Copper Bioavailability and Toxicity to *Mytilus galloprovincialis* in Shelter Island Yacht Basin, San Diego, CA

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INTRODUCTION

Leaching of copper (Cu) from antifouling coatings on boats and vessels is a known source of copper to coastal waters and estuaries. Near marinas and ship berths, antifoulant leaching may elevate [Cu] above background to levels where toxicity may be a concern. Toxicity, however, is driven by the bioavailability of Cu, which is not adequately predicted by total or dissolved [Cu]

Shelter Island Yacht Basin (SIYB) in the San Diego Bay, which harbors approximately 2300 recreational boats, shows consistent elevations in [Cu] and has been the subject of various toxicological studies (Neira et al. 2009, Rivera-Duarte et al. 2005). This study examined the biological effects and chemical activity of Cu in SIYB and whether or not the dissolved [Cu], the form of copper monitored for regulatory compliance, poses a threat to organisms inhabiting this area. The findings of this research are important for making environmental decisions about Cu regulation by predicting potential effects of Cu loading on biological communities.

MATERIALS AND METHODS

Copper and a suite of chemical parameters were measured in filtered and unfiltered water, which was collected 1 m below the surface and 1 m above the bottom of SIYB (Figure 1) in two separate sampling events. The first event occurred March 22, 2011 (15 stations) and represents the wet season. The second event was on July 5, 2011 (16 stations) and represents the dry season.

Two approaches were used to assess toxicity, both of which employed 48 hour embryo-larval development toxicity tests using the mussel *Mytilus galloprovincialis*. In one approach, embryos were exposed to untreated (i.e., unspiked) unfiltered surface and bottom seawater from each of the stations to determine if ambient toxicity was present. A total of 62 ambient samples were tested for mussel embryo toxicity over two seasons. In the second approach, unfiltered surface seawater samples from four of the stations (Stations 1, 4, 10 and 12) were spiked with up to 10 copper concentrations to derive median effective concentrations (EC50 values) for calculating a site-specific criterion for Cu using the US Environmental Protection Agency's Water Effect Ratio (WER) procedure (USEPA 1994). Total and dissolved [Cu] in ambient and spiked samples were measured using in-line preconcentration Flow Injection Analysis with detection by ICP-MS.

The data from this study were compared to the marine Biotic Ligand Model (BLM) for Cu, which is a mathematical model that uses site-specific water chemistry parameters to predict toxicity (HydroQual 2011). Using the BLM, an $EC50_{BLM}$ and estimated chronic limit (ECL_{BLM}) for Cu were predicted for each station, and for the marina as a whole.

Figure 1. Aerial view of Shelter Island Yacht Basin (SIYB), in San Diego Bay, California. Location and number of the stations is presented, the yellow locations are those for the WER. View downloaded from Google Earth.

RESULTS

Total and Dissolved [Cu]

Concentration gradients in surface water show a general trend of total and dissolved [Cu] increasing from the mouth to the head of the basin (Figure 2a-d). There is also a radial gradient of Cu increasing from the main channel towards the inner boat slips (e.g., Stations 3 and 11 in figure 2c). In general, the [Cu] spatial distributions show three areas in SIYB, the mouth of SIYB with concentrations similar to those outside the basin (Stations 1 to 7), an area where [Cu] is at an intermediate concentration (Stations 9 to 12), and an area where there is a gradient of increasing concentrations (Stations 13 to 16).

Figure 2. Spatial distribution of total (orange squares) and dissolved (blue circles) [Cu] (µg L^{-1}), and dissolved organic carbon (mg L^{-1}; black diamonds). Figures a and b are for the wet season sampled on March 22, 2011. Figures c and d are for the dry season sampled on July 5, 2011

Ambient Toxicity Tests

Wet Season: The ambient water toxicity tests for both surface and bottom water in the wet season did not show toxicity. The mean % normal alive (percent of larvae surviving and achieving normal D-shape) was greater than 85% for all stations, and were not significantly lower than the laboratory control.

Dry Season: The ambient toxicity tests for the dry season showed no toxicity in bottom water but statistically lower (based on t-tests, α=0.05) normal development at 5 of the 16 surface water stations. Very low variability within treatments detected statistical differences at values of 92% normal alive. Using a biologically meaningful reduction (e.g. ,80%), only station 16 (74%) was deemed toxic (circled in orange).

