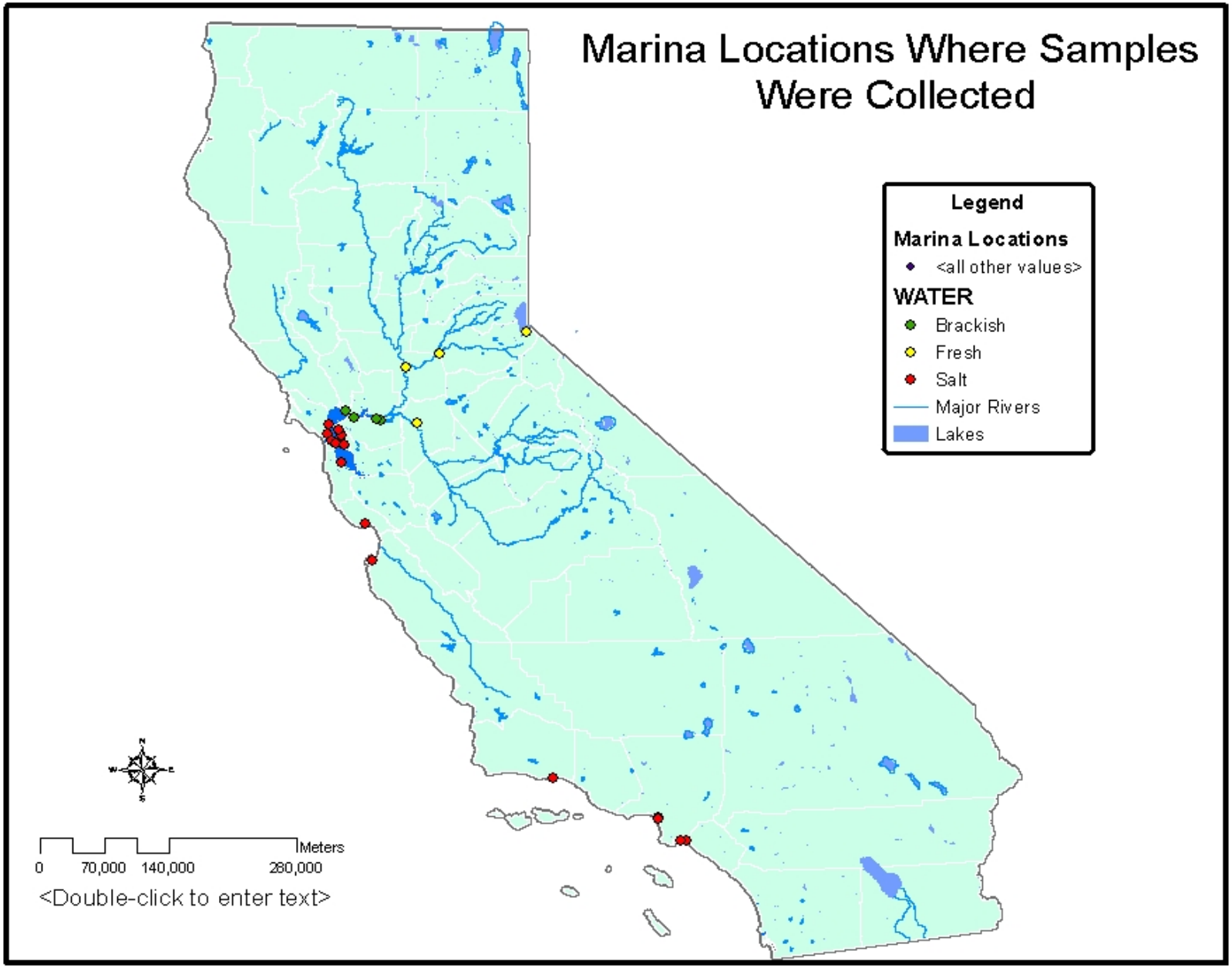
- Are there differences between marina vs. background?
- Are there differences among fresh, brackish, & salt water marinas?
- Measure toxicity of marina waters & confirm w/ Toxicant Identification Evaluation (TIE)
- Apply U.S. EPA's Biotic Ligand Model (BLM) to estimate bioavailability & toxicity of copper

