

Comparison of Biotic Ligand Model (BLM) and Water Effect Ratio (WER) Approaches for Derivation of Site-Specific Criteria for Copper in San Diego Bay

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Presented at the California Stormwater Quality Association Conference, November 7, 2012 San Diego CA



Together We Are Better

Co-authors

- Adam Ryan - HDR|HydroQual, Syracuse NY
- Casey E. Capolupo- University of San Diego, San Diego, CA
- Gunther Rosen, Patrick Earley, Brandon Swope, Ignacio Rivera-Duarte, - SPAWAR System Center Pacific, San Diego, CA
- Charles Delos - US EPA

Overview

- Review ongoing project to propose a revision to the acute and chronic saltwater criteria for copper
 - Update of the saltwater toxicity database
 - Incorporation of bioavailability factors using the saltwater BLM for copper
- Discuss an application of the revised BLM criteria to San Diego Bay

Revision to the US EPA Saltwater Criteria for Copper

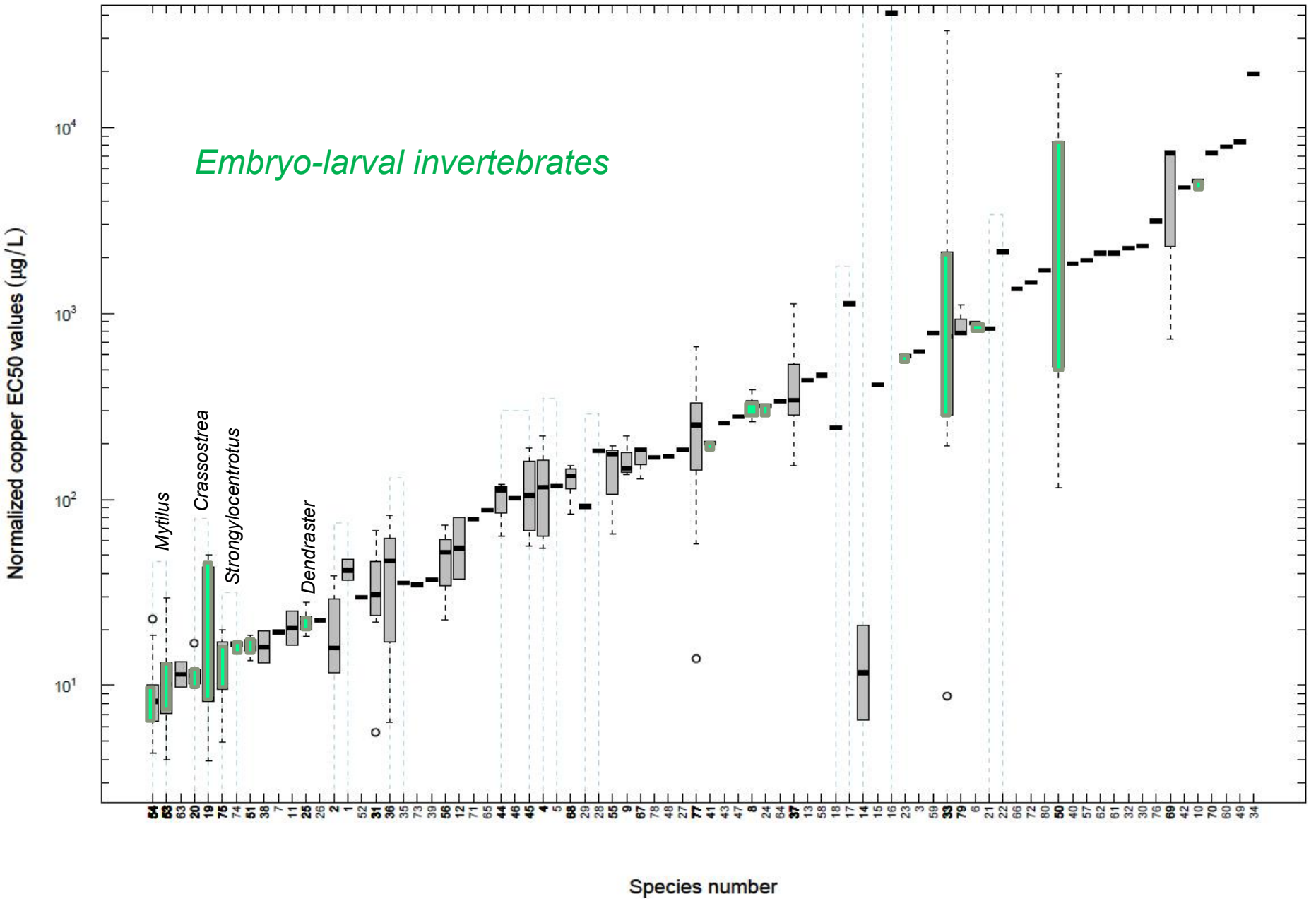
- In review by US EPA, which has participated in oversight of this project and has indicated its interest in revising the ambient saltwater quality criteria for copper while considering these results.
- *Views are those of the authors, and not necessarily those of US EPA*

Saltwater Criteria Data review

- Literature including those included in the 1995* marine document as well as new data published prior to April 2012 were screened for inclusion in this document.
- Data were screened using standard EPA acceptability criteria
- Revision includes toxicity information for 553 acute saltwater toxicity tests using 83 species in 70 genera
- 1995 document included 33 species in 26 genera
- Data were normalized to consistent chemistry conditions using the BLM

*U.S. Environmental Protection Agency, Glen Thursby, and David J. Hansen. 1995. Ambient Water Quality Criteria - Saltwater Copper Addendum (Draft). EPA 440-5-80-036.

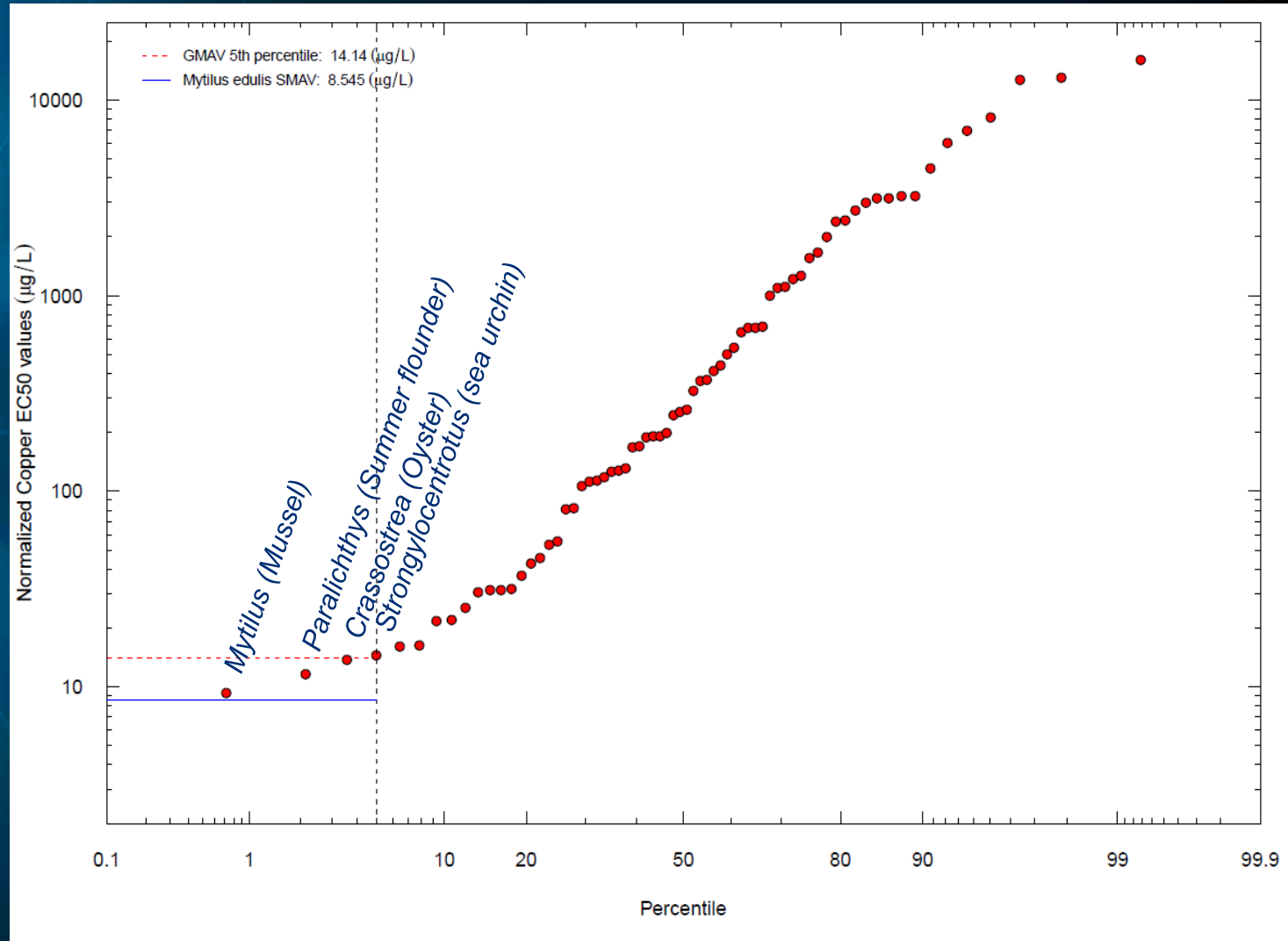
Distribution of copper EC50 values ordered by GMAV rank; 2011 Marine-saltwater copper criteria analysis



Protection of *Mytilus*

- Previous saltwater criteria have lowered the FAV to protect commercially and recreationally important mussel species (*Mytilus*).
- This review also shows that *Mytilus* is both the most sensitive species and is more sensitive than the 5th percentile.
- Recommendation that the FAV should be lowered to protect *Mytilus*.

Saltwater Criteria Data review



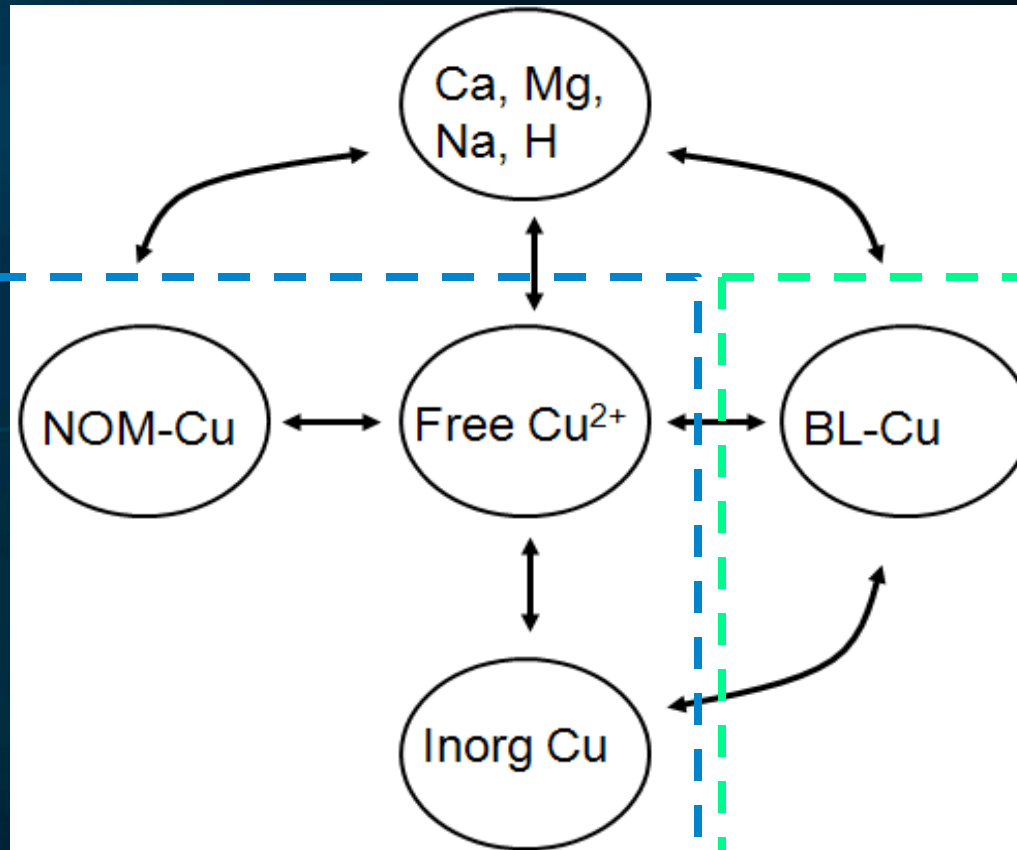
Proposed BLM Acute and Chronic Limits

- 5th Percentile 14.14 µg/L
- *Mytilus edulis*
 - Species mean acute value (EC50) 8.55 µg/L
 - Species mean chronic value (EC10) 7.12 µg/L
- Proposed acute limit = chronic limit = 7.07* µg/L

* as a function of DOC, pH, salinity using BLM
pH = 8, DOC = 1.4, Salinity = 32 ppt