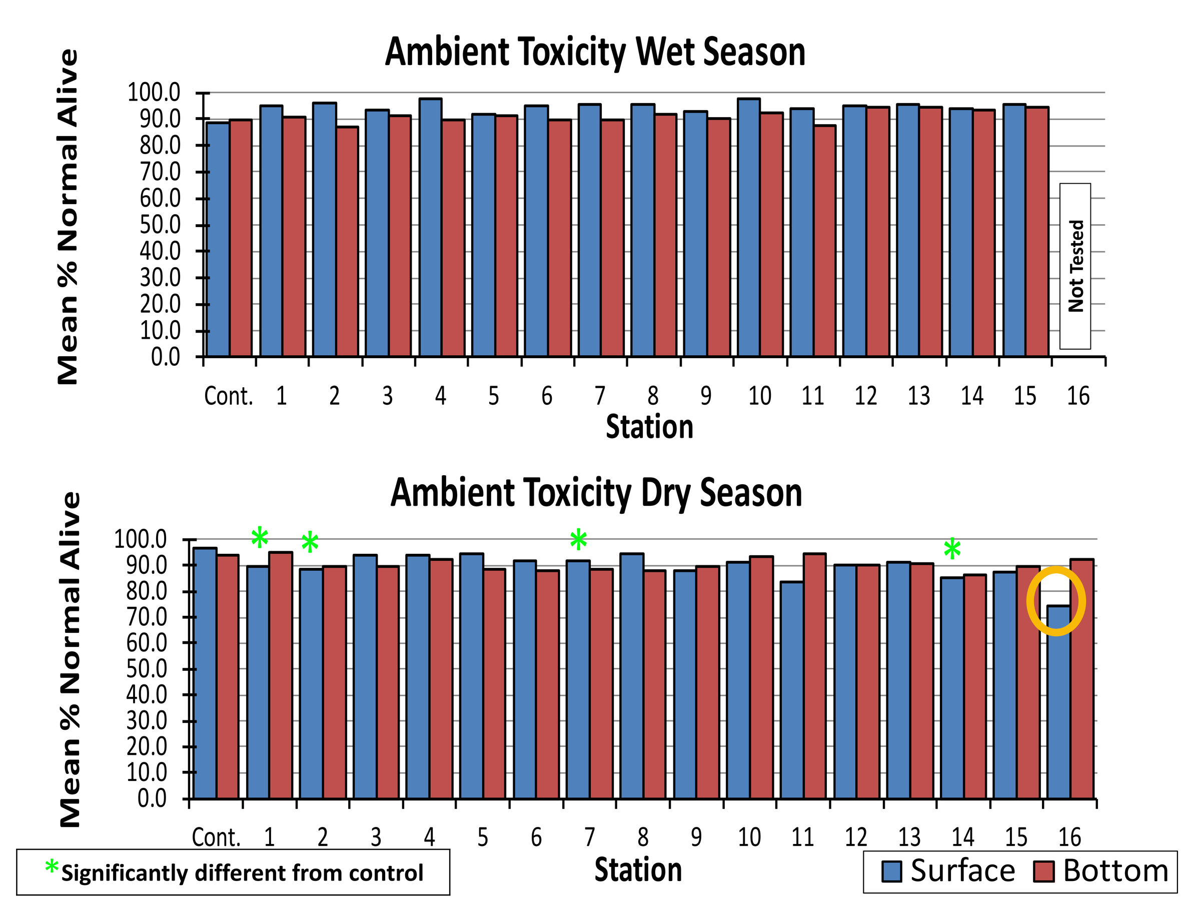

Figure 3 Ambient toxicity observed in SIYB in the wet and dry season sampling events.

EC50 Values and Site-Specific Criteria

The range in EC50 values was from 8.0 to 10.1 [Cu] µg L^{-1} in the wet season, with no spatial gradient. In contrast, during the dry season, the EC50 values ranged from 9.3 to 11.2 µg L^{-1}, with the stations located closer to the mouth having the lowest values. These EC50 values, however, were about twice the measured dissolved concentration of copper at those stations.