Study Design Overview

- Selected 23 (medium to large) CA marinas from 3 water types
- Avoided marinas w/ potential interferences from adjacent sources
- Sampled each marina 3 times during dry season (July-October 2006)
- Collect water samples from 4 points inside marina & 4 points outside marina (local reference sites or LRS)
- Took sub-surface samples from center of fairway & half way down docks
- Followed U.S. EPA ultra-clean collection/handling methods

Marina Sampling Diagram




Marina Locations Where Samples Were Collected
Legend
Marina Locations
<all other values>
WATER
Brackish
Fresh
Salt
Major Rivers
Lakes
Meters
0
70,000
140,000
280,000
<Double-click to enter text>

Antifouling Paint Monitoring

dpr

CF 5730XF
958
YAMAHA

Monitoring Summary

- 67 marina visits
- ~ 600 water samples taken + W.Q.
- ~ 7,000 individual analytical results (most feed into BLM)
- Irgarol/M1, toxicity & TIE analyses done on subset
- Sediment from only 3 marinas collected
- Field & Lab QA/QC very good overall
- Marina survey conducted → source evaluation

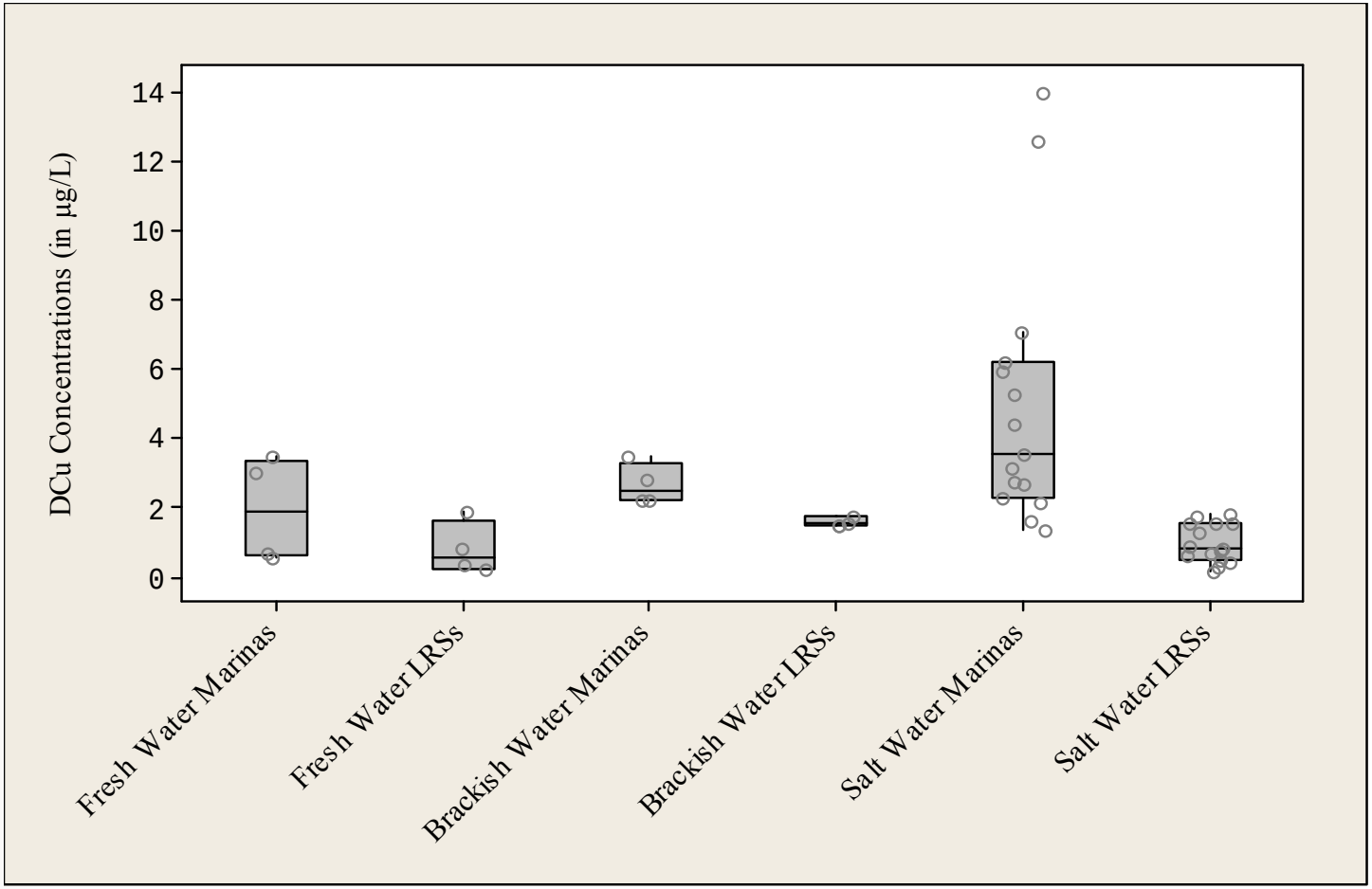
Results

Dissolved Copper (DCu)

Results - DCu

- DCu ranged from 0.1–18.4 µg/L
- High DCu in Central & South Coast marinas (except 1 location)
  - Within range of DCu results from 2 other studies in SoCal
- Low to Moderate in SF Bay Area, brackish & riverine marinas
- Very Low (< 1 µg/L) in the 2 lake marinas
- MdR Basins consistently very high in DCu

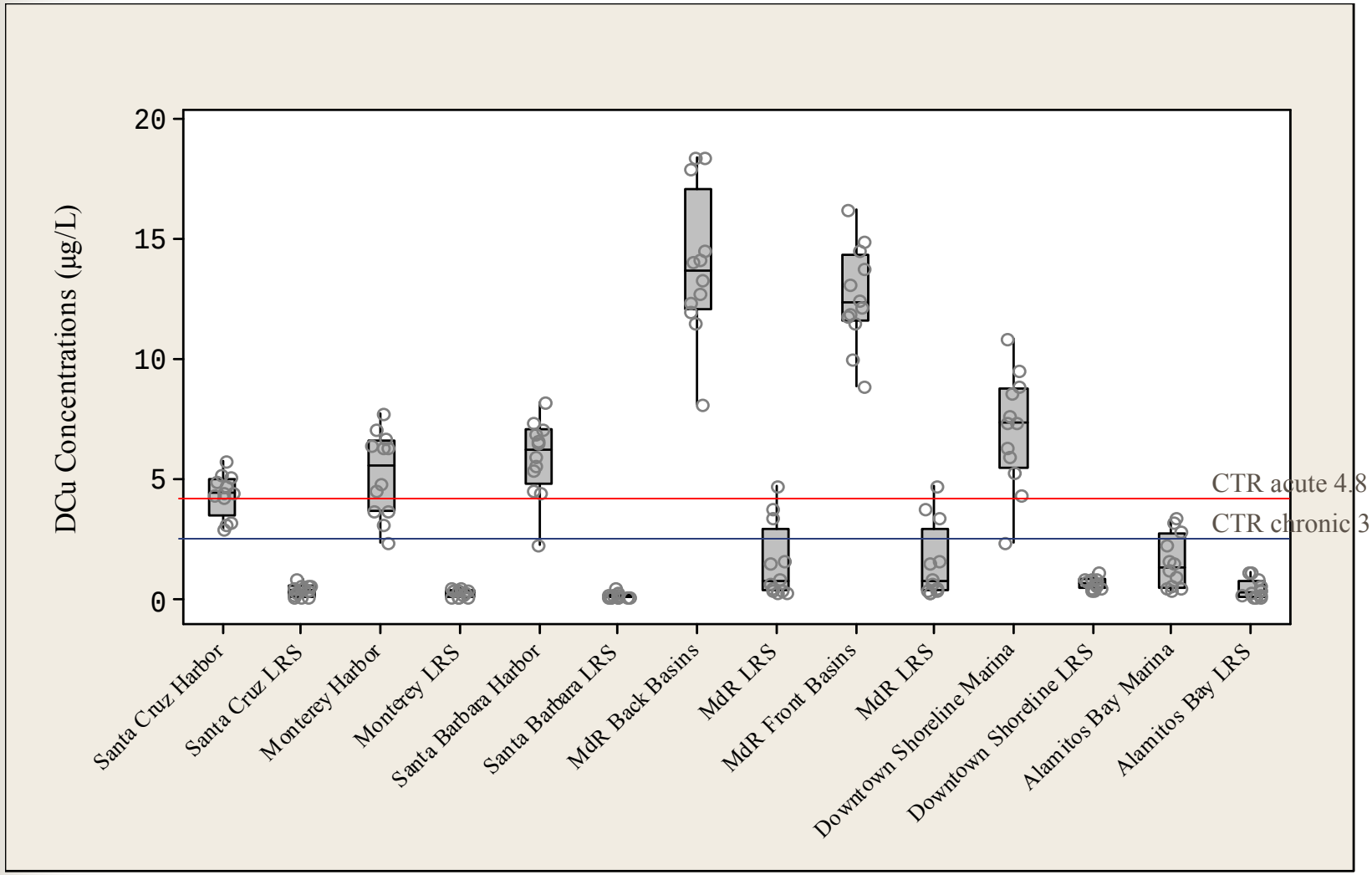
Marina Median DCu Concentrations by Water Types



