FA165

UF UNIVERSITY of FLORIDA
IFAS Extension

Use of Copper in Marine Aquaculture and Aquarium Systems[1]

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Introduction

Copper has been used effectively for many years to control algae and fish parasites in freshwater and marine systems. Because copper does not discolor the water, it is a preferred treatment for use in display aquaria. Water chemistry and other environmental factors will determine how much copper will be biologically available and for how long.

However, the copper concentrations required for effective treatment may be acutely toxic for some species of finfish and are lethal for most invertebrates. Chronic copper exposure will also adversely affect fish health. Sublethal and toxic levels of copper damage gills and other tissues of fish, and also are known to depress the immune system. Because of all these concerns, it is important to understand how copper works and how copper availability is affected by the environment in which it is used (Cardeilhac and Whitaker 1988).

Calculations and follow up procedures required for the use of copper in marine systems are different from the calculations and procedures you would use for copper in freshwater (Watson and Yanong 2006). Factors including parasite life cycle, susceptibility and non-target species sensitivities will also factor in your determination of whether or not to use copper and, if you do use it, how long to continue the treatment to ensure it is both effective and safe.

This publication will concentrate on the use of "bluestone" or "blue copperas" copper sulfate ($CuSO_4 \cdot 5H_2O$; i.e., copper sulfate pentahydrate), the most commonly used form of copper for aquaculture. However, before you use copper or any other chemical or drug, be sure to review local, state, and federal regulations and guidelines for legalities regarding application and discharge of the treated water.

Basic Copper Chemistry

Copper is a heavy metal that can be found naturally in a number of different forms. The form of copper that is most effective for algae and parasite control is the positively charged copper with a 2+ charge, also known as "Cu^{2+}." This is the form that is found in "bluestone" copper sulfate (more properly known as "copper sulfate pentahydrate" because it is attached to 5 water molecules).

1. This document is FA165, one of a series of the Program in Fisheries and Aquatic Sciences, School of Forest Resources and Conservation, Florida Cooperative Extension Service, Institute of Food and Agricultural Sciences, University of Florida. Original publication date December 2009. Visit the EDIS Web Site at http://edis.ifas.ufl.edu.

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When copper sulfate is dissolved into water, copper sulfate splits into separate copper (Cu^{2+}) and sulfate (SO_4^{2-}) ions (and water). Because this "Cu^{2+}" is the "active ingredient" of "bluestone" copper sulfate, this is the ion that must remain in solution and which must be measured. For susceptible marine parasites, including *Amyloodinium* (Reed and Floyd 1994) and *Cryptocaryon* (Yanong 2009), the target concentration is 0.15–0.20 mg/L Cu^{2+}.

Maintaining target concentration levels of copper can be challenging. Keeping copper concentrations high enough is difficult for many reasons. Water has numerous dissolved compounds (for example, bicarbonate ion (HCO_3^-), which can readily "combine" with copper and remove copper from solution. Carbonates—which are part of dolomite, crushed coral, oyster shell, and other common marine substrates—dissolve in the water and complex (or bind) with copper, affecting the level of copper in solution. Copper can also be taken up by living organisms, including bacteria, algae, and brine shrimp, and it can bind to substrates in the system (including activated carbon) (Cardeilhac and Whitaker 1988).

Still other factors can cause the copper concentration to rise too high. Increases in salinity will decrease the binding (adsorption) of copper to surfaces. In salt water at more neutral pH (e.g., pH of around 7), copper is surrounded by chloride molecules. Decreases in pH will release previously bound copper, and increase levels in solution, thereby increasing the risk of toxicity. Also, if some live foods, such as brine shrimp, are present during copper treatments, they may bioaccumulate enough copper to be toxic to fish that eat them (Cardeilhac and Whitaker 1988). (Additional factors are discussed in "Environmental Factors" below.)