A site-specific criterion for SIYB was calculated from the WER results (SSC_{WER}). An estimated chronic limit (ECL_{BLM}) was calculated from the BLM output data for comparison to the SSC_{WER}. The SSC_{WER} was consistent with a spatial and temporal range from 3.2 to 5.0 [Cu] µg L^{-1} (geomean for both events = 4.0 µg L^{-1}). In comparison, ECL_{BLM} were more responsive to spatial and temporal variations, ranging from 4.8 to 11.0 [Cu] µg L^{-1} (Geomean for both events =8.6 [Cu] µg L^{-1}) and are up to two-fold larger than the SSC_{WER}. However, both criteria provide the level of protection intended by regulation, as both are lower than measured EC50 values with the most sensitive marine species- *Mytilus sp.*

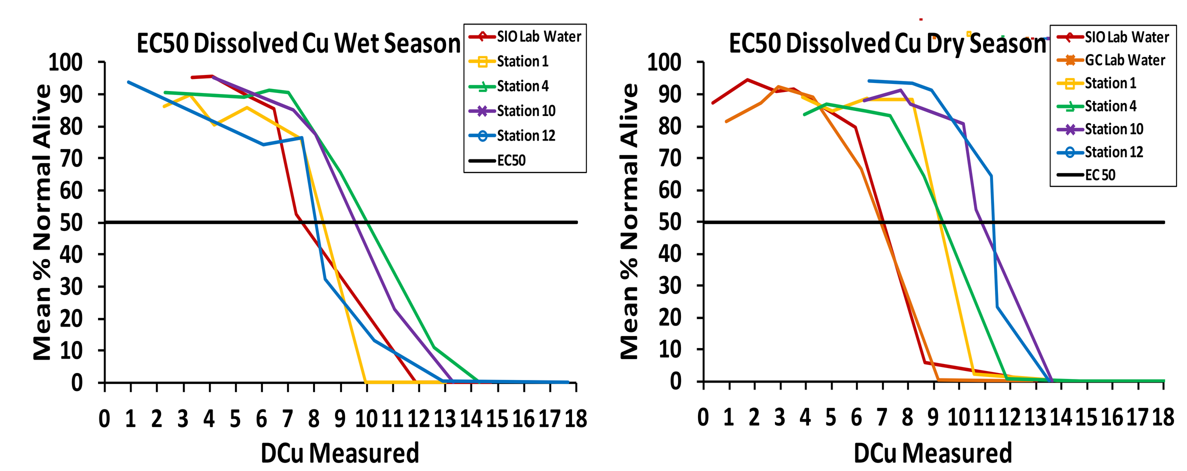

Figure 4. Results for the end point (EC50) measured for the WER under laboratory conditions.

WET SEASON Dissolved Cu						
Station	$EC50_{BLM}$	$EC50_{WER}$	95% LCL WER	95% UCL WER	ECL_{BLM}	SSC_{WER}
SIO (Lab Water)	-	7.9	7.8	8.0	-	-
1	9.4	8.0	7.9	8.1	7.5	3.2
4	8.7	10.1	10.0	10.2	6.9	4.0
10	12.1	9.6	9.4	9.7	9.6	3.8
12	6.1	8.2	8.1	8.3	4.8	3.2
DRY SEASON Dissolved Cu						
SIO (Lab Water)	-	7.0	6.9	7.1	-	-
GC (Lab Water)	-	6.9	6.8	7.0	-	-
1	13.8	9.3	9.3	9.3	11.0	4.1
4	10.3	9.5	9.4	9.6	8.2	4.2
10	9.6	11.2	11.1	11.2	7.6	5.0
12	10.2	11.1	11.1	11.2	8.2	5.0

Table 1 Site-Specific criteria for SIYB derived from the Biotic Ligand Model, and by the USEPA-approved WER approach.