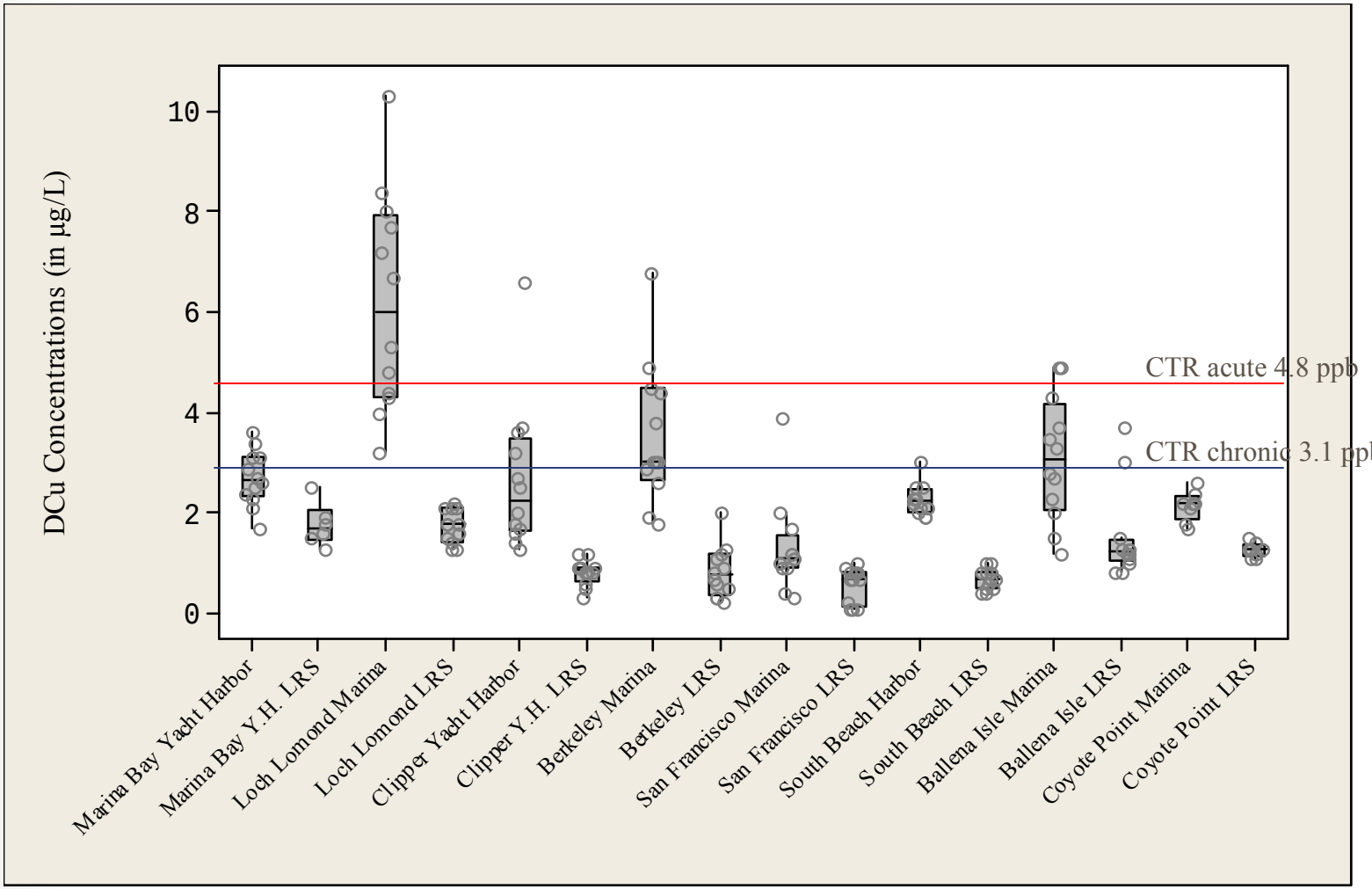
Results - DCu (cont.)

