Multi-Regional Monitoring Study for Indicators of Antifouling Paint Pollution

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Study Background

- Documentation of elevated copper at SIYB in San Diego Bay sparked interests
- Concentrations observed above W.Q. standards
- SIYB TMDL identified boat AFPs as source
- Main question – do similar conditions exist elsewhere in CA?
- DPR planned study under consultation w/ CSG, a sub-workgroup of MRBW
- DPR drafted monitoring plan and QAPP
- Study co-funded by DPR and SWRCB

AFP Use in CA

- ~ 170 AFP pesticide products registered
- More than 90% utilizes copper-based biocides
  - Copper oxide, copper hydroxide, copper thiocyanate
- Booster biocides are often co-formulated
  - Zinc pyrithione (a.k.a. omadine)
  - Irgarol 1051
  - Sea-Nine (DCOI)

Study Objectives

- Determine occurrences & magnitude of AFP-use indicators (i.e., Cu, Zn, and Irgarol/M1) in marina areas
- Determine if these conc. exceed established water quality standards, criteria, guidelines, or other relevant benchmarks
- Determine if a difference exists between marina & background conc.

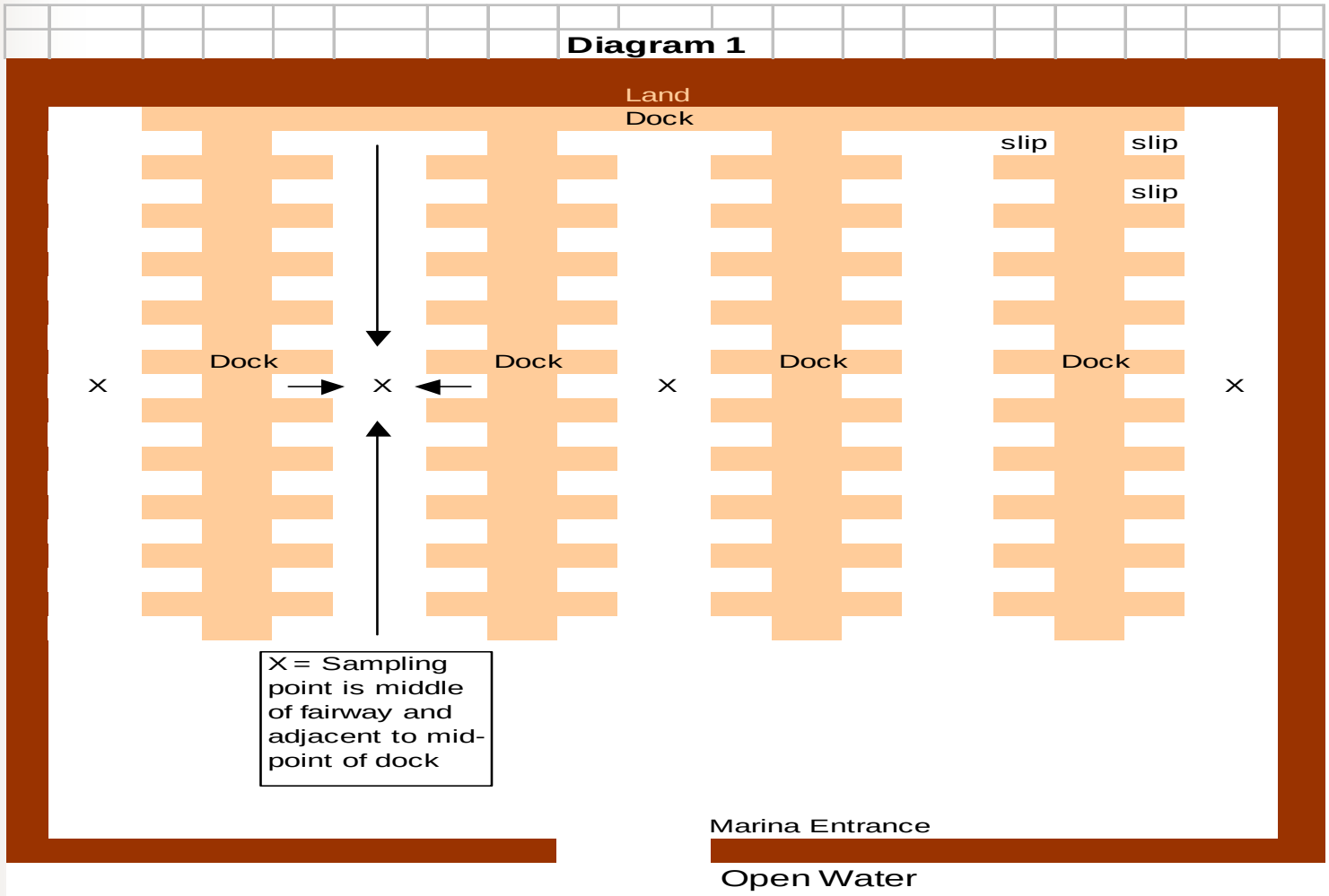
Study Objectives (cont.)