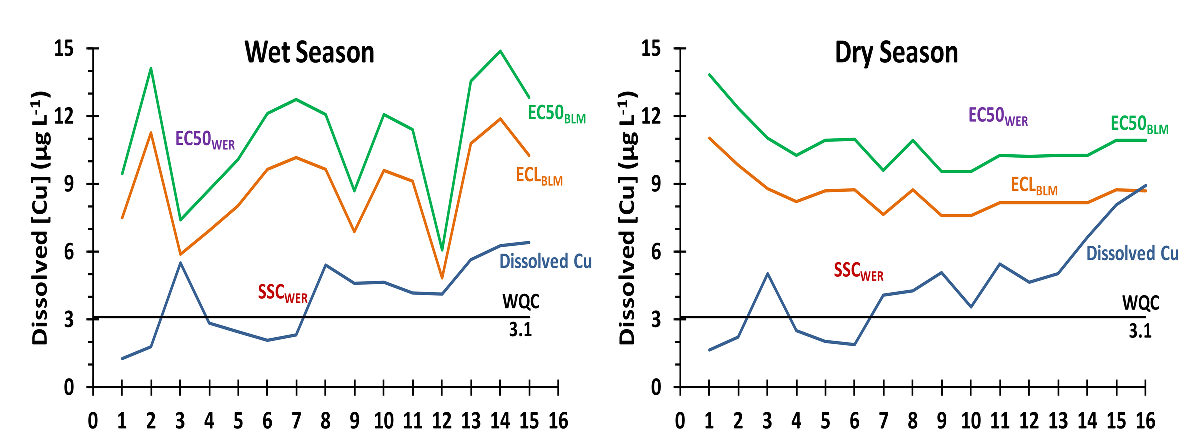

Figure 5. Summary of the different criteria that could be applied to SIYB. These criteria include the 3.1 µg L^{-1} WQC, WER derived and BLM calculated criteria. Dissolved [Cu] (µg L^{-1}) are included for comparison.