- DCu in salt & brackish water marinas ↑ DCu in fresh water marinas *(statistically significant - higher use?)*
- DCu in marina ↑ vs. DCu in LRS for marinas of all 3 water types *(statistically significant - marina source?)*
- What do numbers mean???
- Many salt & brackish marinas exceeded W.Q. stds.
  - 16 of 17 marinas exceeded CTR chronic stds. (3.1 ppb)
  - 10 of these 16 marinas also exceeded acute stds. (4.8 ppb)
- **Few** LRS samples (4) exceeded stds.

DCu Concentrations in Central & South Coast Marinas & LRSs



DCu Concentrations in S.F. Bay Area Marinas & LRSs



Results - DCu (cont.)

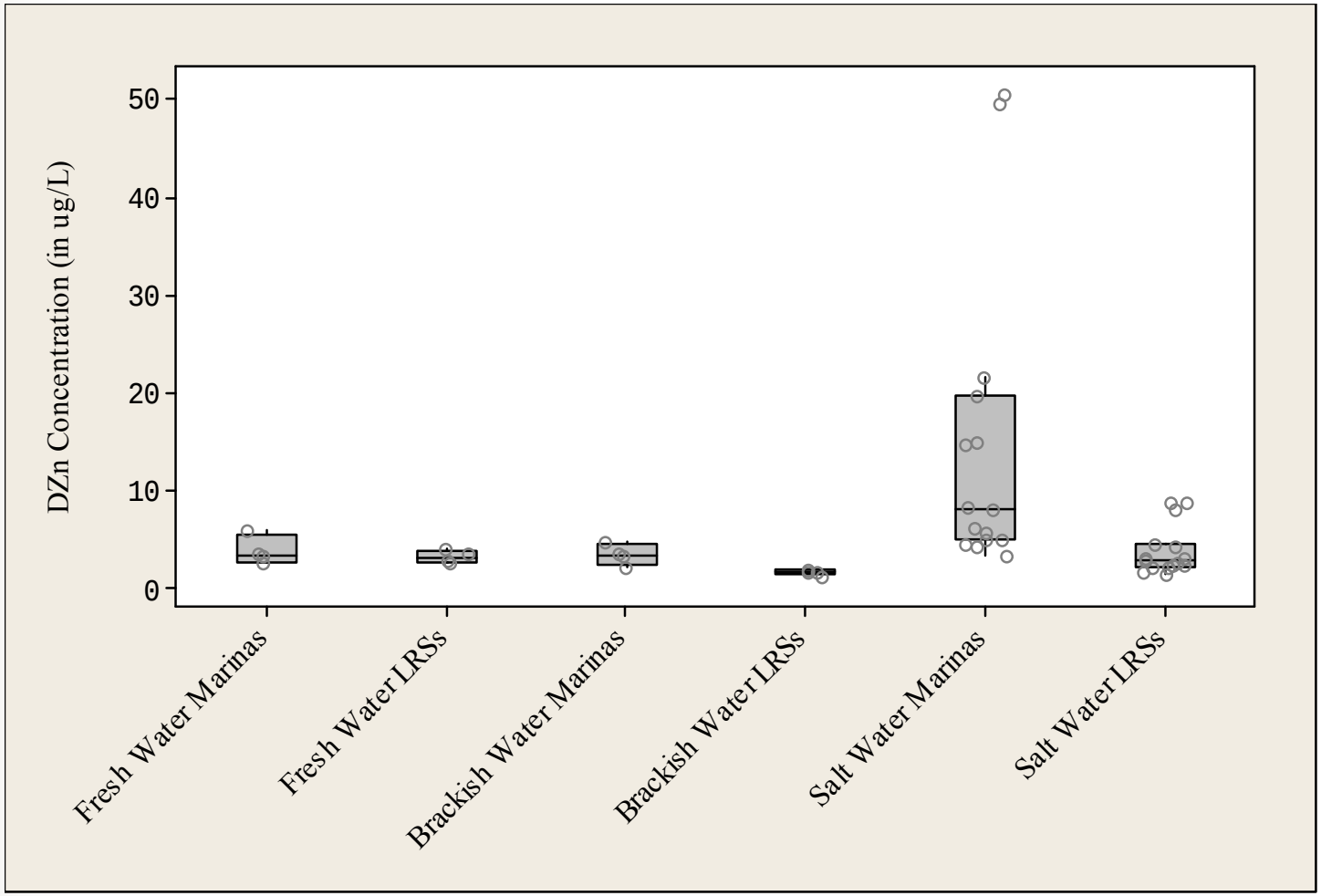
- **30%** of samples from salt & brackish water samples exceeded chronic stds.
- **17%** of these also exceeded acute stds.
- For fresh water, **none** of the samples exceeded fresh water CTR stds.