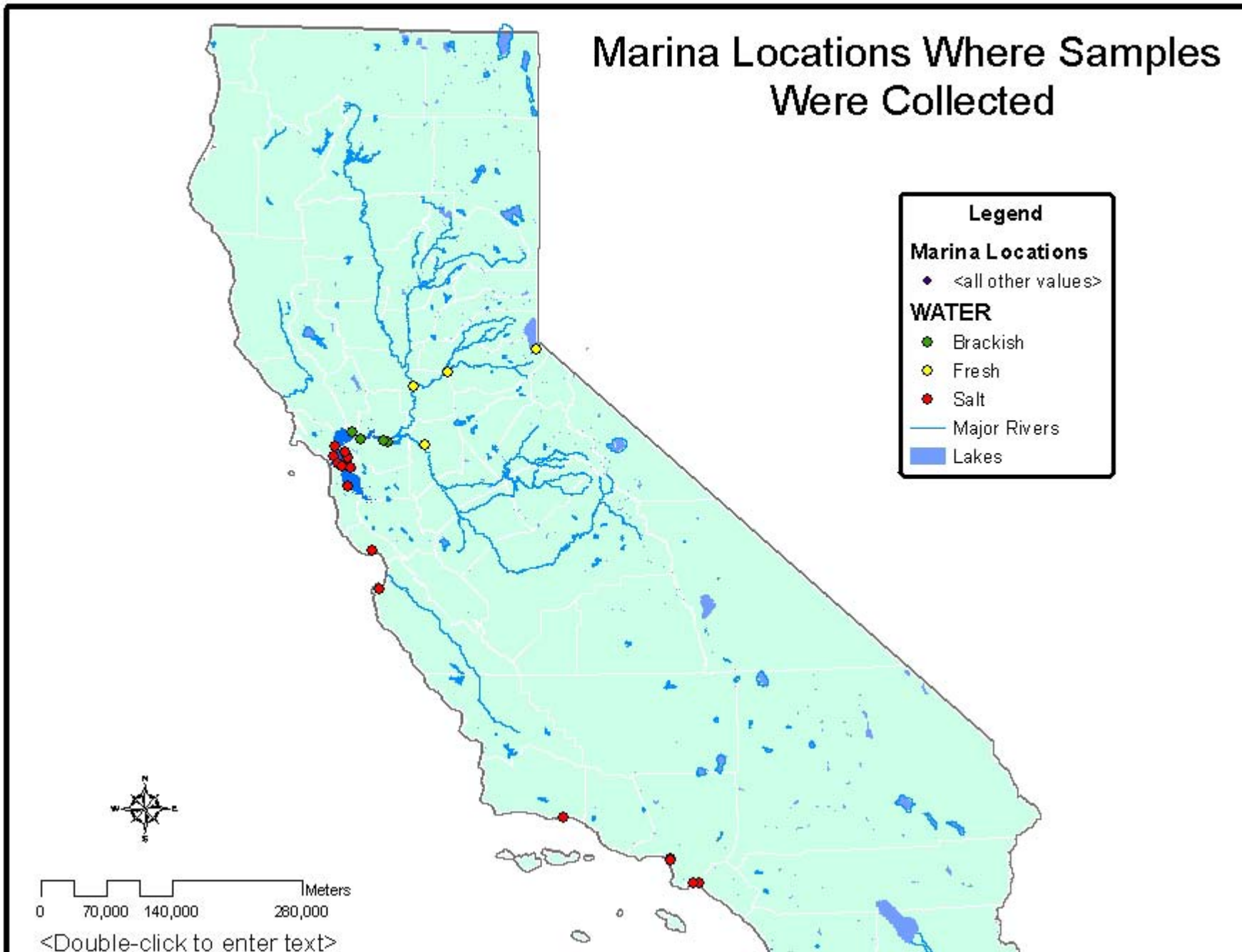
- Determine if differences exist among AFP levels in fresh, brackish, & salt water marinas
- Apply U.S. EPA's Biotic Ligand Model (BLM) or other scientifically-relevant models to estimate bioavailability and toxicity of copper.
- Measure toxicity of marina waters w/ copper-sensitive species & endpoint
- If toxicity exists, identify the likely cause