Biotic Ligand Model

Toxicity Effects showing bioavailability relationships



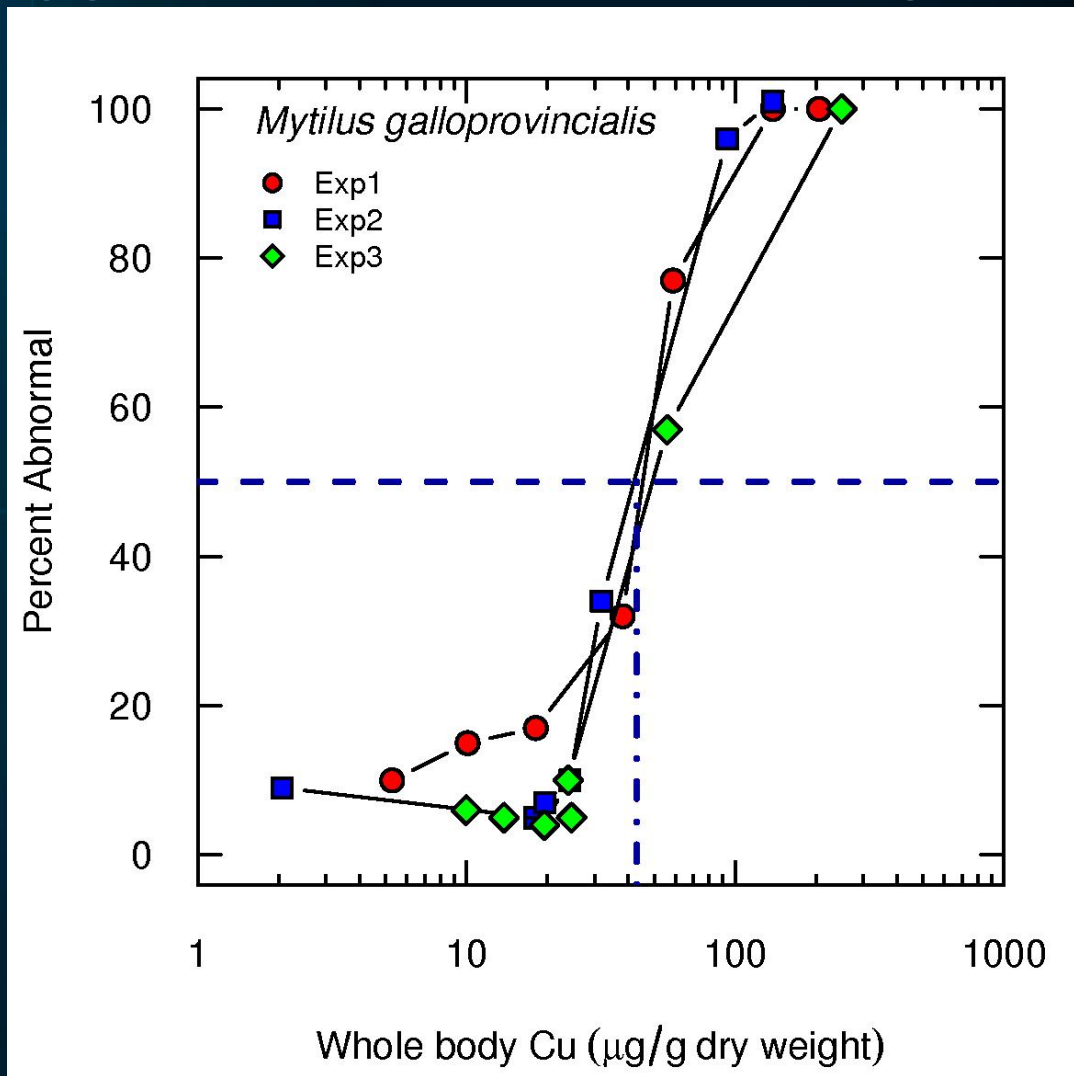
Chemical Speciation

Organism Accumulation

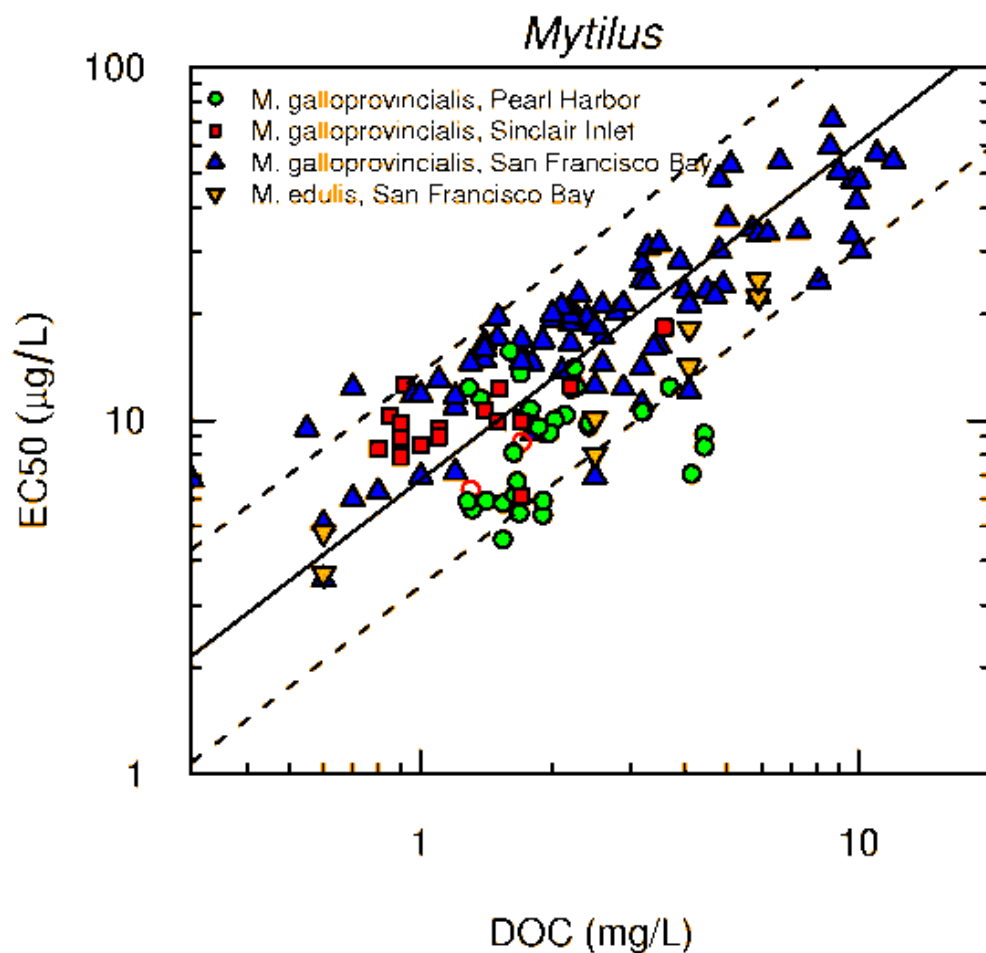
Sensitive Marine Invertebrates used for BLM Development and Testing



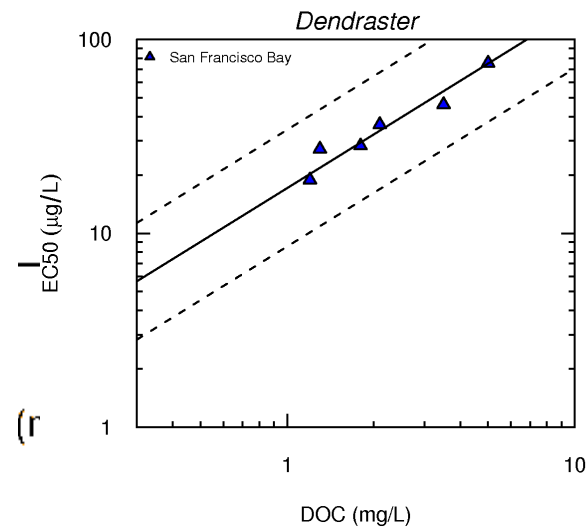
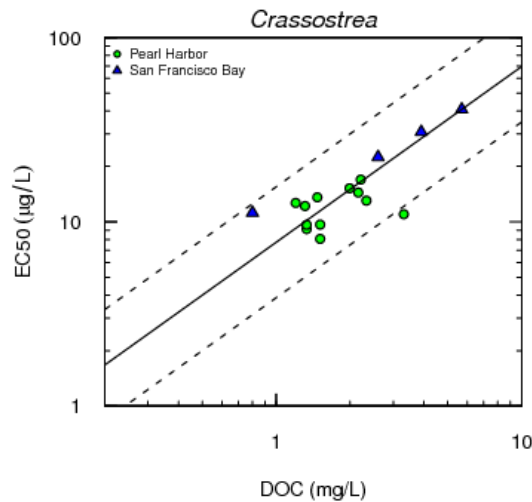
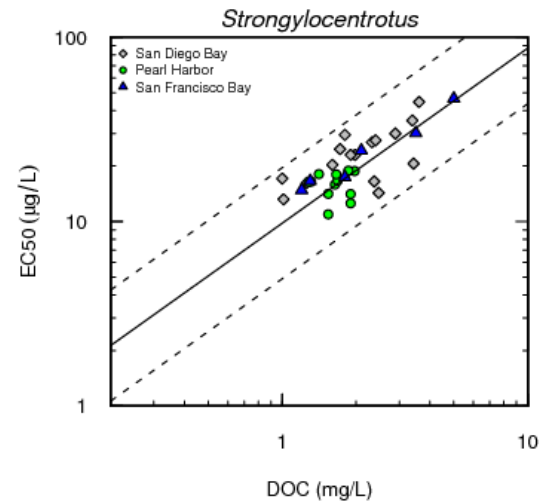
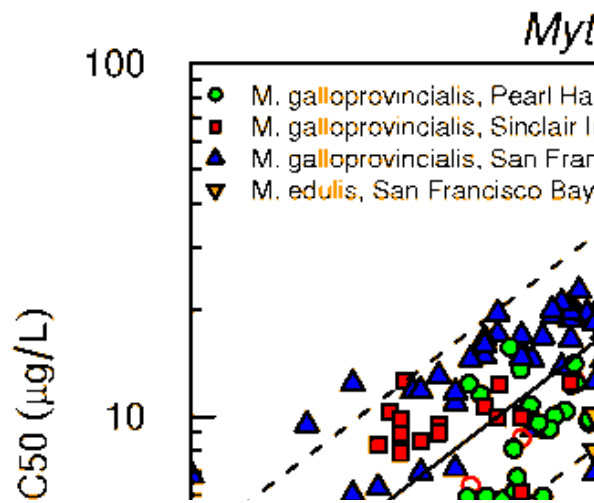
Copper accumulation on *Mytilus*



NOM influence on copper toxicity



NOM influence on copper toxicity



San Diego Bay Case Study

San Diego Bay



Shelter Island Yacht Basin

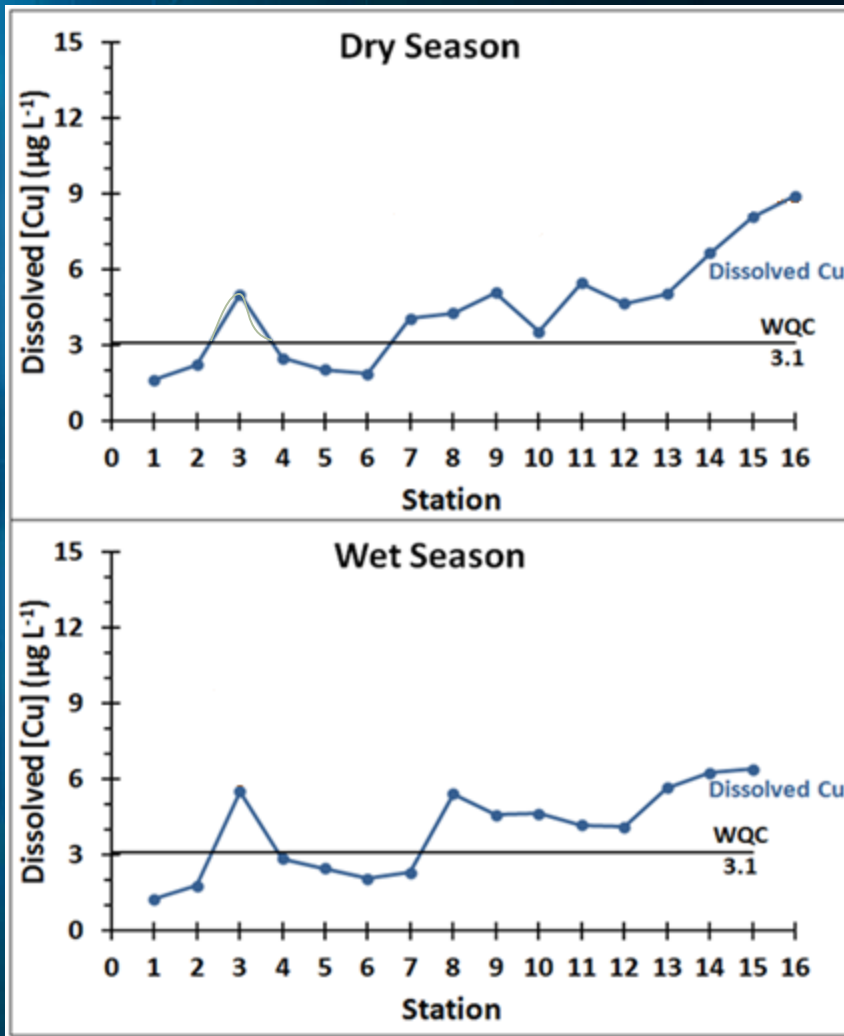


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Images downloaded from Google Earth

Results:

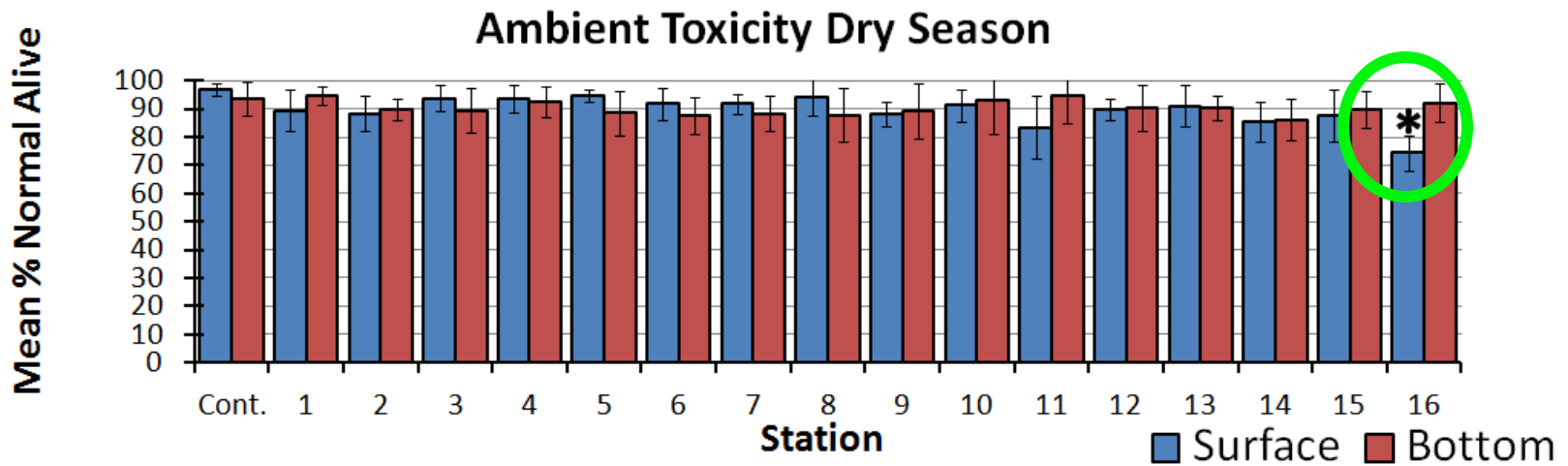
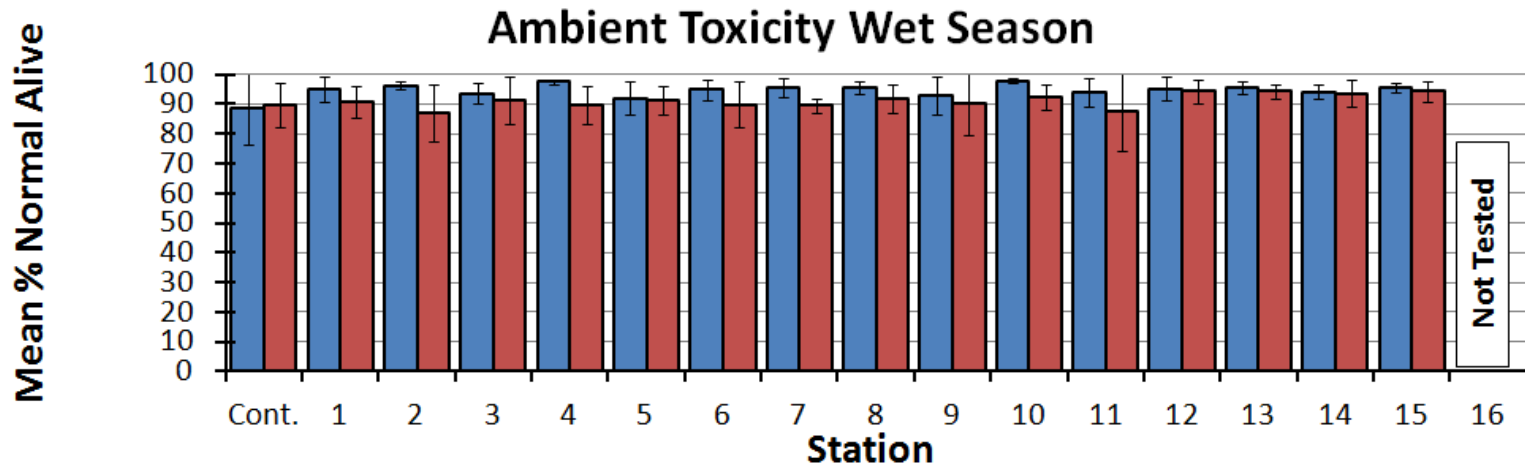
Current US Water Quality Criteria



- Significant portions of SIYB are above the current US EPA Water quality criterion (3.1 ppb)

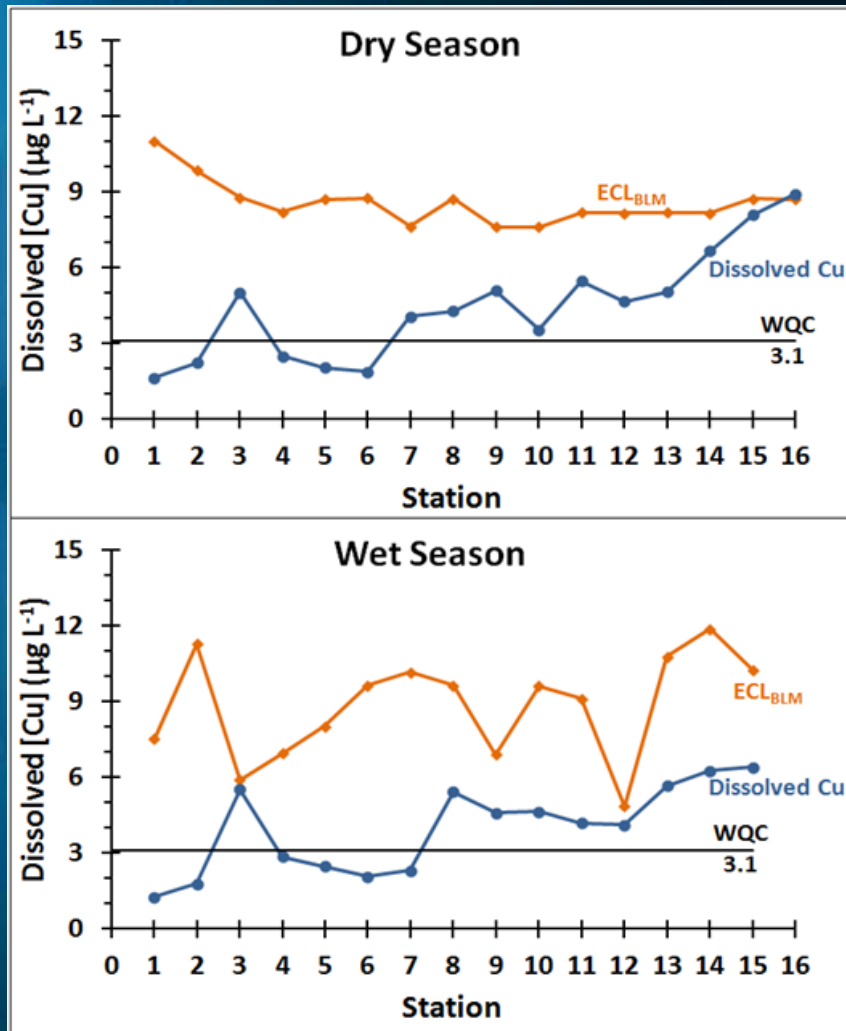
Results:

Ambient Water Toxicity Bioassays



Results:

BLM Predicted Effective Chronic Limit (ECL)



- The ECL predicted by the marine-BLM for *Mytilus* suggests the US EPA WQC is over protective
- Toxicity only observed where dissolved Cu exceeds ECL (one sample)

Measured and Predicted Toxicity SIYB Water Effect Ratio Study (*Mytilus*)

		BLM Predicted <i>Mytilus</i> EC50 µg/L	Measured <i>Mytilus</i> EC50 µg/L
Wet season	Min	6.1	8.0
	Max	12.1	10.1
	Mean	8.8	8.9
Dry season	Min	9.6	9.3
	Max	13.8	11.2
	Mean	10.9	10.2

Summary and Conclusions

- An update to the US EPA saltwater criteria for copper that incorporates the BLM has been developed and is in review by US EPA
- The BLM WQC uses DOC, pH, Salinity to determine a protective criterion that considers local variation
- Both the saltwater BLM and results from a case study in SIYB agree that the existing WQC is overprotective
- The saltwater BLM provides an easy tool that can be used to develop protective marine values for copper using DOC, pH, and salinity

Questions?

For further information:

Bob Santore

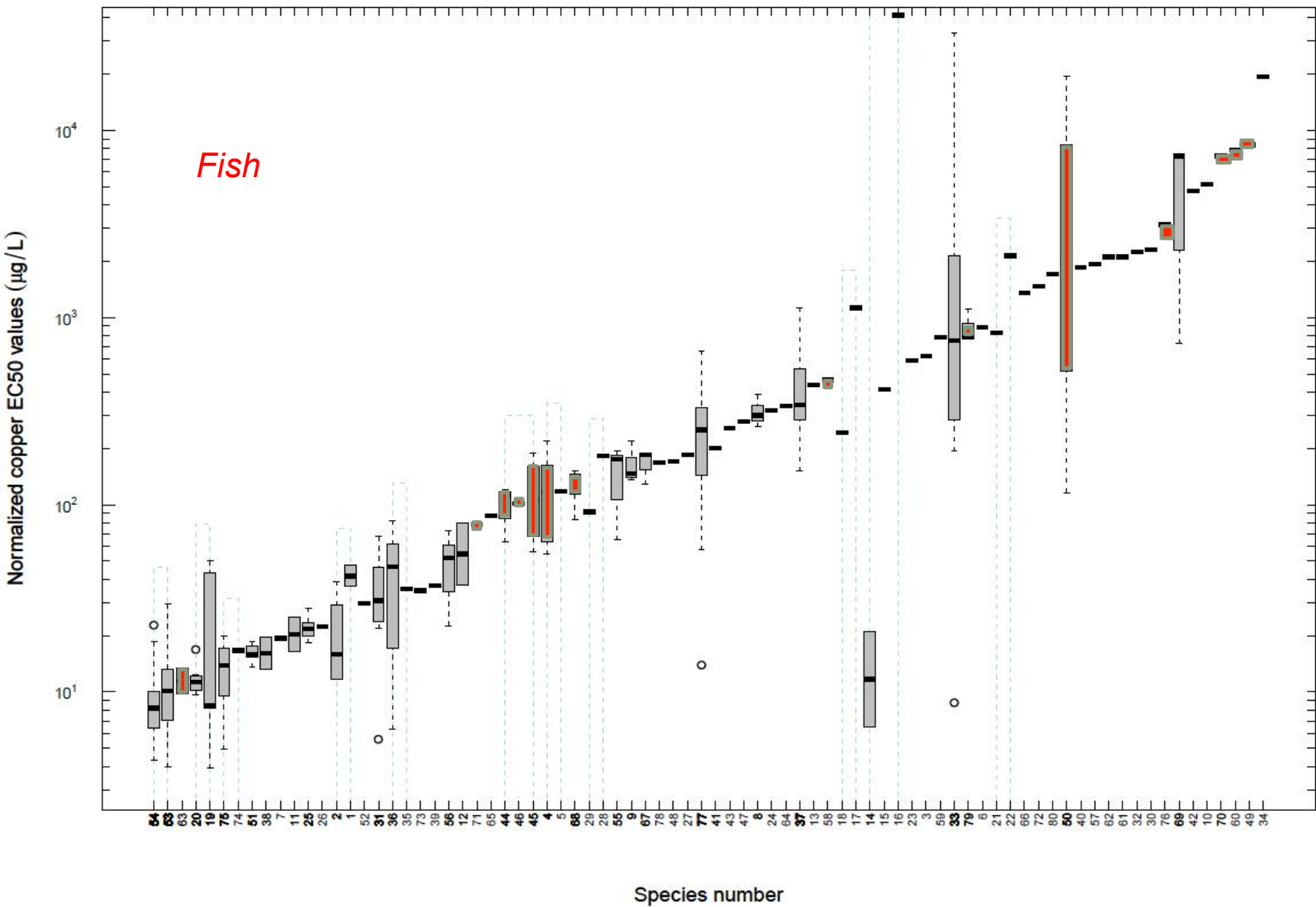
HDR | HydroQual

robert.santore@hdrinc.com

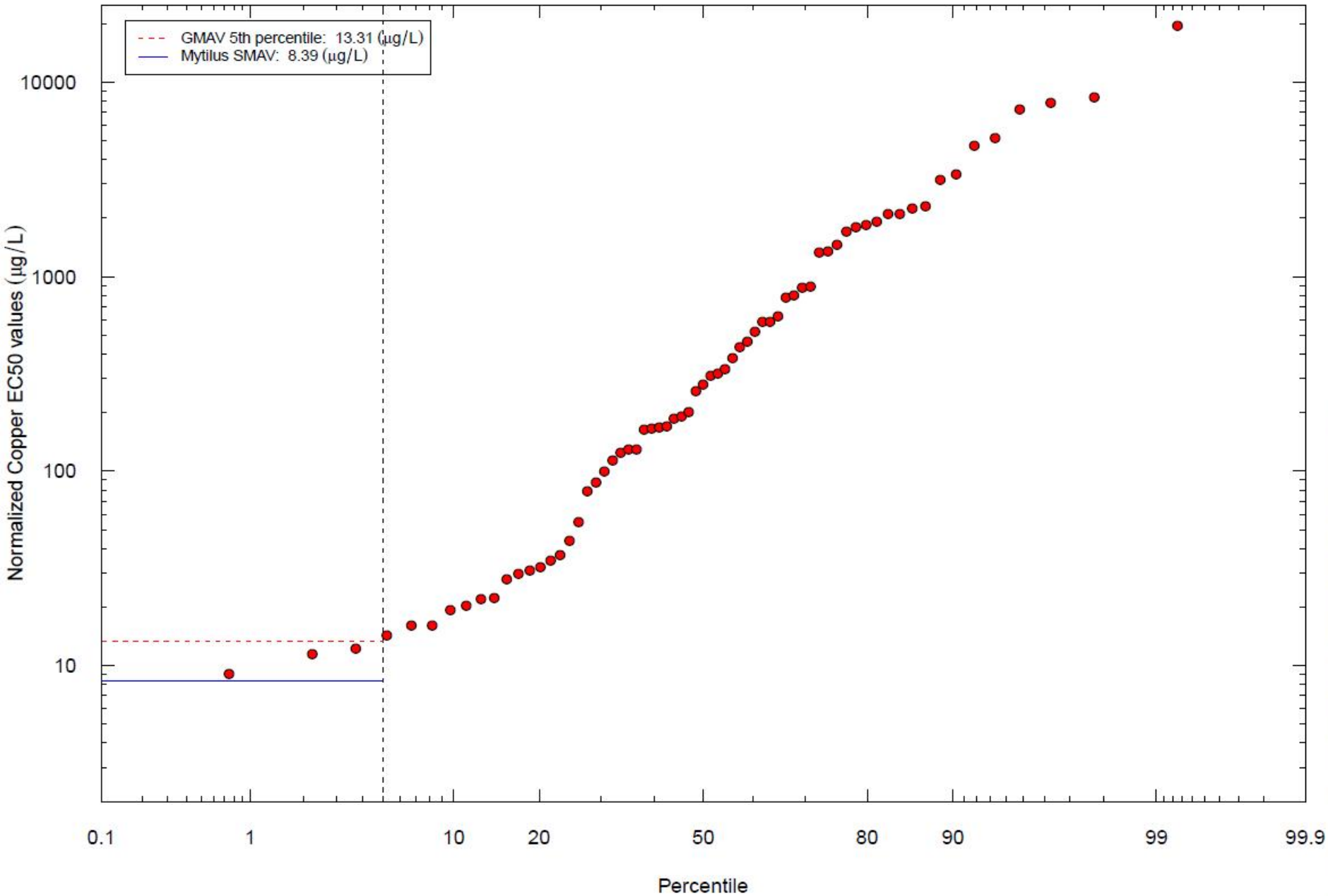


Together We Are Better

Distribution of copper EC50 values ordered by GMAV rank; 2011 Marine-saltwater copper criteria analysis



Probability distribution of copper GMAV values & criteria parameters; 2011 Marine-saltwater copper criteria analysis



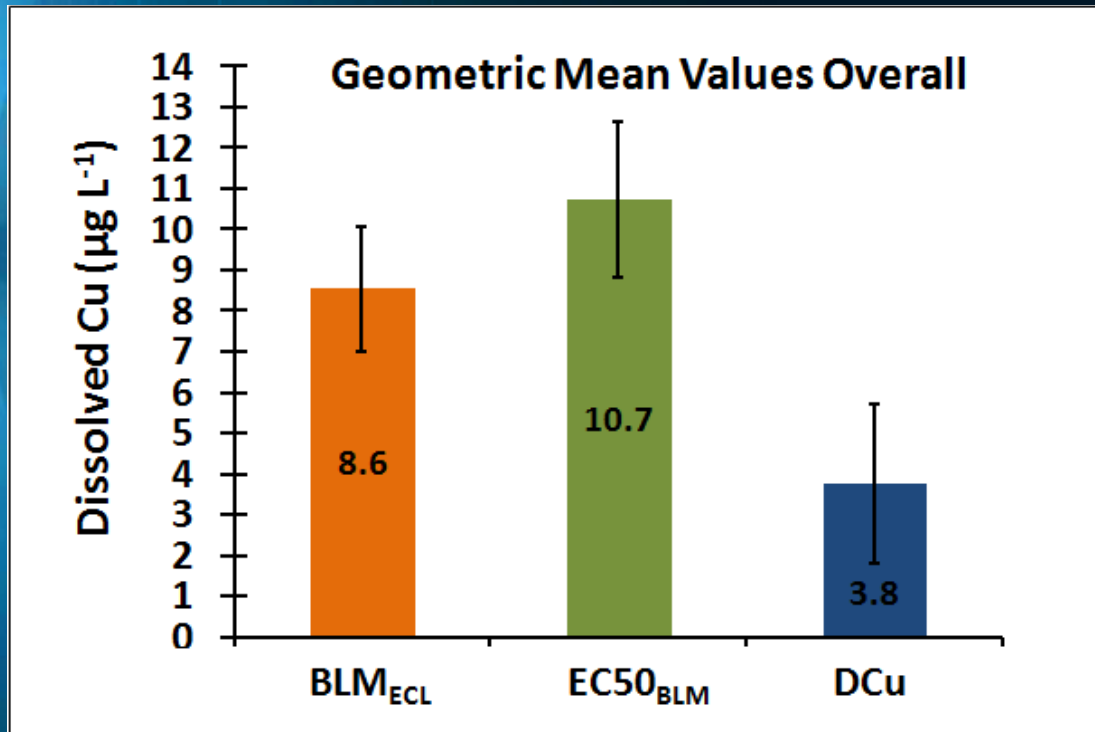
Sampling Stations

Yellow Squares= Water Effect Ratio Stations

Yellow Squares and green circles = Ambient Toxicity Stations

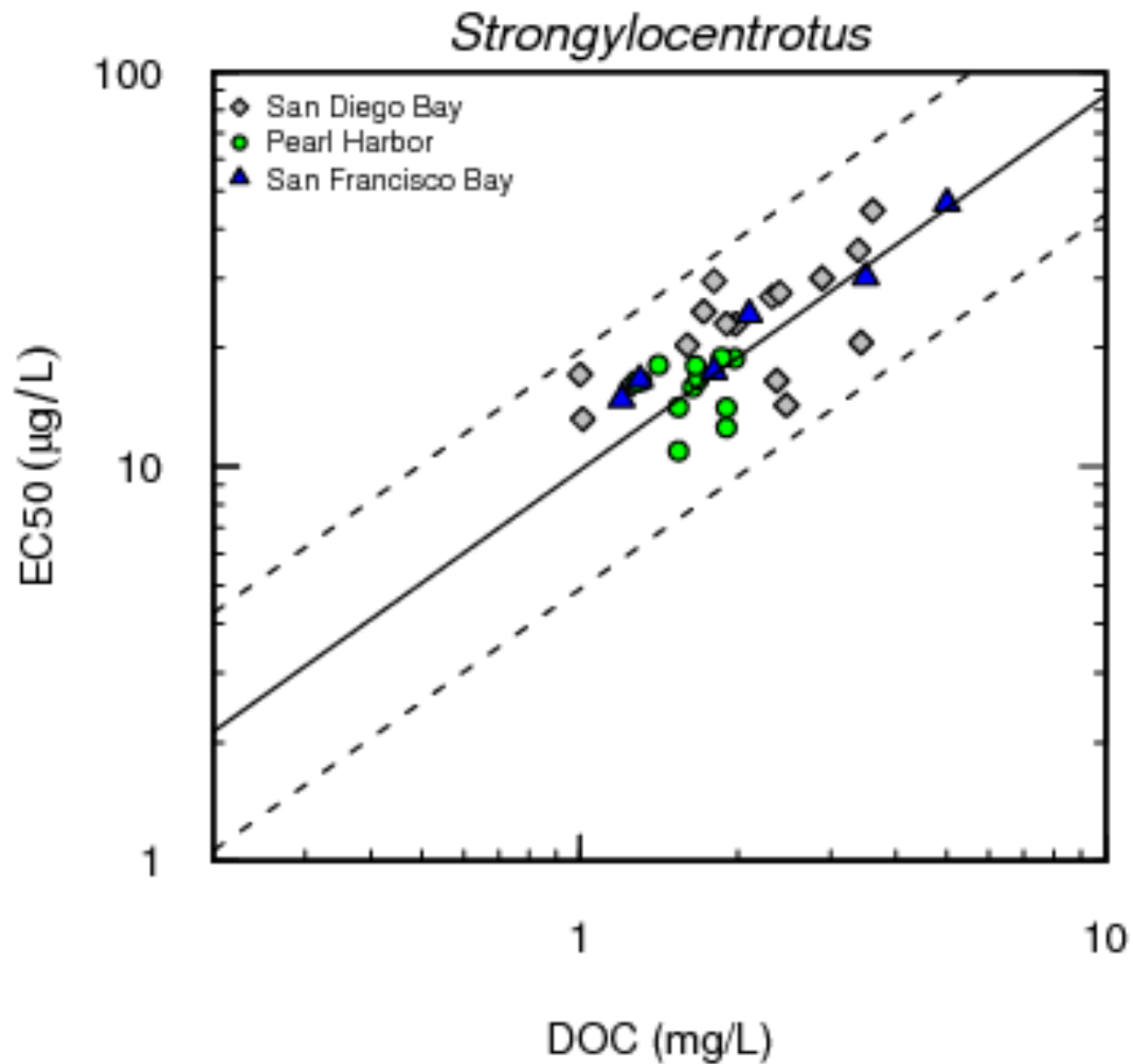


Results marine-BLM

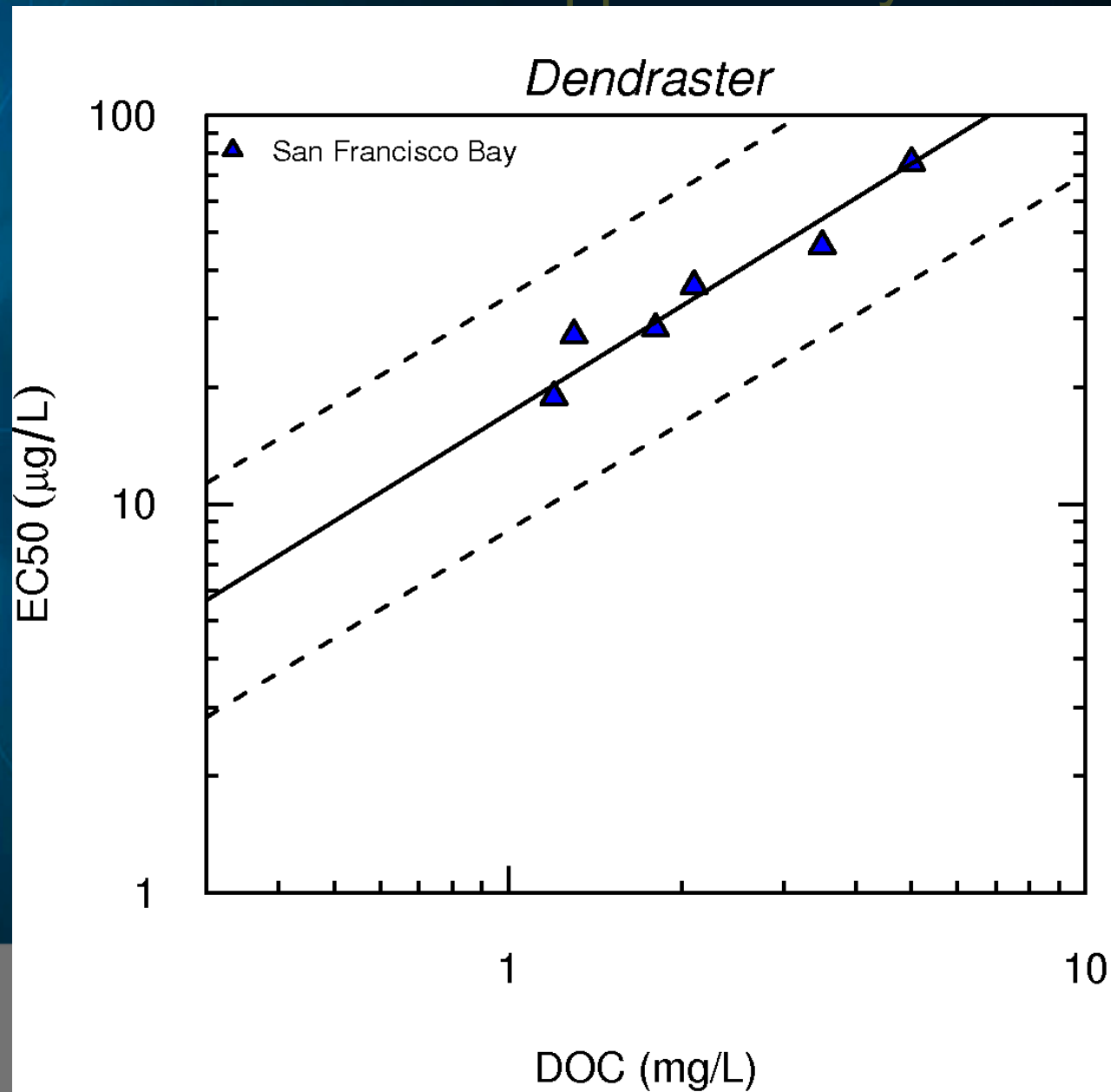


- EC50_{BLM} Averages
 - Wet season 11.1 µg L⁻¹
 - Dry season 10.7 µg L⁻¹
- Estimated chronic limit Averages
 - Wet season 8.8 µg L⁻¹
 - Dry season 8.6 µg L⁻¹
- Difference between DCu and EC50 (6.9 µg L⁻¹) is complexation capacity