- *CTR violation = "likely to present a significant risk to aquatic organisms & their uses"*

Results

Dissolved Zinc (DZn)

Marina Median DZn Concentrations by Water Types



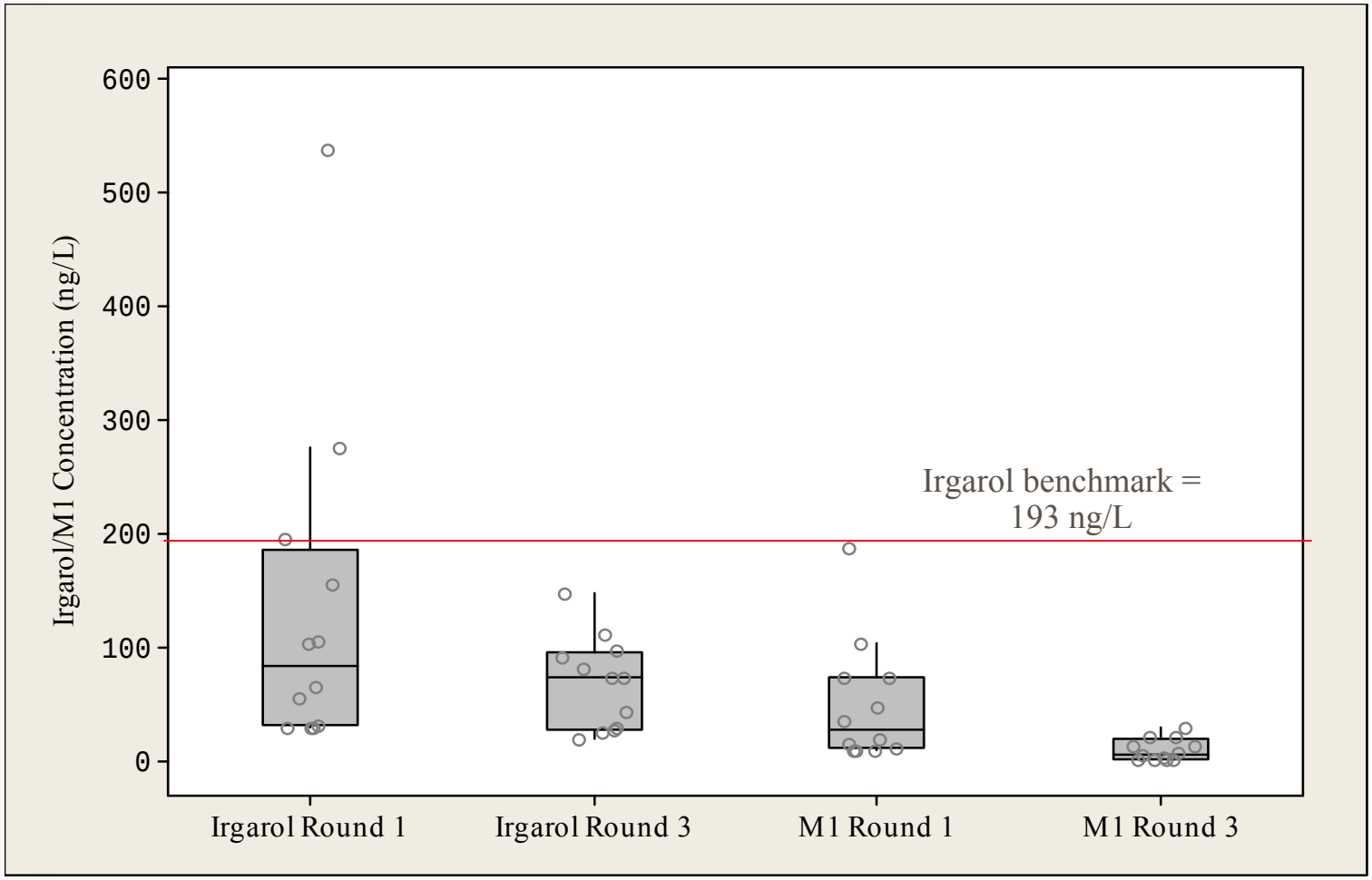
Results - DZn

- Similar to DCu results
- Tends to be higher than DCu by factor of 2–4
  - Ranged from 1.0–66.6 µg/L
- Much ↑ DZn in salt water marinas compared to brackish & fresh water marinas *(statistically significant - sacrificial anodes?)*
- Marina DZn ↑ vs. LRS DZn for salt & brackish water marinas *(statistically significant - marina source?)*
- Zinc stds. **never** exceeded

Results

Irgarol & M1

Irgarol & M1 Concentrations by Rounds



Results - Irgarol/M1

- Irgarol & M1 detected in all 45 samples
  - Irgarol →12–712 ng/L
  - M1 → 1.6–217.1 ng/L
- Irgarol conc. range overlaps more sensitive phytoplankton EC_{50}
  - Photosynthetic activity
  - Reproduction/growth
- Irgarol at 9% of sites also exceeded aquatic plant benchmark (193 ng/L)
  - protective of 90% of aquatic plant species
- M1 never exceeded benchmark (12,500 ng/L)

Results

Toxicity & Toxicity Identification Evaluation

Results - Toxicity/TIE

- Subset only
- Endpoint → abnormal *M. galloprovincialis* embryo development & mortality
- 8 of 47 samples (17%) exhibited statistically significant toxicity
- 7 of 8 toxic samples came from MdR
- TIE → Cu as cause of toxicity

- *Toxicity is <u>violation</u> of Water Boards narrative WQO*

Results