General Study Design

- Selected 23 (medium–large) CA marinas
- Avoided marinas w/ potential interferences from adjacent sources
- Sampled each marina 3 times (replicates) over dry period between July & October 2006
- Water and sediment from 4 points inside marina area & 4 points outside of the marina area (local reference sites or LRS)
- Took sub-surface samples from center of fairway & half way down docks

Marina Sampling Diagram




Marina Locations Where Samples Were Collected
Legend
Marina Locations
<all other values>
WATER
Brackish
Fresh
Salt
Major Rivers
Lakes
N
W
E
S
0
70,000
140,000
280,000
Meters
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CF 5730XF
958
YAMAHA

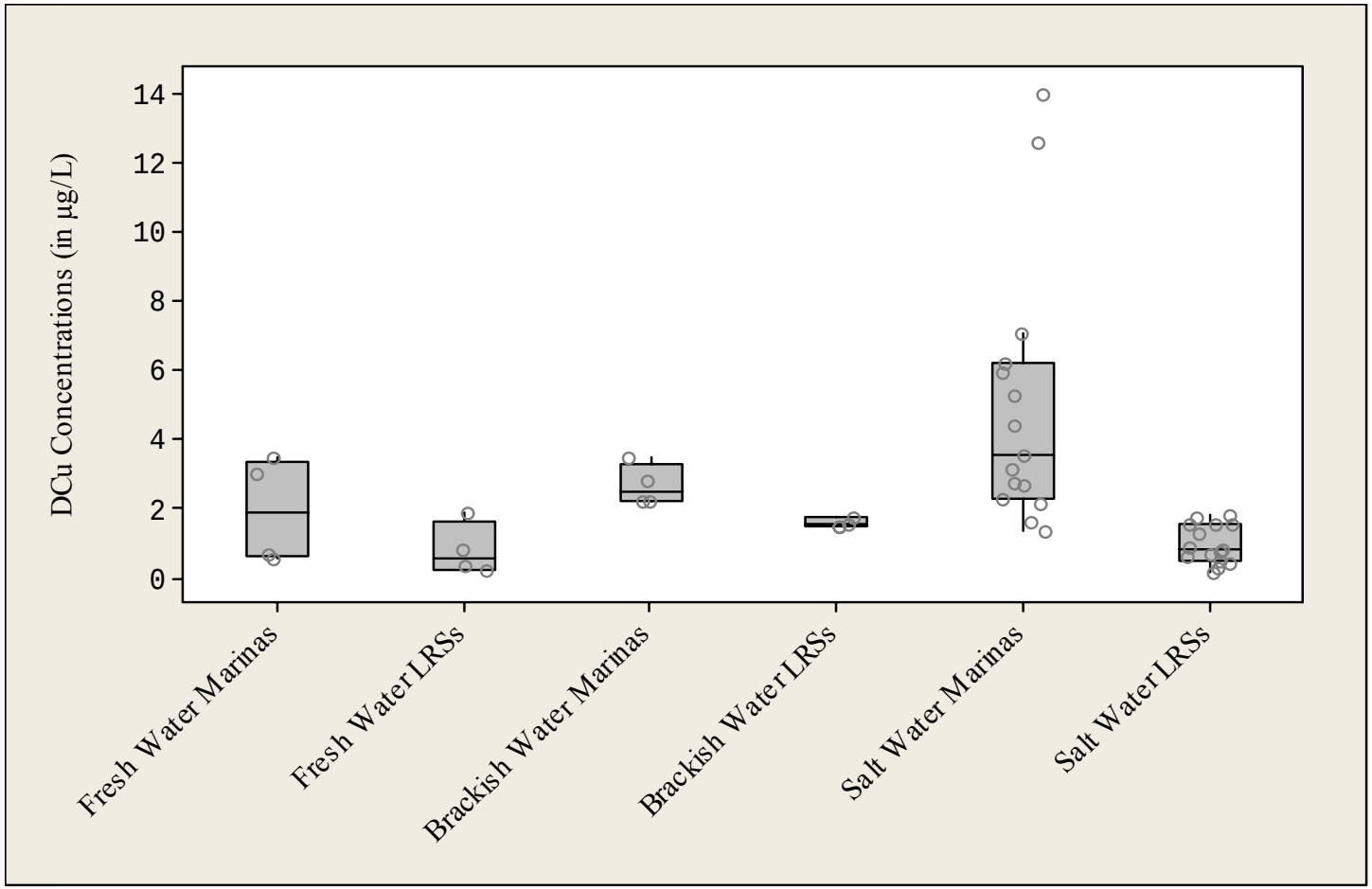
Monitoring Summary

- 67 of 69 total events sampled
- ~ 600 water samples taken, ~ 7,000 individual analytical results (most feed into BLM)
- Sediment from only 3 marinas collected (fresh water). Remainder of sediment worked cancelled due to safety & liability concerns
- Field & Lab QA/QC very good overall