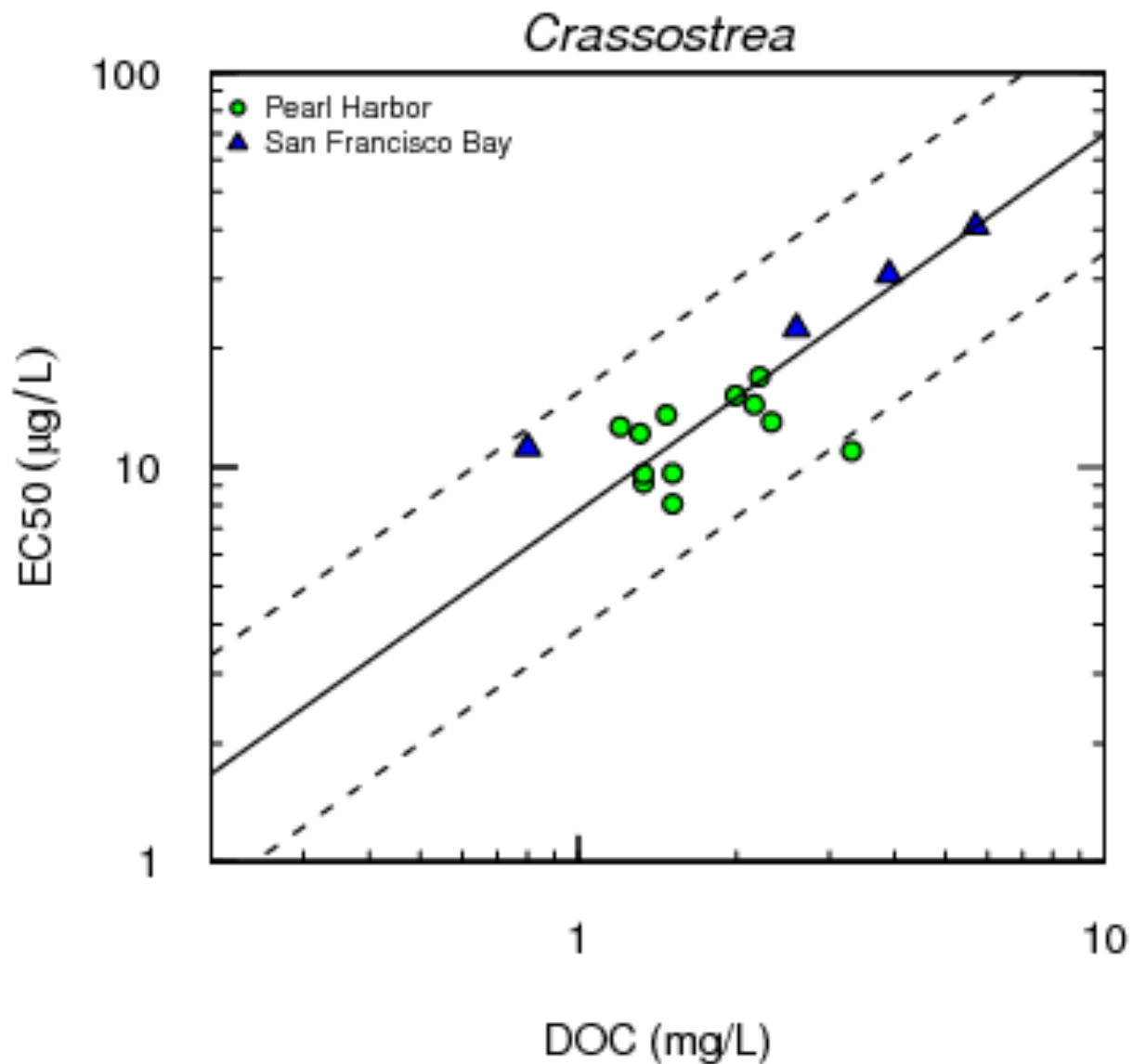
NOM influence on copper toxicity to *Strongylocentrotus*



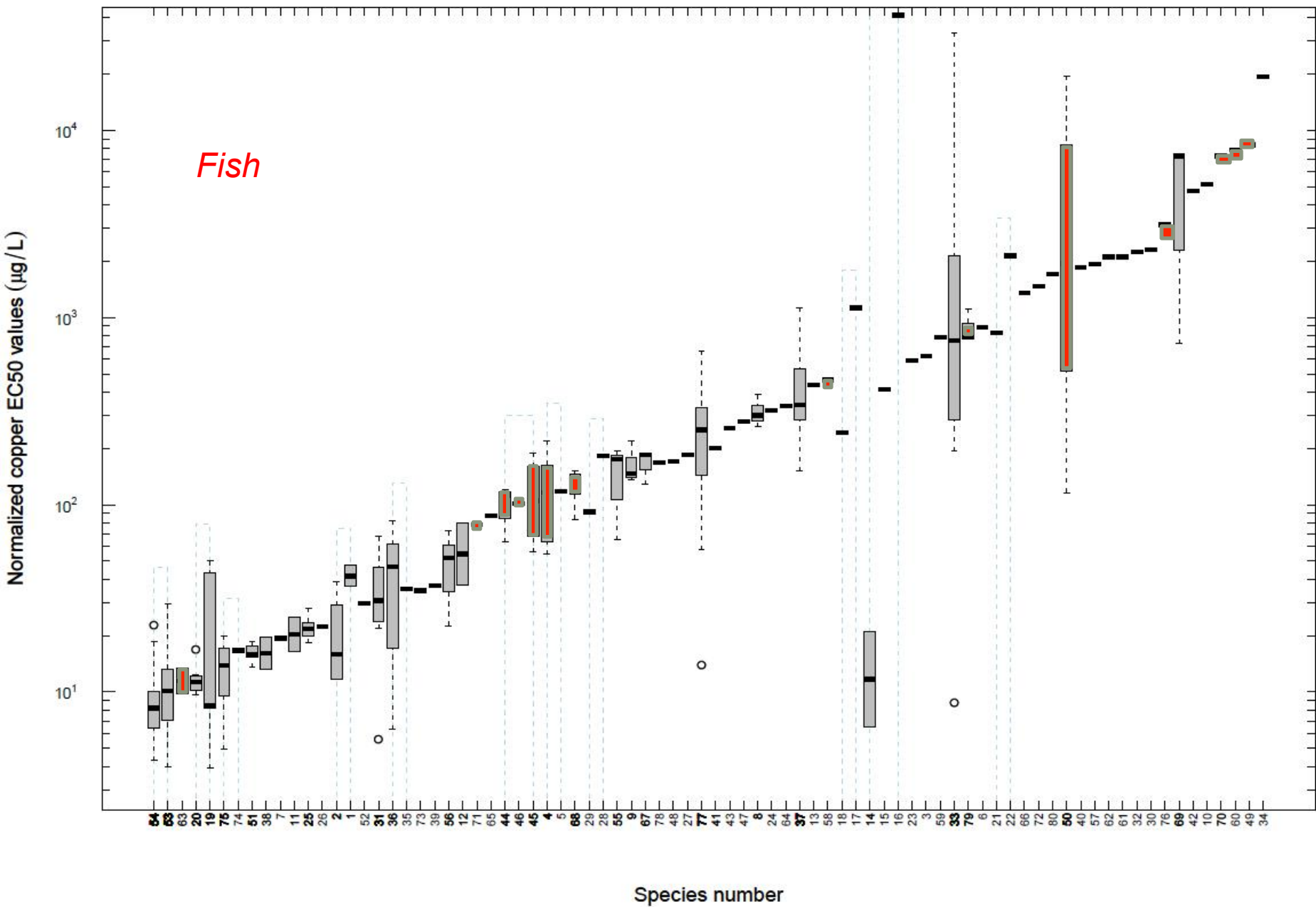
NOM influence on copper toxicity to *Dendraster*



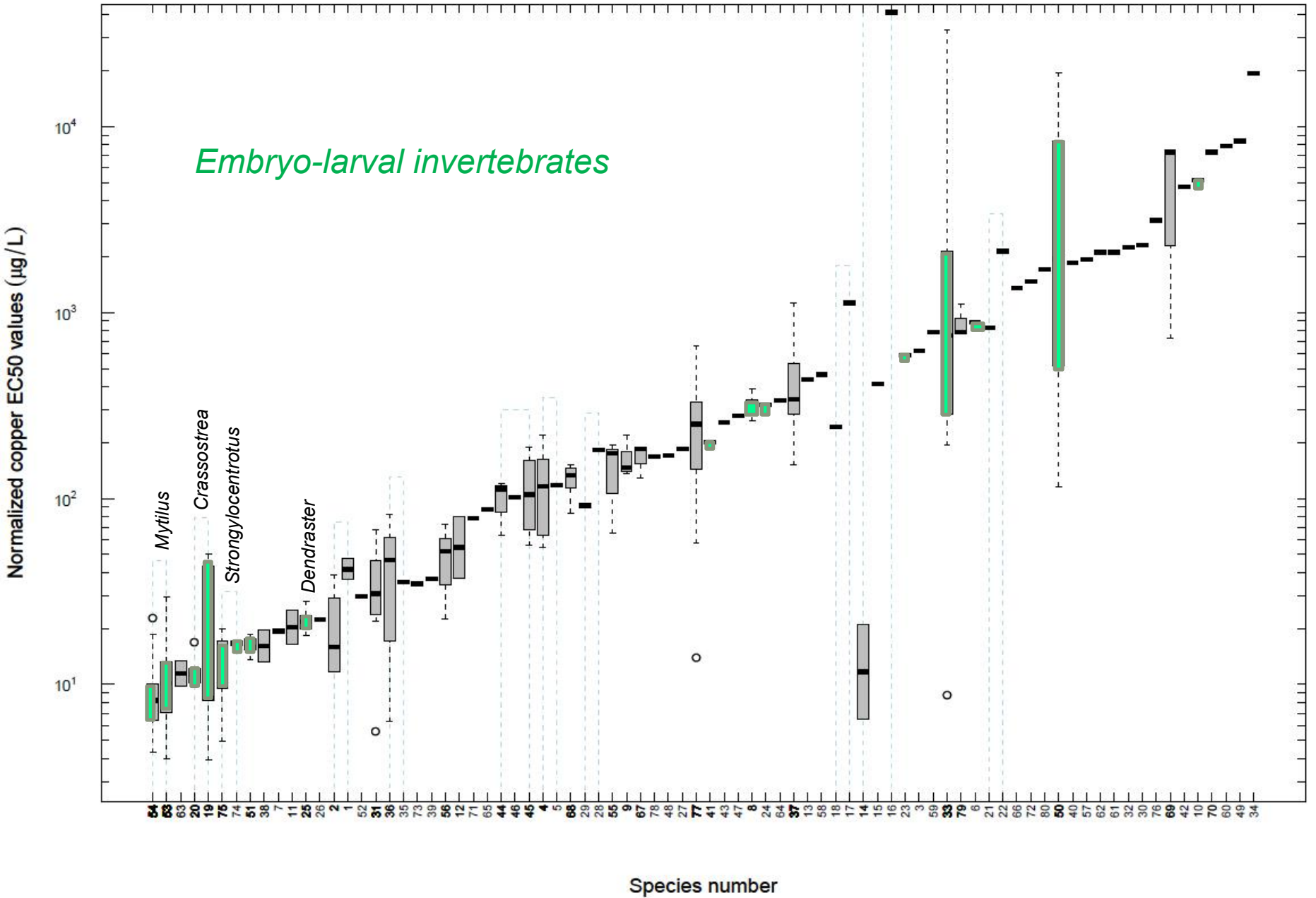
NOM influence on copper toxicity to *Crassostrea*