Predictive Toxicity Modeling

Results - Predicted Toxicity Models (BLM & DOC)

- For all samples… site specific
- In fresh water BLM (fish gill model) predicted virtually no Cu toxicity
- Salt water BLM predicted toxicity to mussel embryo in 18% of samples
- 98% of samples w/ predicted toxicity were marina samples
- DOC Model → similar results

- *Models → inexpensive way of gauging toxicity*

Conclusions

- Marinas are localized sources of Cu, Zn, and Irgarol/M1
- In salt & brackish water marinas, high DCu conc. could adversely impact sensitive invertebrate species
- Boat AFPs are likely a significant source of Cu in salt & brackish water marinas during dry periods
- Ecological impacts from Cu are unlikely in fresh water marinas
- Ecological impacts from Zn are unlikely in marinas of all 3 water types
  - Pyrithione a better AFP indicator?

Conclusions

- Irgarol conc. occasionally exceed benchmark in salt water marinas & may adversely impact sensitive aquatic plants & algae
- Salt water BLM is a reliable predictor of Cu toxicity
  - *Accounts for site-specific bioavailability*
  - *Consistent predicted outcome*
  - *More accurate >2 Toxic Units*
- For "full experience" go to:
  http://www.cdpr.ca.gov/docs/emon/pubs/ehapreps/eh0805.pdf
  http://www.cdpr.ca.gov/docs/emon/pubs/ehapreps/eh0805_apdxA.pdf

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Thank you…

Questions?

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