Results

Dissolved Copper (DCu)

Marina Median DCu Concentrations by Water Types



Median DCu Concentrations by Marina Areas

Marina	Marina Median Concentration (ug/L)	LRS Median Concentration (ug/L)	Estimated Number of Slips
Folsom Lake Marina	0.5	0.3	675
Tahoe Keys Marina	0.6	0.2	250
San Francisco Marina	1.1	0.4	700
Alamitos Bay Marina	1.2	0.3	1,191
Coyote Point Marina	2.1	1.3	565
Antioch Marina	2.2	1.5	310
Pittsburg Marina	2.1	1.5	486
South Beach Harbor	2.2	0.7	700
Clipper Yacht Harbor	2.4	0.8	735
Marina Bay Yacht Harbor	2.6	1.7	850
Benicia Marina	2.7	1.7	320
Sacramento Marina	3.0	0.7	547
Ballena Isle Marina	2.8	1.4	504
Village West Marina	3.4	1.8	700
Vallejo Marina	3.4	1.5	800
Berkeley Marina	3.3	0.7	1,052
Santa Cruz Harbor	4.3	0.3	1,000
Monterey Harbor	4.9	0.2	413
Santa Barbara Harbor	5.7	0.1	1,133
Loch Lomond Marina	5.8	1.7	517
Downtown Shoreline Marina	6.6	0.7	1,800
Marina del Rey Front Basins	12.4	1.0	~ 5000
Marina del Rey Back Basins	13.6	1.0	~ 3000

fresh water
brackish water
salt water

Findings – DCu

- DCu ranged from 0.1–18.4 µg/L
- Particularly elevated levels in Central & South Coast marinas – except Alamitos Bay Marina
- MdR Back & Front Basins consistently very high in DCu
- Low to Moderate levels in SF Bay Area and brackish water marinas
- Very Low to Moderate levels observed in fresh water marinas

Findings – DCu (cont.)

- Salt & brackish water marinas are distinctly higher than fresh water marinas *(higher use?)*
- Marina vs. LRS are statistically significant for marinas of all 3 water types
- In salt & brackish water areas, 16 of 17 marinas exceeded CTR chronic stds. (3.1 ppb); 10 of these 16 marinas also exceeded acute stds. (4.8 ppb)

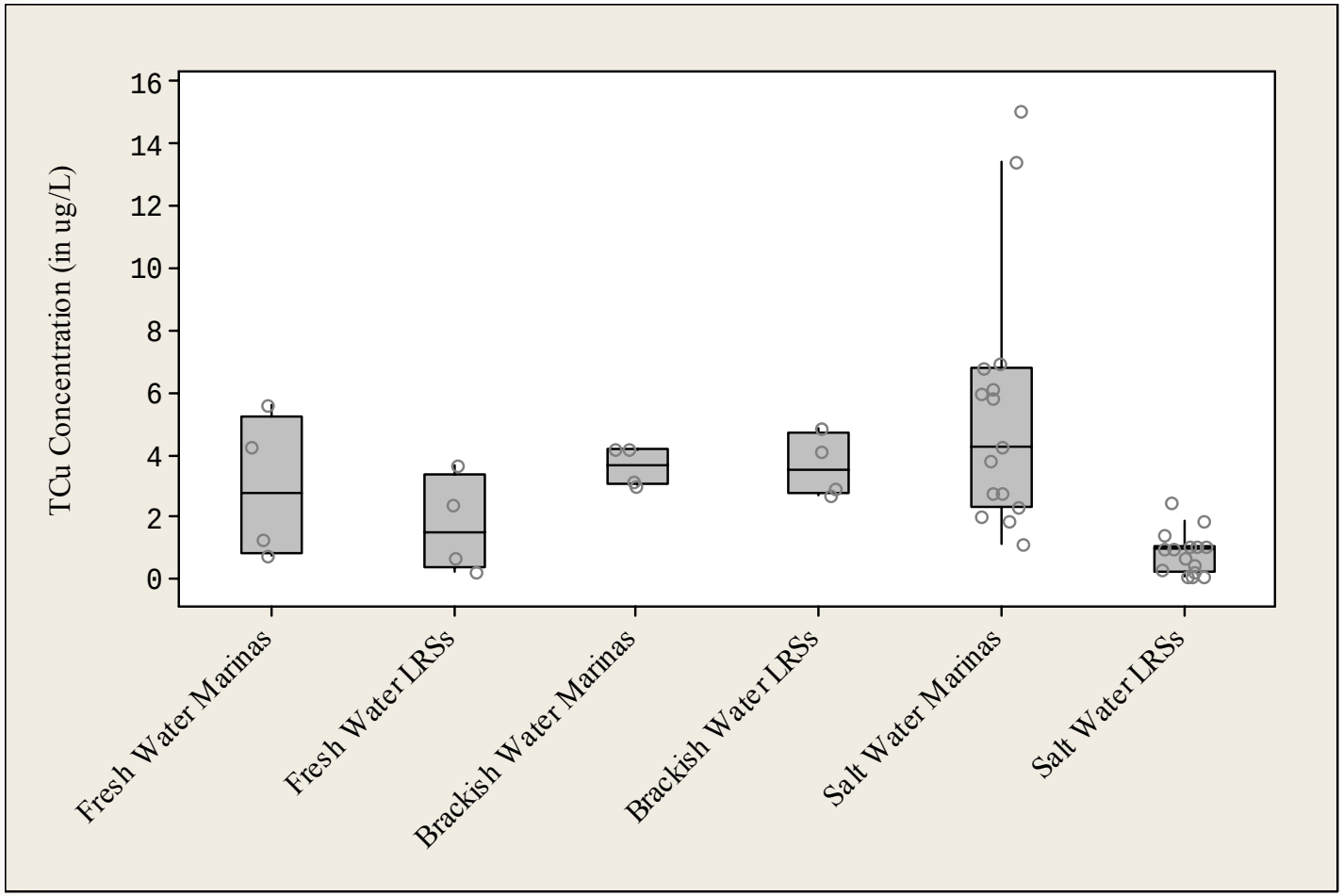
Findings – DCu (cont.)