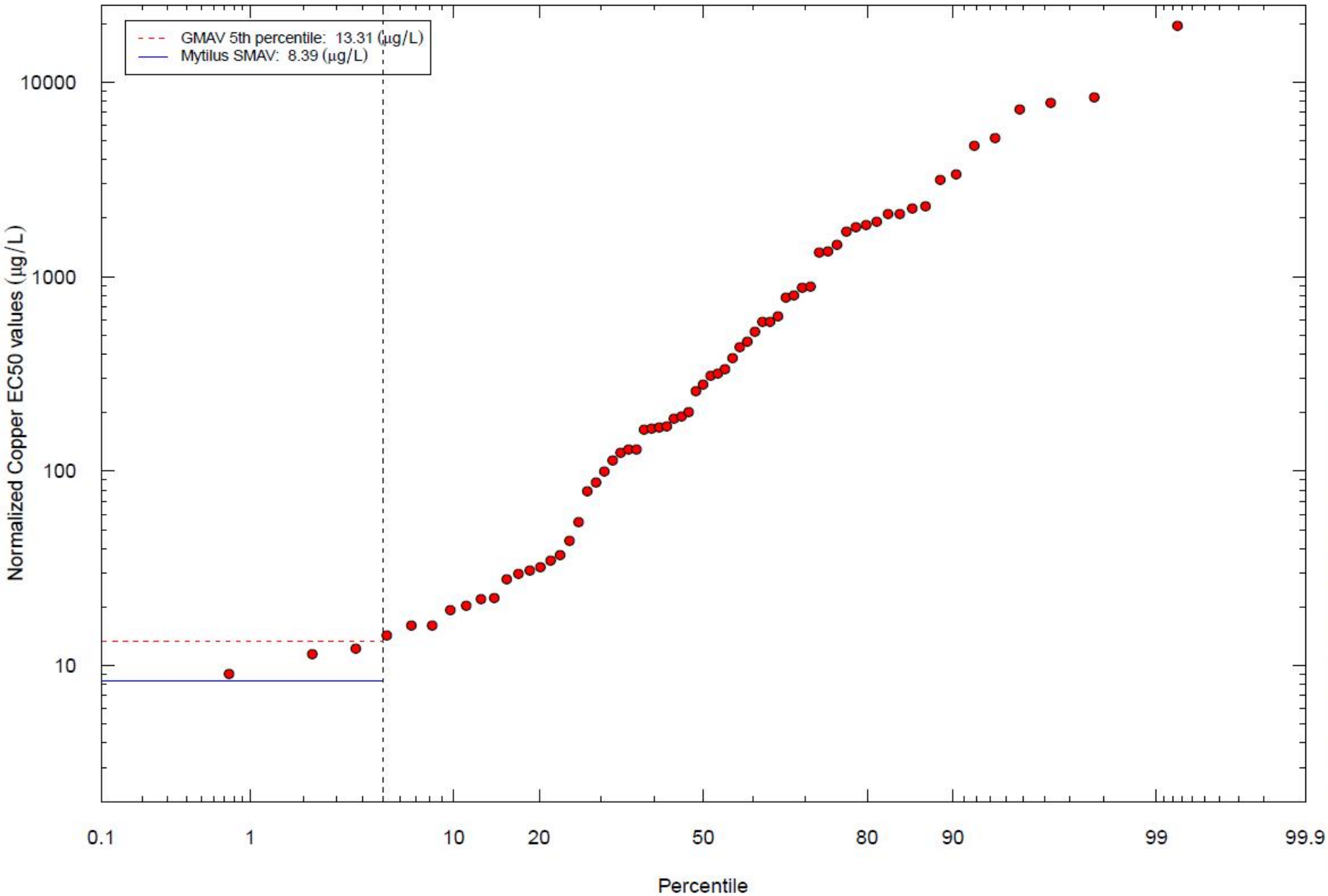
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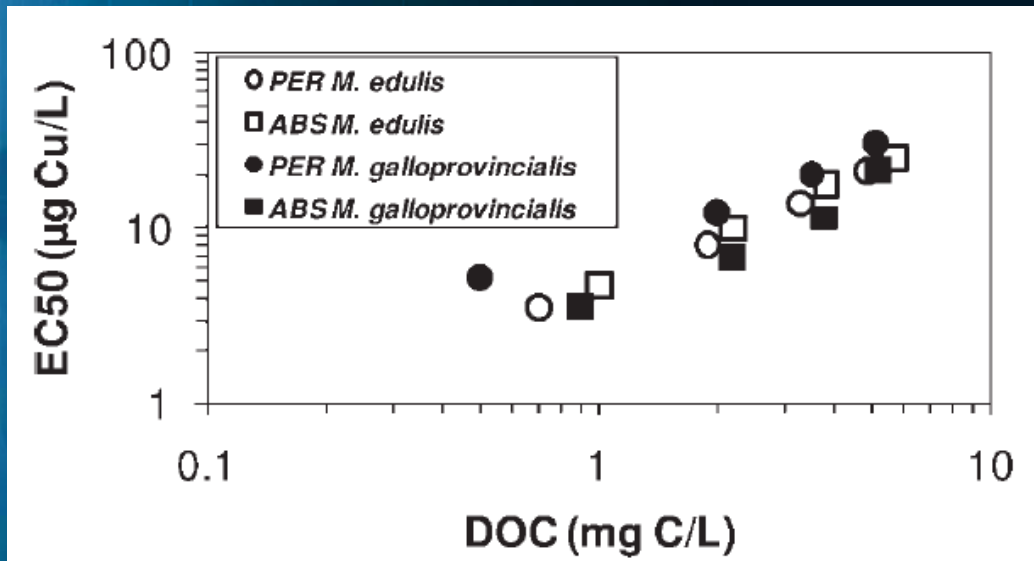
Probability distribution of copper GMAV values & criteria parameters; 2011 Marine-saltwater copper criteria analysis



Protection of *Mytilus*

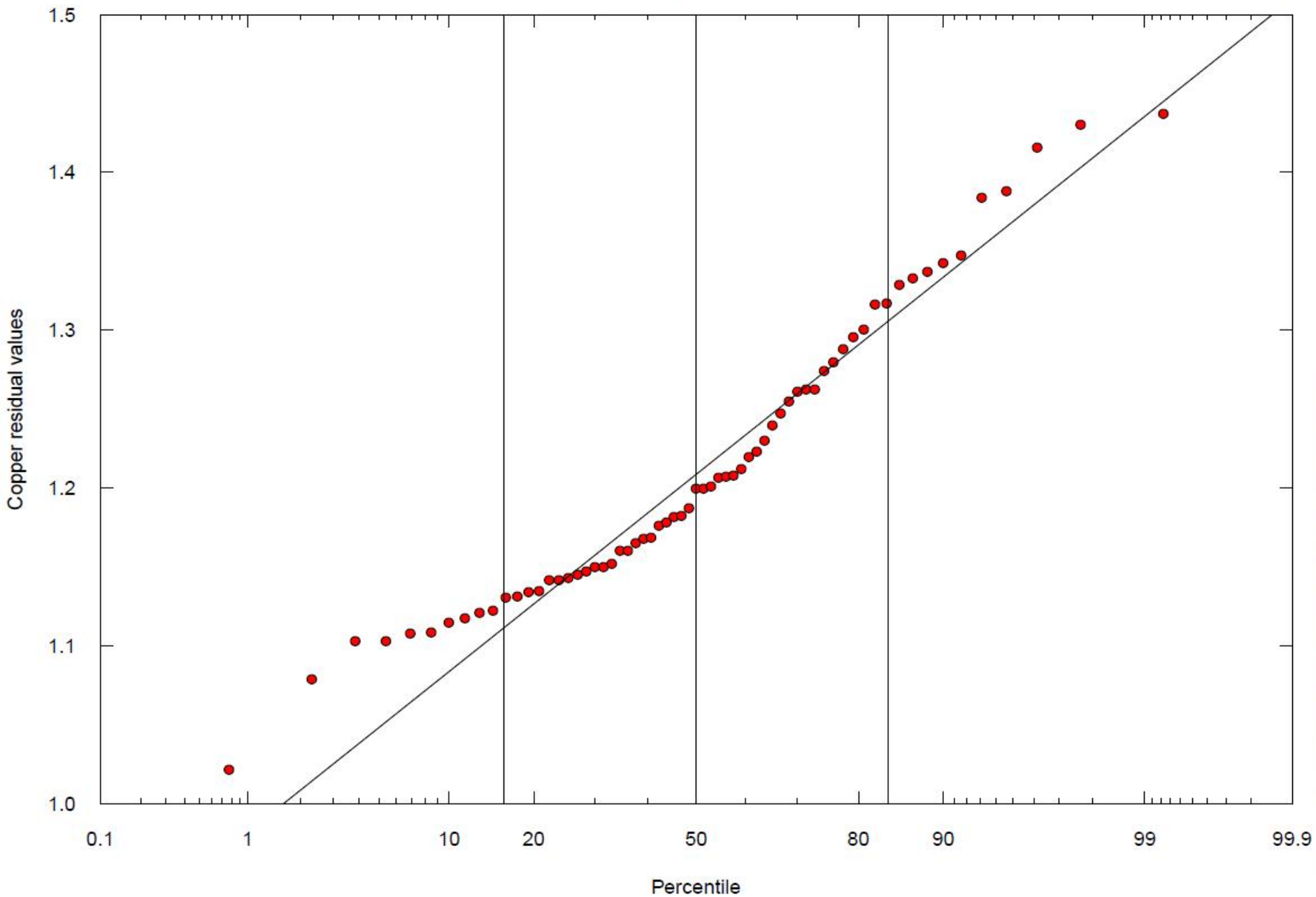
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- Recommendation that the FAV should be lowered to protect *Mytilus*.

Comparison of *M edulis* and *M galloprovincialis* sensitivity



- Two *Mytilus* species have nearly identical sensitivity
- Differences in SMAVs may not be meaningful
- Could use combined GMAV as the basis for FAV rather than SMAV

Probability distribution of copper EC50/EC10 residual values for Mytilus from Arnold data; 2011 Marine-saltwater copper criteria analysis



Recommendation

- Recommendation is to lower the FAV below the 5th percentile to protect *Mytilus edulis*
- 80th percentile of the EC50/EC10 ratio provides a conservative concentration that is protective of *Mytilus*
- Proposed CMC developed as the *Mytilus* SMAV or GMAV divided by 1.3 (1.02 – 1.44)
- Similar EC50/EC10 ratios observed for other sensitive invertebrates such as *Crassostrea* (1.09 – 1.21) and *Strongylocentrotus*
- Furthermore, since this results in a conservatively protective concentration for the most sensitive life stage, we propose that the CMC and CCC are set to the same numeric value

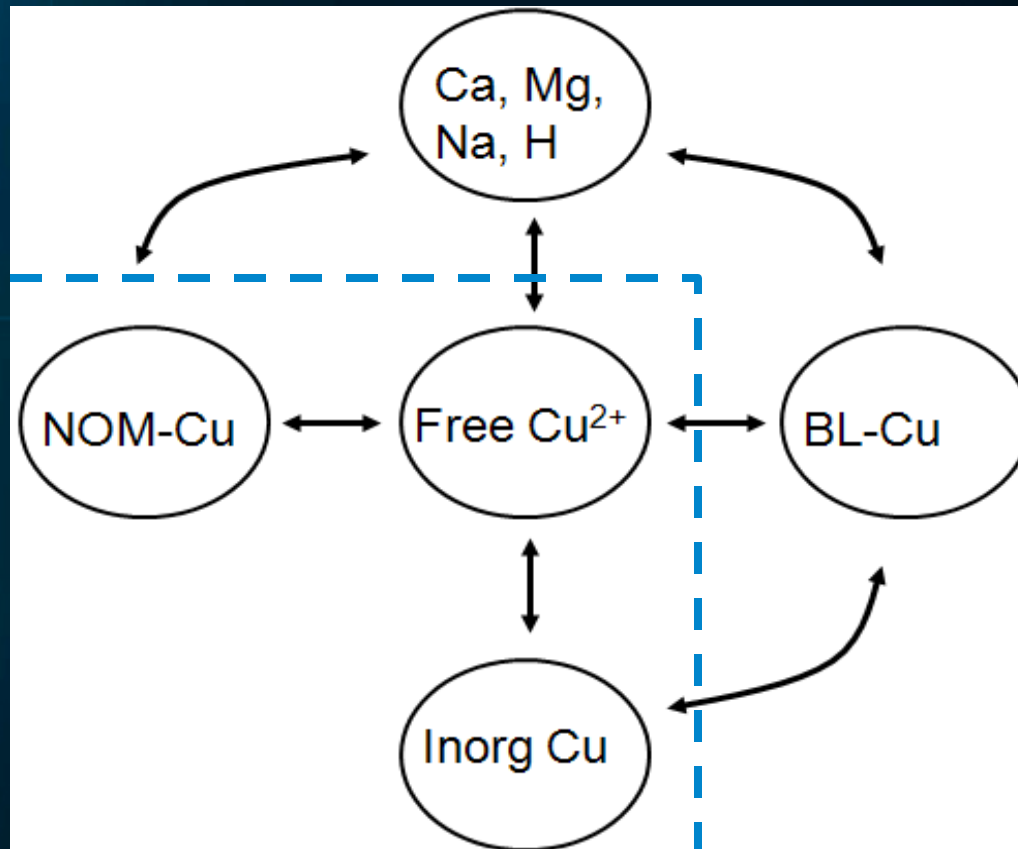
FAV and CMC Calculation

Small difference depending on whether SMAV or GMAV is used:

– 6.45 $\mu\text{g/L}$, *M. edulis* SMAV/1.3

– 6.97 $\mu\text{g/L}$, *Mytilus* GMAV/1.3

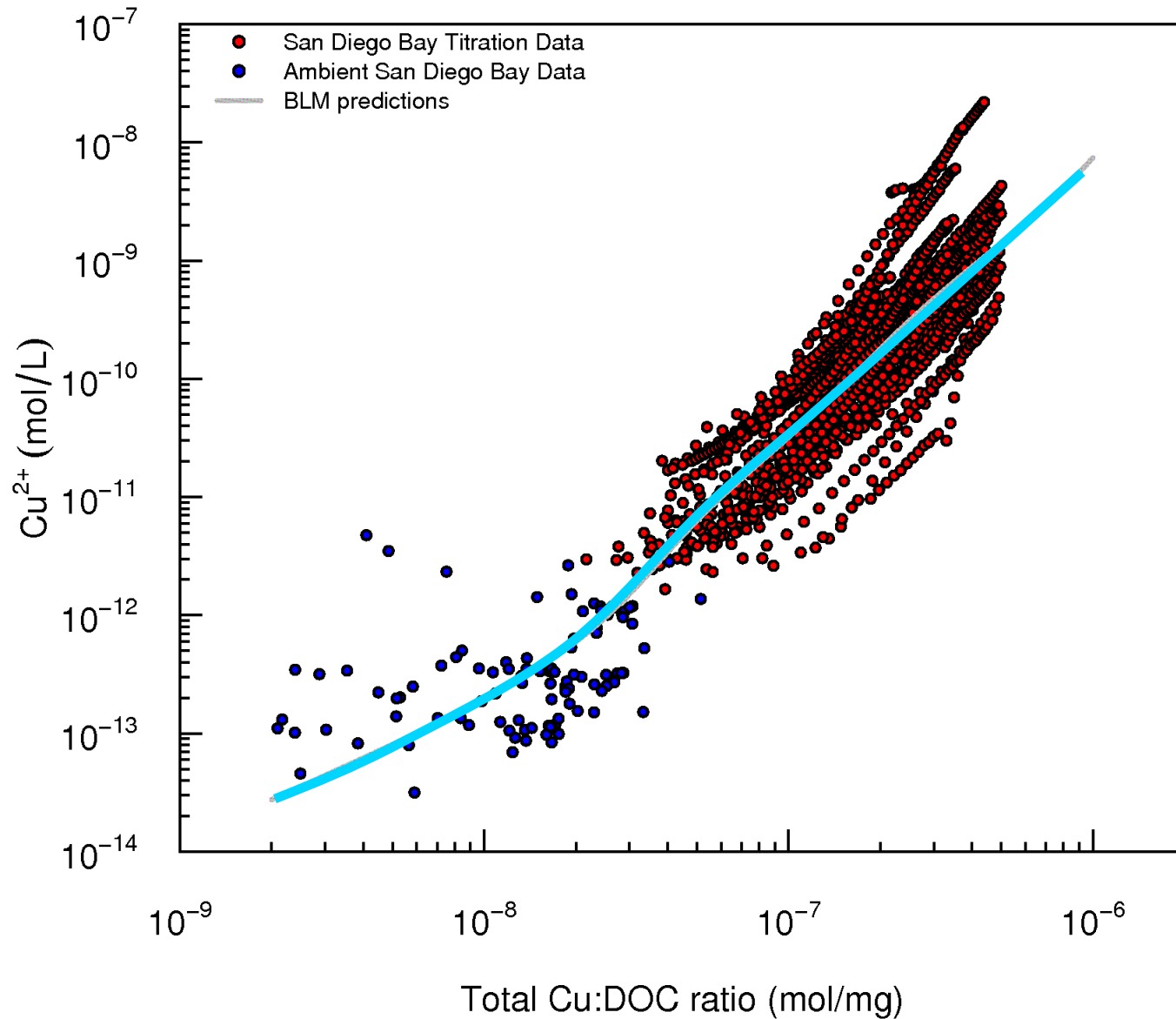
Conceptual Model and Data Needs



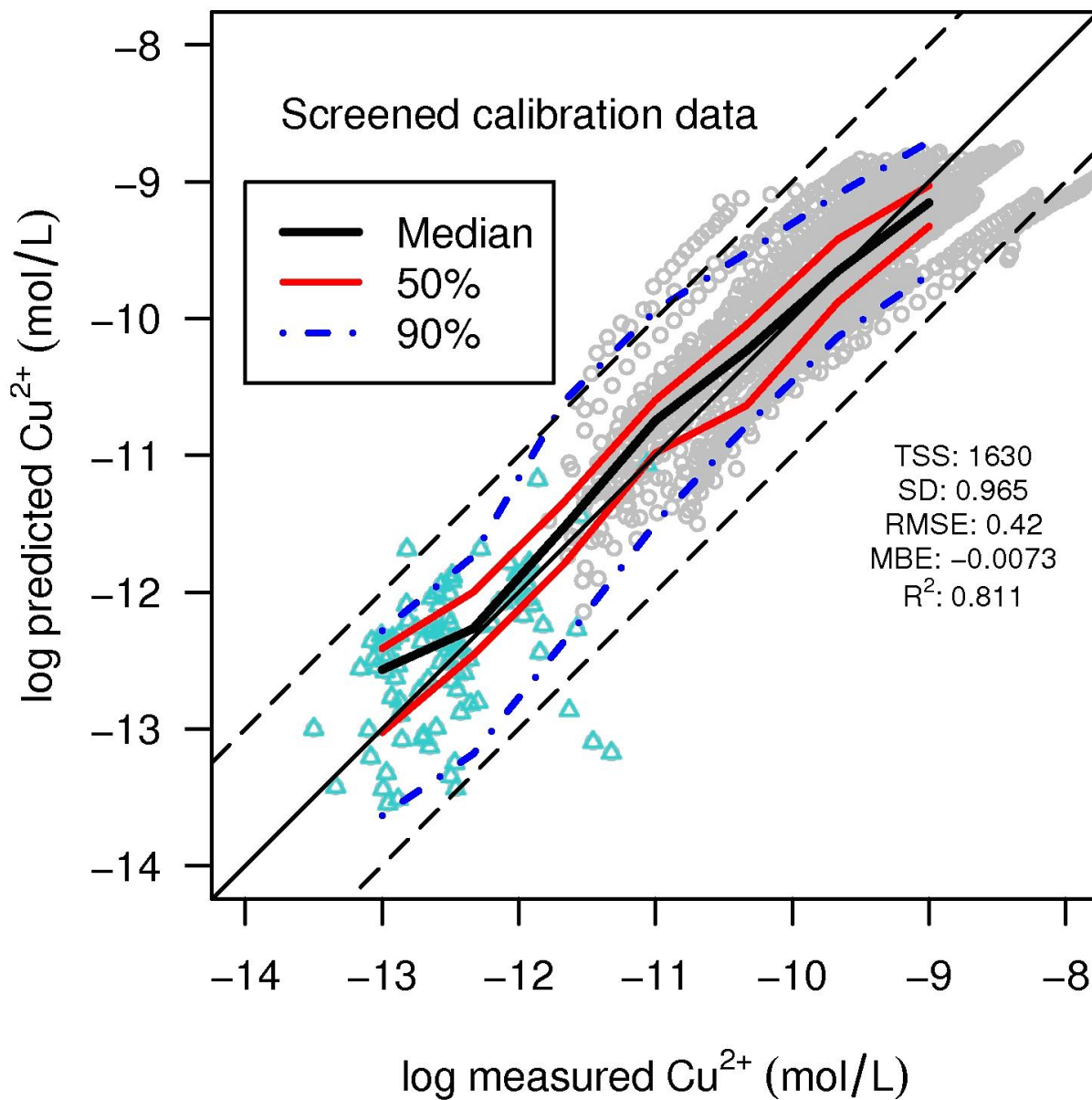
Speciation modeling needs

- Determine the copper complexation behavior of marine natural organic matter (NOM) including binding capacity and binding strength
- Compare copper binding characteristics from NOM at different sites
- Use dissolved organic carbon (DOC) as a measure of NOM quantity
- Model inputs: T, pH, DOC, Salinity