Chelated Copper

Chelating agents are compounds added to copper sulfate in water. These agents help keep copper in solution by forming a ring-structured complex with copper. These complexes vary in their stability, depending upon the agent used. EDTA, one such agent, is very stable in solution. Citrate is also used, but citrate-copper complexes are less stable. However, citrate-copper complexes have more biological activity than EDTA-copper complexes, and are also easier to remove after treatment (Cardeilhac and Whitaker 1988).

In general, larger aquaculture facilities and public aquaria prefer to use copper sulfate rather than chelated copper complexes, because strength and activity of chelated copper complexes are more uncertain, and chelated copper compounds are also more difficult to remove.

Copper Toxicity to Target Organisms

At recommended Cu^{2+} concentrations of 0.15–0.20 mg/L, free copper is toxic to a number of organisms that are pathogens of fish, including the marine parasites *Cryptocaryon irritans* and *Amyloodinium ocellatum*. However, copper is effective primarily against the free-swimming, infective stages of these parasites—the *Cryptocaryon* theronts and the *Amyloodinium* dinospores (Cardeilhac and Whitaker 1988). Therefore, an understanding of the life cycle of these parasites is critical, and prolonged treatments (a minimum of 3–4 weeks for *Cryptocaryon* and 10–14 days for *Amyloodinium*) are generally required (Yanong 2009; Reed and Francis-Floyd 1994).

Copper Toxicity to Non-Targeted Organisms

Animal Considerations

Some species of fish are highly sensitive to copper and will die even at concentrations below therapeutic levels (i.e., less than 0.15 mg/L free copper). Other considerations that will affect survival include acclimation period (exposing fish to slowly increasing concentrations of free copper over the course of several days until the treatment target concentration is reached), as well as age or life stage of the fish. In one study, larvae acclimated to copper exposure more quickly than juvenile and adult fish and had better survival (Sellin et al. 2005). In some fish species, younger fish are more resistant to copper toxicity than older fish; in others, the reverse is true (Howarth and Sprague 1978; Pickering and

Lazorchak 1995; Furata et al. 2008). Copper will damage a number of organs and systems, including the gills, liver, kidney, immune system, and nervous system (Cardeilhac and Whitaker 1988). Gills appear to be the most affected organ during acute toxicity, and will become blunt and thickened and lose ability to regulate body fluid ion concentrations. Copper also suppresses immune system function, and can affect the lateral line of fish. Prolonged copper exposure also may result in reduced growth (Wong et al. 1999). During toxicity, in addition to general signs of distress (e.g., increased respiration), fish may display darkening and behavioral abnormalities: lethargy, incoordination, problems with posture and balance, and, eventually, death (Cardeilhac and Whitaker 1988).

Most invertebrates are highly sensitive to copper and will not survive a copper treatment. If systems with invertebrates are to be treated, the invertebrates should be moved and not returned until Cu^{2+} concentrations are 0.01 mg/L or less, but ideally zero (Cardeilhac and Whitaker 1988). Copper levels should be monitored for some time after treatment, because copper bound to substrate (e.g., coral, shells, decorations) may be released if pH drops or other changes in water quality parameters occur (see Environmental Factors below).

Environmental Factors

A number of factors will determine the toxicity of copper in water: a) the amount of free copper (Cu^{2+}) in the water; b) the sensitivity of the fish or invertebrate species exposed; c) the age of the fish; d) the acclimation time to target concentration; e) the presence of substrates, especially those made of calcium or magnesium carbonate (including dolomite, oysters shell, and coral), that may remove copper from the water by adsorption; f) the presence of dissolved substances that may bind with copper and reduce its activity, including carbonates; g) the presence of "live foods" that may absorb and bioaccumulate (biologically concentrate) copper in their bodies; and h) the tank water pH (Cardeilhac and Whitaker 1988). Because copper levels can vary over time--for instance, they may suddenly increase with a drop in pH--copper concentration should be measured at least twice a day and adjusted accordingly (see section below).

