Copper & Water Quality

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What is Copper Sulfate?

- The pentahydrate formulation ($CuSO_4\ 5H_2O$), as shown above, is a fungicide, algaecide, germacide and herbicide used to maintain the aesthetic appearance of lakes, reservoirs and ponds.

- $CuSO_4$ treatment as an algaecide addresses only the signs and symptoms of a water body's degraded state, not the causes.

- Free hydrated Cu^{+2} (cupric ion) acts as the toxicant to algae by inhibiting the uptake of divalent micronutrients (e.g., Mn^{+2} and Zn^{+2}) necessary for photosynthesis and growth.

- $CuSO_4$ treatment has the potential to result in dissolved Cu concentrations that exceed water quality criteria, thus posing a potential risk to non-target aquatic species.

- The toxicity of $CuSO_4$ to both algae and non-target species declines rapidly after application, as Cu forms complexes with a host of ligands or settles out of the water column upon adsorption to sediments and particulates.

Dissolved vs. Total Copper

- Total Cu includes that dissolved in water and adsorbed to suspended sediments and particulates (i.e., **particle bound**). As was done in the Eagle's Pointe study, a dissolved Cu analysis is typically performed by removing particulates with a 0.45 μm filter, then analyzing the filtered water sample.

- Total Cu should always be greater than or equal to dissolved Cu, as dissolved Cu is a subset of total Cu (thus , the two "anomalous" findings in the Eagle's Pointe study).

- Dissolved Cu can be "**free**" or "**complexed**" with a number of ligands. The "free" fraction is the ultimate toxicant, whereas most dissolved Cu complexes are inert and non-bioavailable.

- In all water types (saltwater, brackish water and freshwater), the concentration of potential ligands usually exceeds the total dissolved Cu concentration, effectively sequestering Cu and reducing its bioavailability and toxicity (consider the humic acid addition system at SRS).

- Cu toxicity can be grossly overestimated if it is based on total Cu concentration alone. Likewise, total dissolved Cu can result in such an overestimation.

Why is Copper a Problem?

- Cu is toxic to a host of aquatic receptors (e.g., fish, invertebrates and amphibians), with some effects seen at concentrations below those measured pre-treatment at Eagle's Pointe.

- In many aquatic animals, Cu causes toxicity by inhibiting enzymes and disrupting ion flow, resulting in cellular toxicity and changes in pH balance and osmoregulation.

- At environmentally-relevant concentrations, Cu can disrupt sperm and egg production in fish and shellfish, be neurotoxic to fish olfaction, and produce structural and functional changes to gills.

- Cu is a permanent addition to the environment and will bioconcentrate. In other words, the concentration of Cu is often higher in plants and animals than in the water or sediments in which they live.

Why is Copper a Problem?

- Whereas algae is temporarily killed as intended, its decaying matter contributes heavily to dissolved oxygen depletion, fish kills and the accelerated recycling of phosphorus which actually promotes algal blooms.

- The use of $CuSO_4$ decreases the environment's ability to manage the nutrients in fertilizers. As a germicide, it destroys the beneficial bacteria that would naturally break down nutrients and, as an herbicide, kills plant life that would absorb them.

- As of 2010, there were 5 known creeks or rivers in Beaufort Co. impaired for Cu: 1) Huspah Creek at RR trestle, 2) Coosaw River near mouth of Bull River, 3) Port Royal Sound 1.8 miles SW of the tip of Parris Is., 4) tidal creek near confluenc of Coosaw and Bull Rivers near Chisolm Is. and 5) tributary to Sparrow Nest Creek near Dataw Island.

Copper Standards

- Cu standards are of two general types: 1) state-specific values loosely based on U.S. EPA's National Water Quality Criteria and 2) site-specific values derived using the biotic ligand model (BLM).

South Carolina Water Quality Criteria

Saltwater (assume 83% of total Cu is dissolved): 5.8 ppb (acute) and 3.7 ppb (chronic) as total Cu

Freshwater (assume 96% of total Cu is dissolved): 3.8 ppb (acute) and 2.9 ppb (chronic) as total Cu

Standards Derived Using the Biotic Ligand Model

The BLM is a metal bioavailability model that uses information on water chemistry to calculate a site-specific standard. As present, the BLM is only applied to freshwater, although a saltwater version is in development. The BLM is based on the premise that toxicity is related to the amount of metal bound to a biochemical receptor on an organism (e.g., gill membrane on a fish). As such, model inputs, all of which could affect receptor binding, include temperature, pH, dissolved organic carbon, major cations (Ca, Mg, Na, K), major anions (SO_4 and Cl), and alkalinity (the buffering capacity of water against a pH change). Model output includes a criterion maximum concentration (highest 1-hour average without unacceptable toxicity) and a criterion continuous concentration (highest 4-day average without unacceptable toxicity).