- 30% (118/388) of samples from salt & brackish water samples exceeded CCC; 17% (67/388) exceeded CMC
- Very few LRS samples (4) exceeded CCC
- For fresh water, none of the samples exceeded fresh water CTR standards

Results

Total Copper (TCu)

Marina Median TCu Concentrations by Water Types



Findings - TCu

- Ranged from 0.1–20.2 µg/L
- Trend in TCu data very similar to DCu
- TCu tends to be slightly higher than DCu
- Main exception: brackish LRSs
  - TCu relatively high
  - Likely related to high TSS
- High TSS may be elevating TCu & depressing DCu

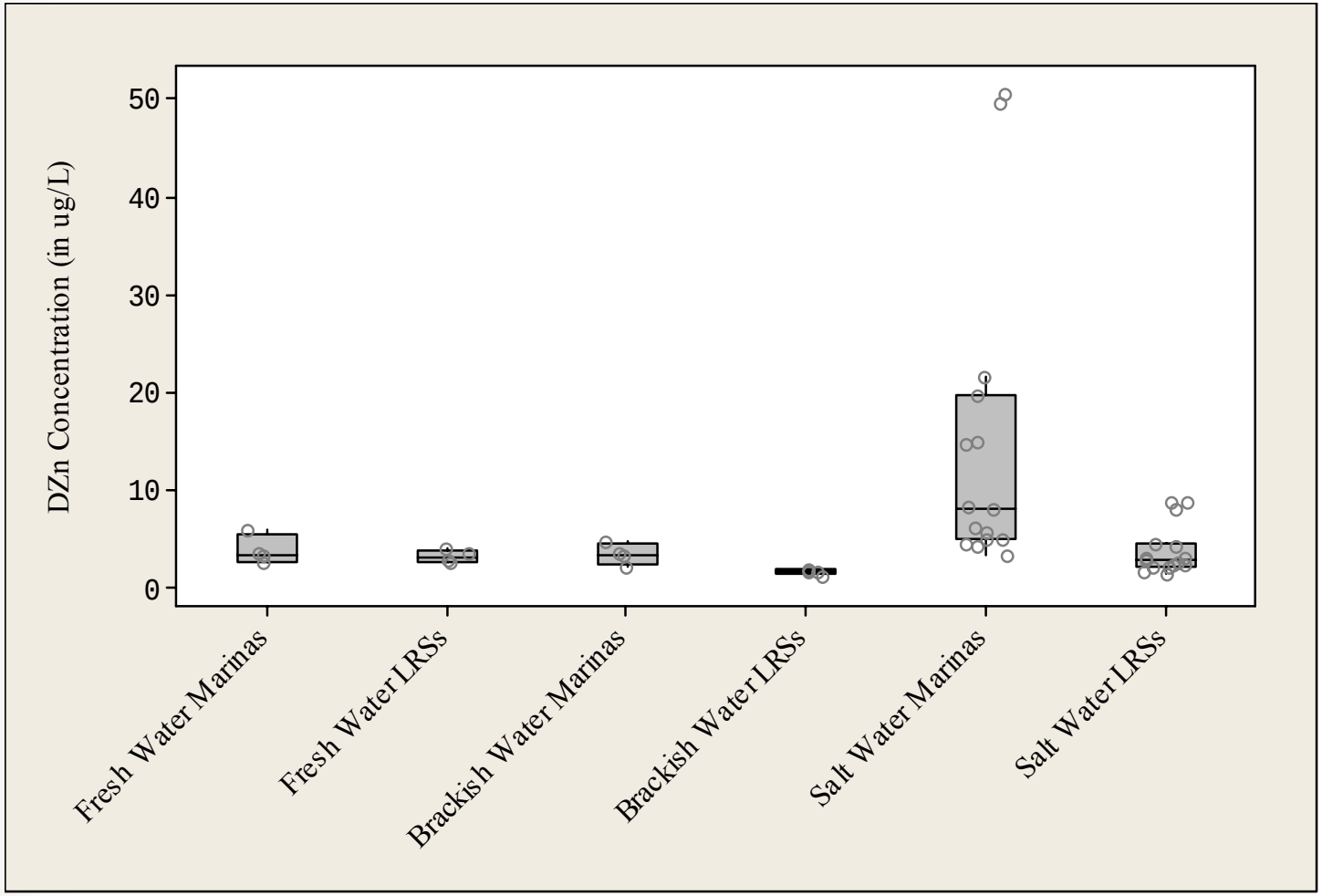
Findings – TCu (cont.)