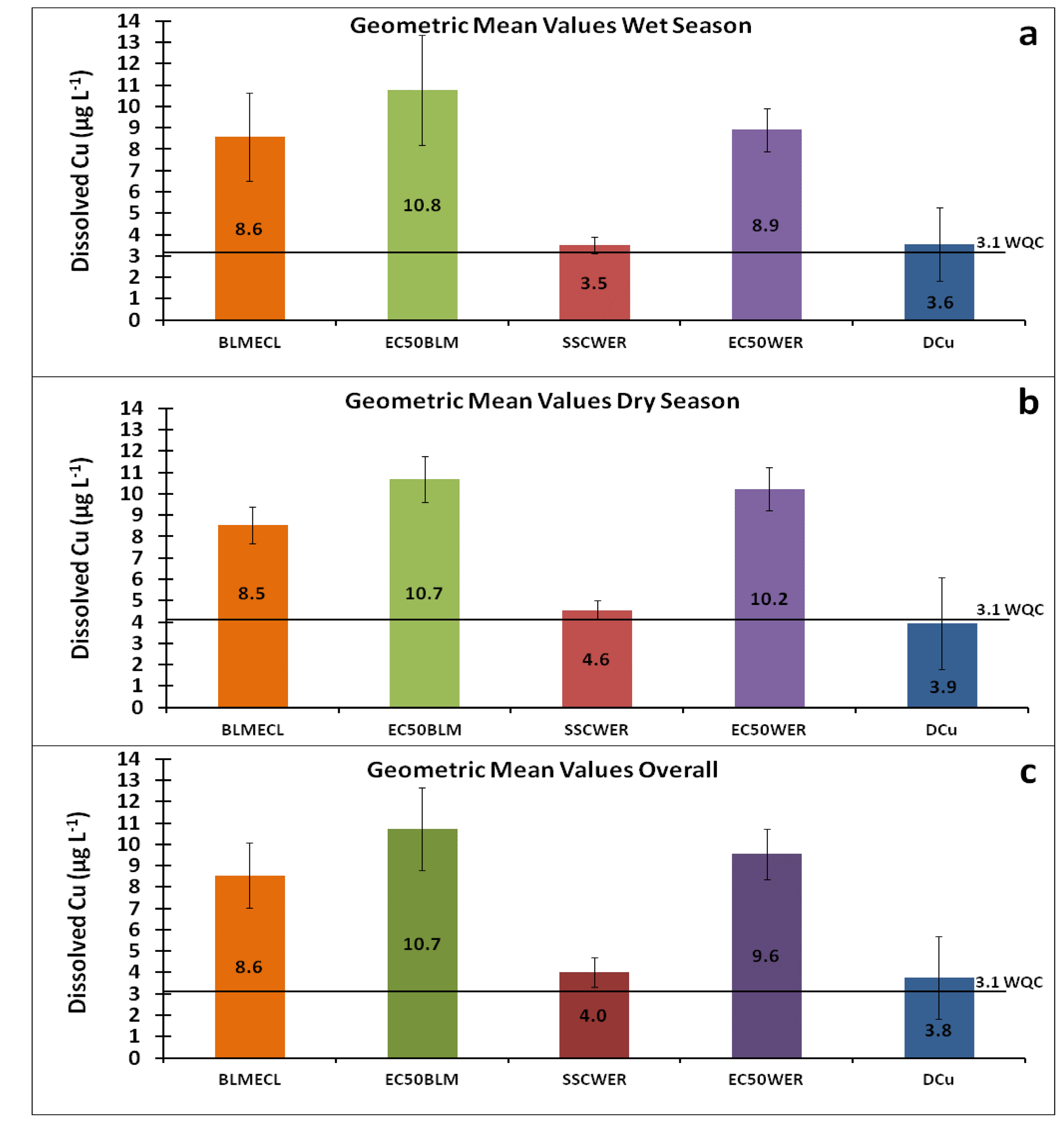

Figure 6. Geometric mean values for the site-specific criteria applied to the dry season (a), wet season (b), and the overall values (c).

CONCLUSIONS

- Two gradients are apparent in surface water total and dissolved [Cu] in SIYB, an increase from the mouth to the head, and an increase from the main channel towards the boats
- The elevated [Cu] at stations 3 and 8 (wet season) and stations 3 and 11 (dry season) appear to be related to proximity and density of boats surrounding the area
- Although [Cu] in SIYB are elevated in comparison to the main body of San Diego Bay, the ambient water is generally not toxic to mussel embryos (1 out of 62 samples somewhat toxic)
- Dissolved [Cu] as high as 8.8 µg L^{-1} were not toxic to mussel embryos
- The BLM estimated chronic limit (ECL) for Cu (mean of 8.6 µg L^{-1} for wet season and 8.5 µg L^{-1} for dry season) is protective of *M. galloprovincialis* based on the ambient toxicity data
- Traditional water effects ration calculation (SSC_{WER}) for Cu is overly conservative based on EPA's intended level of protection. EPA suggested WQC (3.1 µg L^{-1} dissolved Cu) is over conservative as well
- Lack of ambient toxicity and verified protection by BLM suggest that SIYB is not impaired due to copper

REFERENCES

HydroQual 2011. Draft update of aquatic life ambient saltwater quality criteria for copper

Neira, C., Delgadillo-Hinojosa, F., Zirino, A., Mendoza, G., Lenis, L.A., Porrachia, M. and Deheyn, D. 2009. Spatial distribution of copper in relation to recreational boating in a California shallow-water basin. Chemistry and Ecology 25: 417-433

Rivera-Duarte, I., Rosen, G., Lapota, D., Chadwick, D., Kear-Padilla, L. and Zirino, A. 2005. Copper toxicity to larval stages of three marine invertebrates and copper complexation capacity in San Diego Bay, California. Environmental Science and Technology 39: 1542-1546.

Rosen, G., Rivera-Duarte, I., Chadwick, B. D., Ryan, A., Santore, R. C. and Paquin, P. R. 2008. Critical tissue copper residues for marine bivalve (*Mytilus galloprovincialis*) and echinoderm (*Strongylocentrotus purpuratus*) embryonic development: Conceptual, regulatory and environmental implications. Marine Environmental Research 66: 327–336.

U.S. EPA 1994 a. Interim guidance on determination and use of water effect ratios for metals. EPA-823-B-94-001

U.S. EPA 1995. Short-term methods for estimating the chronic toxicity of estuarine organisms: Section 15. EPA 600-R-95-136.

United States Environmental Protection Agency 2000. Water quality standards; establishment of numeric criteria for priority toxic pollutants for the State of California. United States Environmental Protection Agency. Federal Register. Vol. 65, No.97, May 18, 2000. Rules and Regulations

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