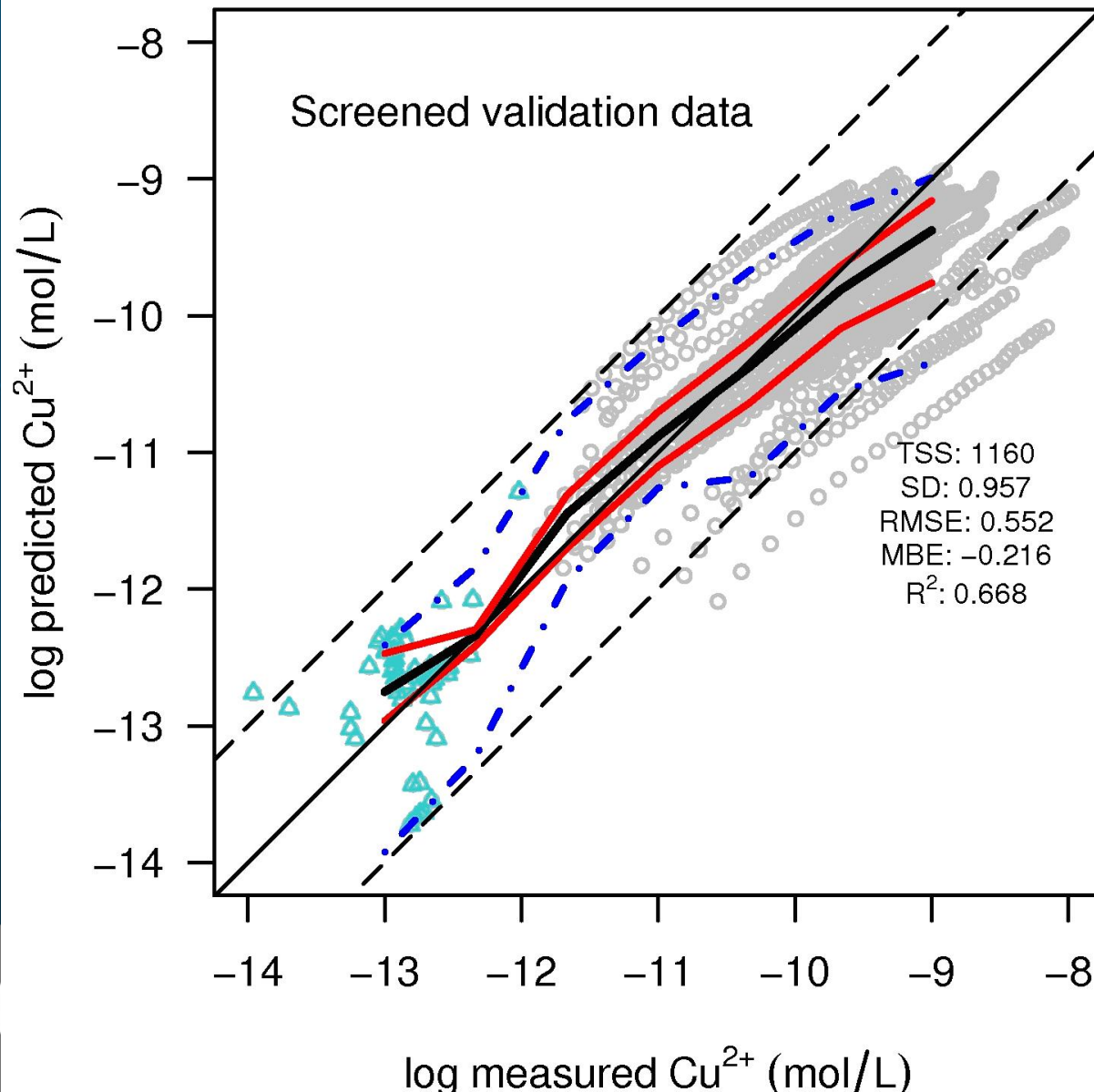
Titration and Ambient Speciation Data



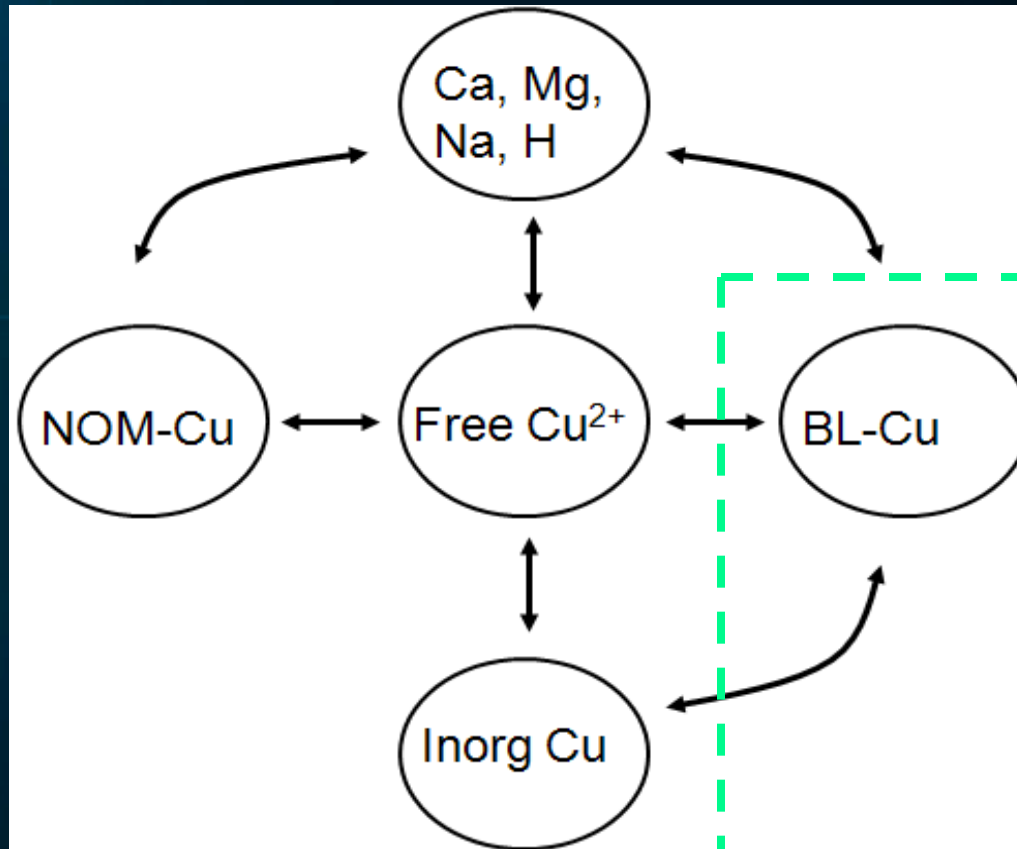
San Diego Bay Chemistry Calibration



San Diego Bay Chemistry Validation



Conceptual Model and Data Needs

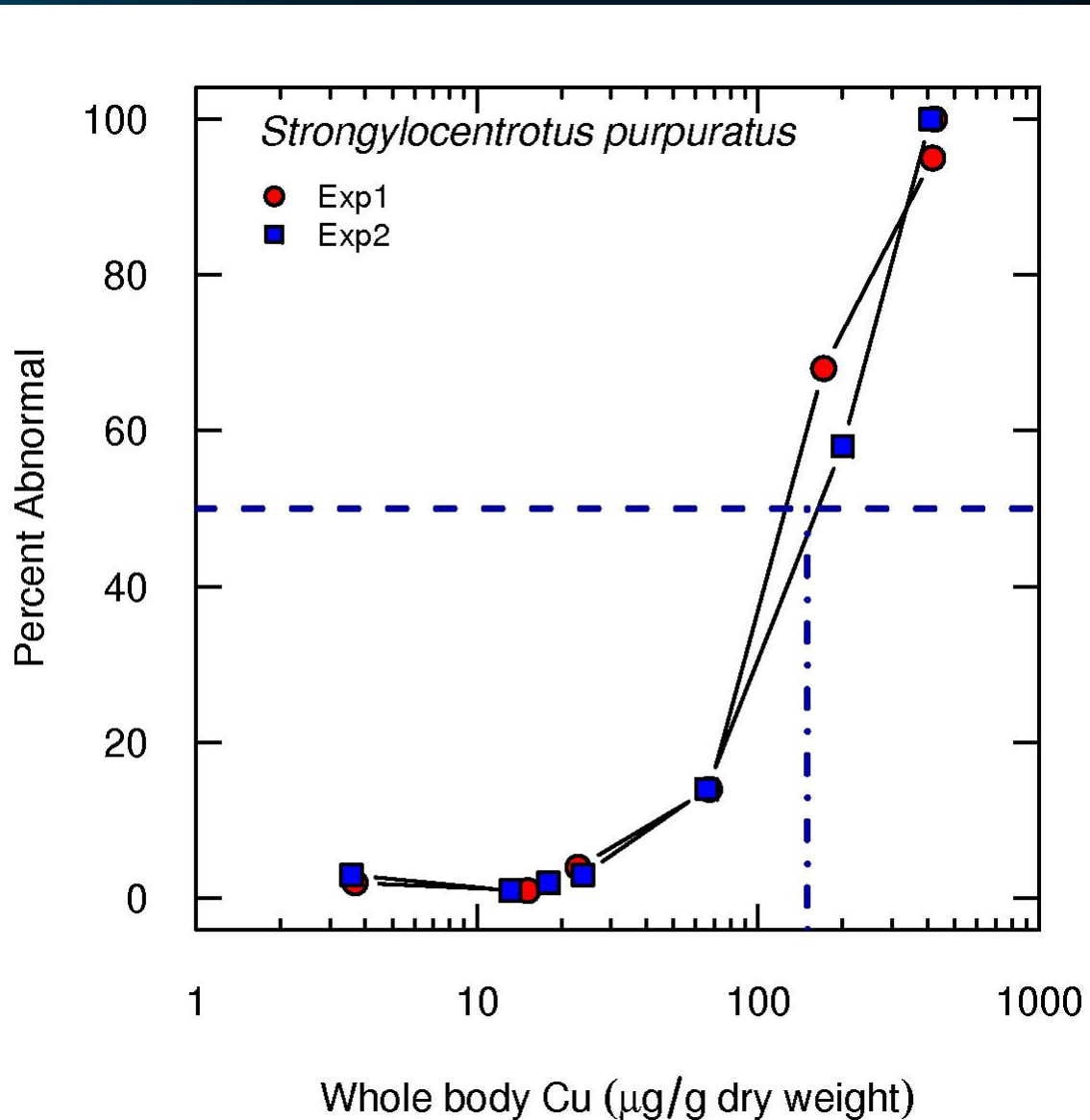


Data review

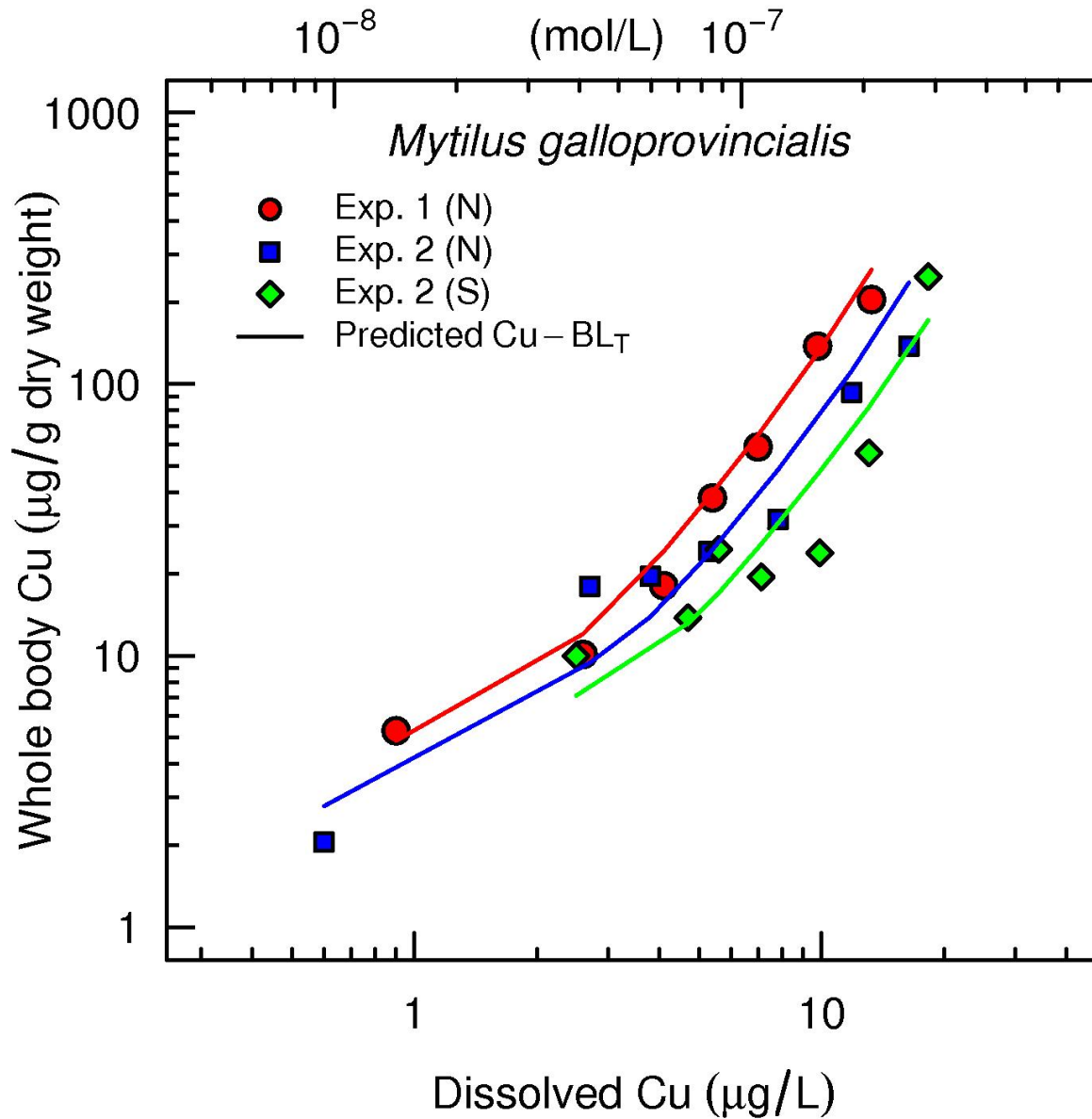
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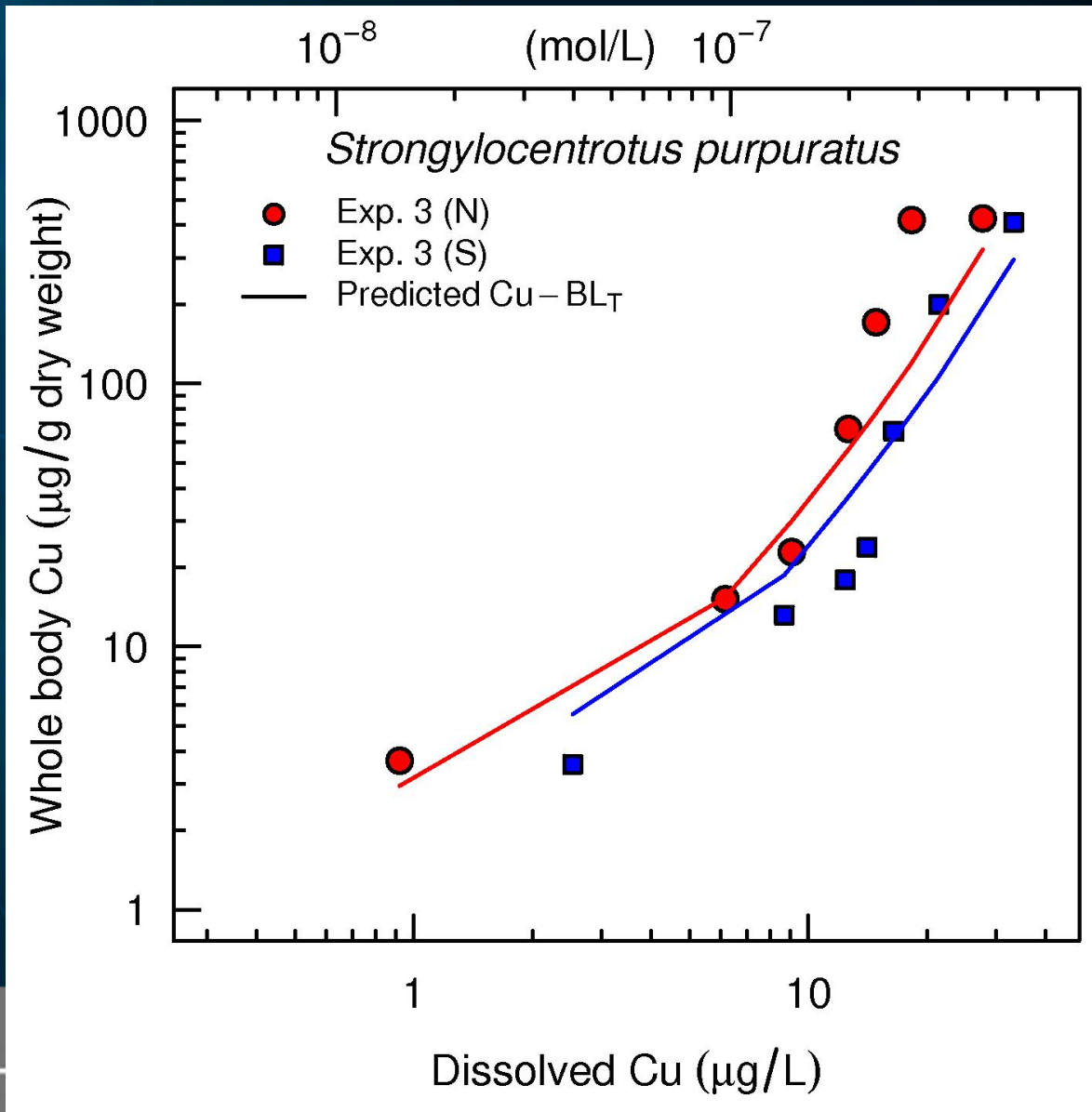
Copper accumulation on *Strongylocentrotus*



Predicted Copper Accumulation on *Mytilus*

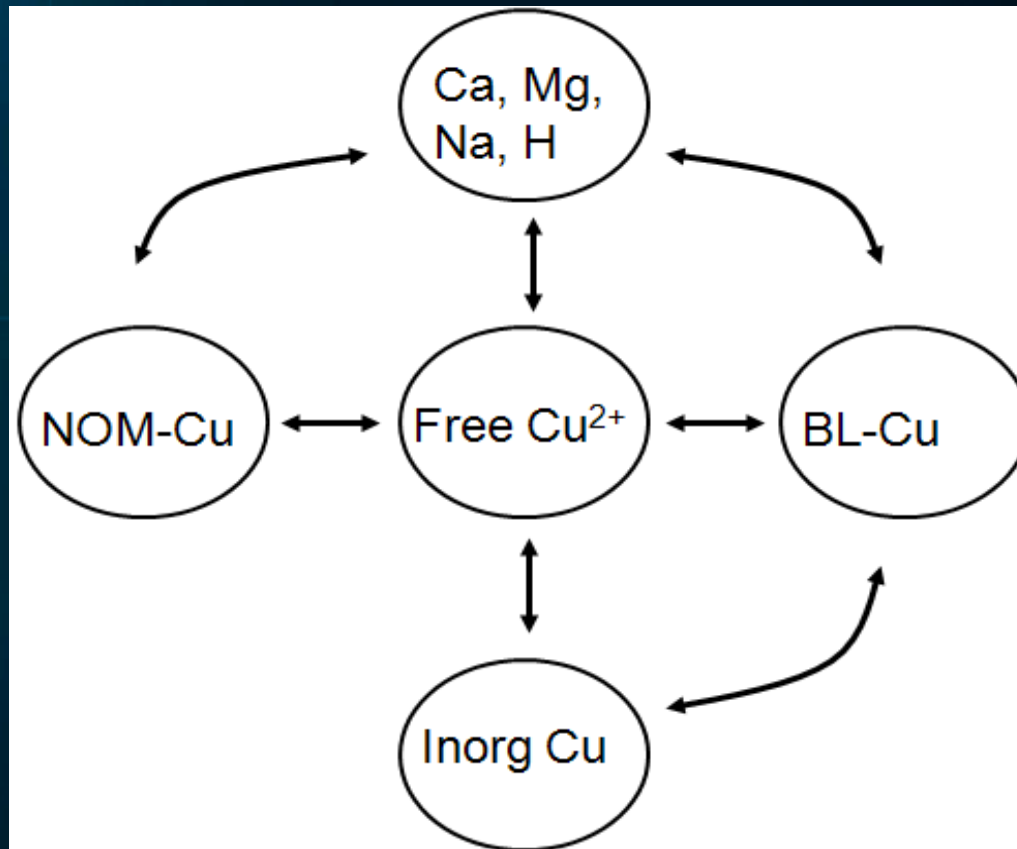


Predicted Copper Accumulation on *S. purpuratus*



Conceptual Model and Data Needs

Toxicity Effects showing bioavailability relationships



Introduction

- Shelter Island Yacht Basin
 - Antifoulant leaching elevates [Cu]
 - Reported gradient
 - Toxicity may be a concern
 - Toxicity controlled by bioavailability
 - Not adequately predicted by TCu or DCu alone



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