- Marinas in all 3 water types are similar w/ marginal difference for salt and fresh water marinas
- Marina vs. LRS are statistically significant for salt & fresh water marinas
- No statistically significant difference for brackish marinas (high LRS TCu)

Results

Dissolved Zinc (DZn)

Marina Median DZn Concentrations by Water Types



Findings - DZn

- Ranged from 1.0–66.6 µg/L
- Trend also similar to DCu & TCu
- MdR Back & Front Basins consistently very high in DZn
- Exception: Alamitos Bay ranked much higher
- Tends to be higher than DCu by factor of 2–4

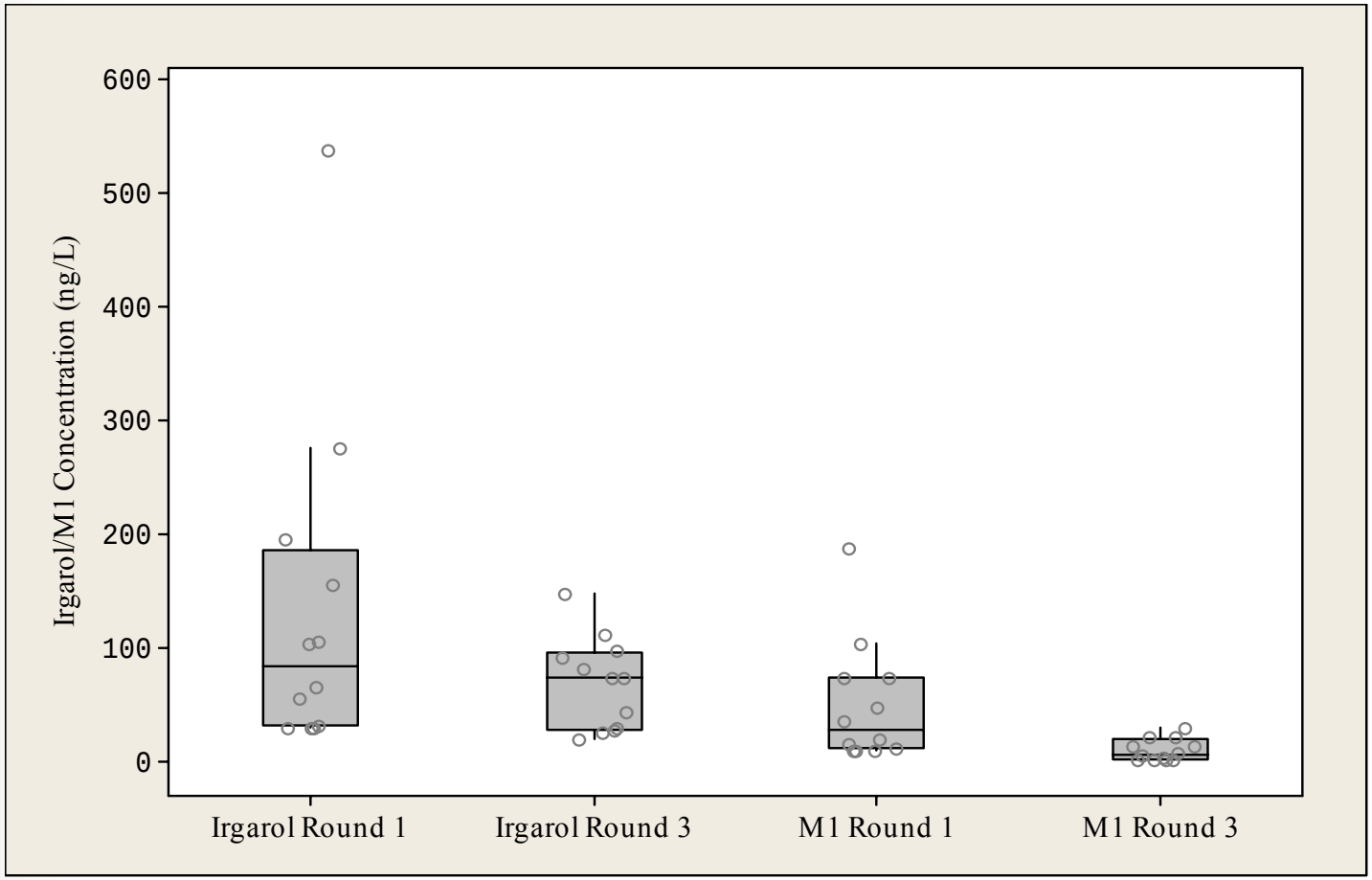
Findings - DZn (cont.)