Bacterial Considerations

Copper is also toxic to the nitrifying bacteria in the biofilter. At 0.3 mg/L Cu^{2+}, copper sulfate inhibits ammonia and nitrite oxidation; therefore, increases in ammonia or nitrite levels in the system should be monitored closely during copper treatments. By contrast, bacteria that can cause disease in fish are much more resistant to copper, with some only inhibited or killed at free copper levels as high as 1.25 mg/L (Cardeilhac and Whitaker 1988).

Determining Copper Dose (Concentration)

Copper sulfate ("bluestone" copper; blue copperas; copper sulfate pentahydrate) is 25.5% free copper (Cu^{2+}), the active ingredient used to treat marine systems. Correct copper sulfate dosing is based on the free copper portion of the preparation; in marine systems, the recommended dose of Cu^{2+} for treatment of parasites, including *Cryptocaryon* sp. and *Amyloodinium* sp., is 0.15–0.20 mg/L Cu^{2+}

To determine the grams (g) of copper sulfate estimated to be necessary to treat a given volume of water at a given desired concentration of free copper, use one of the formulas below:

If volume is known in **gallons:** Volume in gallons x 0.0038 (conversion factor) x (concentration of free copper desired in mg/L) x 3.92 = quantity required in grams

EXAMPLE 1 (gallons).

100-gallon tank; desired concentration of free copper: 0.15 mg/L

Formula (gallons): Volume in gallons x 0.0038 (conversion factor) x (concentration of free copper desired in mg/L) x 3.92 = quantity required in grams

100 x 0.0038 x 0.15 mg/L x 3.92 = 0.223 grams of copper sulfate pentahydrate needed

If volume is known in **liters:** Volume in liters x (concentration of free copper desired in mg/L) x 0.00392 = quantity required in grams

EXAMPLE 2 (liters).

1000-liter system; desired concentration of free copper: 0.20 mg/L

Formula (liters): Volume in liters x (concentration of free copper desired in mg/L) x 0.00392 = quantity required in grams

1000 x 0.20 mg/L x 0.00392 = 0.784 grams of copper sulfate pentahydrate needed

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If using over-the-counter copper products, follow the manufacturer's directions.

Reaching and Maintaining Desired Concentrations

When treating a tank of marine fish with copper, any materials or filtration components (e.g., activated carbon) that may bind copper should be removed; if necessary, organic loading and detritus should be removed. Baseline water quality parameters that should be measured prior to treatment include ammonia, nitrite, pH, temperature, alkalinity, and salinity. The recommended dose range of 0.15–0.20 mg/L free copper (Cu^{2+}) should be reached gradually, over 2–3 days. This approach allows fish time to increase internal substances and physiological mechanisms that protect their bodies against toxicity, including the production of copper-binding proteins, such as metallothioneins (De Boeck et al. 2003).

Because water quality, substrates, and other factors determine measured levels of free copper, achieving any specific dose in a system can be challenging. After calculating the amount of copper needed (and always have your calculations checked by one or two others!), add half of the amount to the system. This can best be done by first mixing the copper sulfate with distilled water (as long as the volume of distilled water doesn't drastically change the salinity of the system) and distributing half of the solution proportionately throughout each tank and the sump, avoiding the formation of "hot spots."

Alternatively, the copper solution can be poured gradually into the sump; however, this acute, high-dose exposure may damage the biofilter by killing beneficial bacteria. After water in the system has cycled long enough that the copper should be evenly distributed, measure the free copper levels. Add more copper, allow time to mix, and re-measure. Do this until the desired concentration is reached.

Often, due to binding (adsorption) of copper to components of the system, more copper than the amount calculated initially will be needed to reach the appropriate concentration. Copper measurements should be taken twice a day, with more copper added if necessary. As discussed previously, treatment may last 3–4 weeks or more, depending upon the target organism and specific situation. Consult with a fish health specialist to determine duration of treatment and effectiveness.