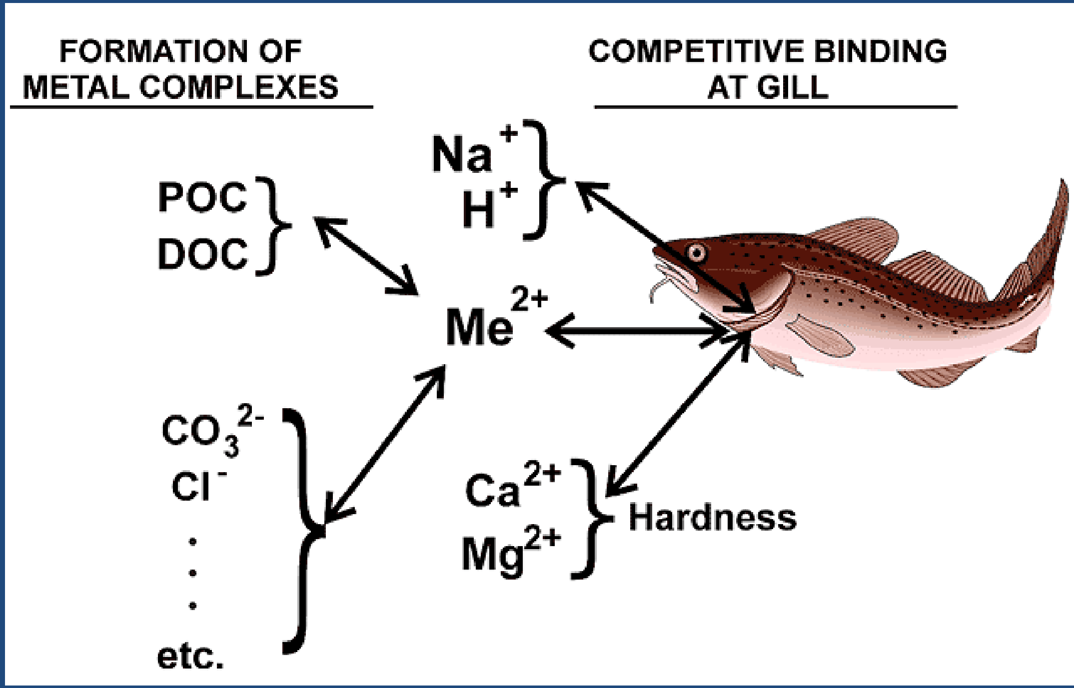
Why can Copper Concentrations Exceed the Standard and Still be OK?

- Quite simply, most regulatory standards are inherently conservative due to application of the precautionary principal. Granted, the BLM is a less conservative means of deriving acceptable concentrations, but is conservative nonetheless.

- Regardless of the means of derivation, regulatory values are not "bright lines“. In other words, they do not represent values between acceptable and unacceptable concentrations.

- Cu concentrations that are toxic to an ecological receptor under controlled laboratory conditions are often non-toxic in the “real world”. The converse may also be true, but with less frequency.

Why Apply the BLM to Eagles Pointe?



Because variations in pH, cation and anion concentrations, alkalinity and the presence of natural organic matter can all have a significant effect on Cu toxicity. The BLM obviates the need for default assumptions that lead to overly conservative regulatory limits. As a result, as in the case of Eagle's Pointe, BLM-derived acceptable concentrations are frequently less stringent (higher) than those derived by other means.

Copper Sampling Report

	Sample Set 1 - 6/29/2010		Sample Set 2 - 7/20/2010		Sample Set 3 - 8/3/2010		Sample Set 4 - 8/17/2010	
	Total Cu	Dissolved Cu	Total Cu	Dissolved Cu	Total Cu	Dissolved Cu	Total Cu	Dissolved Cu
Pre-Treatment	11.5	17.7*	13.4	78.1*	19.3	11.2	11.5	7.6
Post-Treatment	11.9	9.5	27.9	24.1	158.0	65.2	125.0	79.4
24 Hours	38.7	27.1	21.4	14.8	47.7	23.5	31.6	20.9
48 Hours	20.0	16.0	30.8	13.1	184.0	42.1	25.0	15.9
Week	16.2	11.9	32.8	9.9	16.4	11.1	12.4	9.8

All results are reported in micrograms per liter (ug/L)

* These results are anomalous, however, this does not alter the findings.

Biotic Ligand Model Results

	May 5 Results (ug/l)	Nov 5 Results (ug/l)	Jan 6 Results (ug/l)
Criterion Maximum Concentration (CMC)	66.15	36.9	45.6
Criterion Continuous Concentration (CCC)	41.08	22.4	28.32
Acute Toxic Units	0.5744	0.3861	0.195
Dissolved Copper (measured in sample)	38.2	13.9	8.89

Is the Problem Too Much Application ?

- What problem? According to the GEL report, there is no problem. Consider, however, …

- What are we concerned about – toxicity to ecological receptors in treated ponds, the river into which treated ponds discharge or both?

- If the river is our concern, why run the BLM with input parameters from the treated pond?

- When was the last application of $CuSO_4$ relative to BLM data collection? Can we even make a judgment as to the potential impact of $CuSO_4$ on ecological receptors residing in treated ponds?

- Is there any value in comparing dissolved Cu concentrations as measured in June, July and August to criterion maximum and continuous concentrations based on BLM input parameters collected in May, November and January?

- Can one infer anything about the impact on river water quality of pond discharge? Consider that equal concentrations of dissolved Cu are apt to be more toxic in freshwater than saltwater. Also, Cu adsorbed to sediments and particulates in freshwater may be released as soluble Cu when it comes into contact with seawater in estuarine environments. Is the old adage, "the solution to pollution is dilution", applicable here?

Prohibit Pond Discharge for 24 hr After Treatment?

- *A prudent practice, but why 24 hr?*

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