- Salt water marinas are distinctly higher than brackish & fresh water marinas *(higher use?)*
- Marina vs. LRS are statistically significant for salt & brackish water marinas *(sacrificial anode difference?)*
- Zinc CTR fresh and salt water standards never exceeded

Results

Irgarol & M1

Irgarol & M1 Concentrations by Rounds



Findings - Irgarol/M1

- Irgarol & M1 detected in all 45 samples
- Irgarol ranged from 12–712 ng/L
- M1 ranged from 1.6–217.1 ng/L
- Highest Irgarol & M1 conc. documented @ Loch Lomond Marina
- Higher conc. in salt water marinas
- Higher conc. in Round 1 (Summer) vs. Round 2 (Fall) *(higher leaching?)*

Findings - Irgarol/M1 (cont.)

- Irgarol conc. range overlaps more sensitive phytoplankton endpoints
  - photosynthetic activity
  - growth
- Irgarol conc. exceed aquatic PERA benchmark values (i.e., 136 & 251 ng/L) protective of 90% of aquatic plant species
- M1 never exceeded benchmark (12,500 ng/L)

Results

Toxicity & Toxicity Identification Evaluation

Findings - Toxicity/TIE

- 8 of 47 samples (17%) exhibited statistically significant toxicity
- 7 of 8 toxic samples came from MdR; remaining sample from MBYH in Richmond
- TIE strongly points to metal (most likely copper) as the cause of toxicity