Removing Copper from the System

High quality, activated carbon effectively removes dissolved free copper from systems. One recommendation is to place a separate filtration unit containing fresh, activated charcoal at the rate of 170 grams per 57 liters of water (about 0.375 lbs per 15 gallons) on a system to be purged of copper (Cardeilhac and Whitaker 1988). Once all the water is believed to have cycled through the carbon, test for free copper concentration. If chelated copper has been used, water changes will be necessary. Dolomite may also be used, if it is removed afterward (Cardeilhac and Whitaker 1988). If tests continue to show a high free copper concentration, a complete water change may still be required to remove copper from the water. Copper levels should be monitored throughout this process and for several weeks afterward, in case copper that was previously bound to substrate or complexed in solution, is released as free copper.

Summary

Before treating any system with copper, check local, state and federal regulations to ensure legal use.

Copper at a dosage rate of 0.15–0.20 mg/L Cu^{2+} is effective for control of important fish parasites, including *Amyloodinium* and *Cryptocaryon*, many species of algae, unwanted invertebrates, and fish parasites.

Copper sulfate (copper sulfate pentahydrate) is the most commonly used form of copper in marine aquarium and marine aquaculture systems. Because saltwater has greater ion content than freshwater, copper chemistry in marine systems is more complicated than in freshwater systems. In addition, many other factors affect the final concentration of free copper in water.

Copper can be toxic to some sensitive fish species and is highly toxic to many invertebrate species. Even for more tolerant species, chronic copper use can damage gills, kidneys, spleens, and other organs and systems. Copper will depress the immune system. Copper can also damage the beneficial bacteria in the biofilter.

Consult a fish health specialist during any disease outbreak or other situation for which you may consider using copper. If unsure about the effect on a given species, test on one or a few individuals before treating an entire group of fish. Invertebrates should be removed prior to treatment with copper.

Dosage calculation for use of copper in marine systems is different from that developed for use in freshwater systems, and is based on measured concentration of free copper ion (Cu^{2+}). By contrast, in freshwater systems, measured alkalinity is normally used to calculate dosage rate (Watson and Yanong 2006). Copper sulfate pentahydrate (bluestone copper) is composed of 25.5% of the active ingredient (Cu^{2+}) used to treat marine systems.

When dosing a system, therapeutic levels (0.15–0.20 mg/L) should be reached gradually over 2–3 days to allow fish to acclimate. Copper levels should be measured at least twice a day.

Activated carbon and water changes can be used to remove copper, once treatment is completed, but ideally, levels should be checked regularly for several weeks afterward, in case of copper leaching.

References and Suggested Reading

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Table 1.

Compound	Concentration	Duration	Comments
Copper sulfate (copper sulfate pentahydrate) ($CuSO_4 \cdot 5H_20$)	0.15–0.20 mg/L Cu^{2+}	3–6 weeks	— gradually increase concentration over 2–3 days until target dose — measure free copper (Cu^{2+}) concentration twice a day during treatment period — immunosuppressive
Hyposalinity (for sensitive strains of *Cryptocaryon*)	15 g/L (ppt) sea salt	21–30 days	— reduce salinity gradually by 5 to 10 g/L per day until 15 g/L obtained
Chloroquine	10 mg/L	2–3 weeks	— additional time may be required — fairly stable in solution
Formalin and hyposalinity combination	25 mg/L formalin and 16–18 g/L (ppt) sea salt	4 weeks; dose with formalin every other day, water changes as needed; keep hyposaline for duration	— formalin chemically removes oxygen from system

Table 2.

Method	**Concentration**	**Duration**	**Life stage killed**
Benzalkonium chloride	100 mg/L	1 hr	tomont, theront
Chlorine	2.4 mg/L	1 hr	theront
Chlorine	60 mg/L	24 hr	tomont, theront
Drying/dessication	-----	24 hr	tomont, theront
Heat	40°C	1 hr	tomont, theront
Reference: Hirazawa et al. 2003			