Results

Bioavailability & Predictive Toxicity Modeling

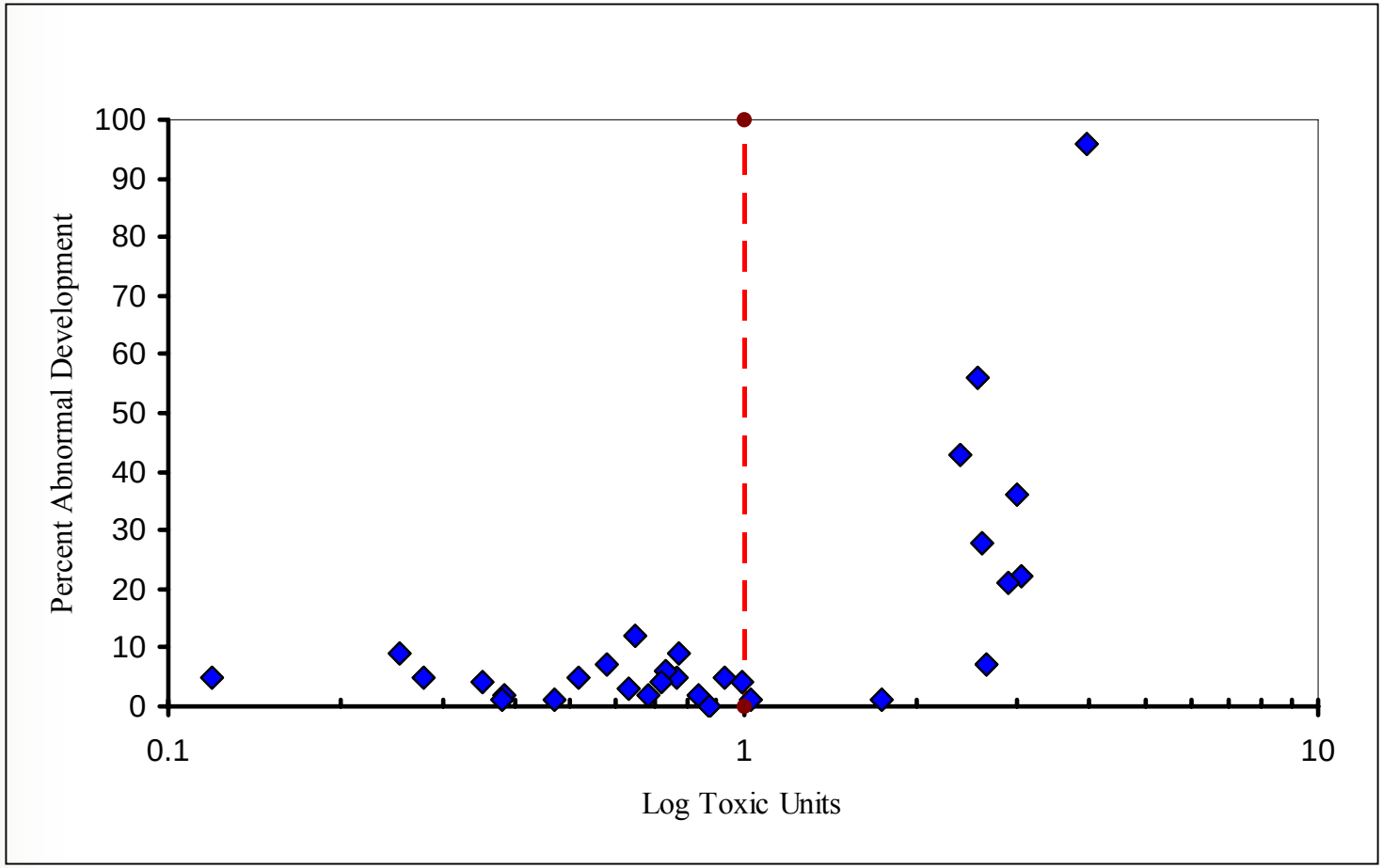
Findings - Modeling

- Fresh water - BLM predicted 7 samples would have had DCu > 1 Toxic Unit (all from Sacramento Marina)
- Salt & brackish water - DOC Model predicted:
  - 86 samples would exceed chronic toxicity threshold
  - Of the 86, 54 would exceed acute threshold
- Comparison of DOC model to actual toxicity showed good agreement

Findings - Modeling (cont.)

- Salt & brackish water - draft BLM predicted:
  - 67 samples would exceed *M. galloprovincialis* EC_{50} (acute only)
- BLM & DOC model showed similar results
- Comparison of BLM to actual toxicity showed good agreement
- However, both models tend to still slightly over-predict toxicity

BLM-Predicted Toxic Units vs. Observed Toxicity



Conclusions

- CTR fresh water standards are not threatened by marina DCu conc.
- Water samples from CA salt & brackish marinas regularly exceed CTR salt water copper standards.
- Higher background DCu loads in S.F. Bay Area, brackish, & fresh water marinas account for a larger portion of marina DCu loads than Central & South Coast marinas.

Conclusion (cont.)

- Considering study results, scientific literature, leaching estimates, & marina source surveys - AFPs are likely the major source of Cu in salt water marinas, particularly during dry periods.
- Toxicity in a commonly-employed copper-sensitive test may not occur until DCu conc. is well over CTR standards.

Conclusions (cont.)

- Copper-sensitive aquatic species in CA salt water marinas that exhibit high DCu conc. (like those observed @ MdR) may be adversely impacted by exposure to copper
- DOC Model & BLM predict actual toxicity with good precision & are promising tools in assessing biological effects of copper.

Conclusion (cont.)

- Zinc CTR standards are not threatened by marina concentrations of DZn – non-AFP zinc applications may be an important factor in determining DZn concentrations in salt & brackish marinas.
- Irgarol may be adversely affecting more-sensitive phytoplankton species in CA's salt water marinas.

Questions?

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