Copper Sulfate Toxicity in Aquatic Ecosystems

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Copper Sulfate (or $CuSO_4$) is a widely applied pesticide used to destroy surface algae in freshwater. When a pond or lake has an algal bloom, chemical applicators use $CuSO_4$ to bind with proteins on the surface of the algae cells. This binding action limits cell growth and eventually kills the algal cells. Advocates for copper sulfate argue that this chemical will quickly rid the water of algae so that other aquatic organisms can reestablish lost habitat. The problem is that the use of copper sulfate comes with a severe biological cost. Simply stated, copper sulfate not only kills algae it eliminates "non-target" species:

> *The U.S. EPA considers copper to be practically nontoxic to bees and moderately toxic to birds. Studies with several aquatic species have found copper to be highly to very highly toxic to fish and aquatic life. Trout, Koi and juvenile fish of several species are known to be particularly sensitive to copper. Fish kills have been reported after copper sulfate applications for algae control in ponds and lakes. Oxygen depletion and increased debris have been cited as the cause of most fish deaths. This is sometimes due to the sudden death and decay of algae and plants after an application. Even small concentrations of copper can be harmful to fish and water organisms.* [1]

Copper is well used in a variety of applications in industry and of course in currency. Trace amounts of copper are needed in many plants and animals. The problem is that when the levels of copper exceed the trace chemical needs of aquatic organisms, copper becomes toxic.

Consider when we take a daily vitamin for human health. Many vitamins for women come with iron, since iron is a necessary component of blood. Younger women in particular need additional iron supplementation since each month they lose blood through menstruation. Since men lose iron by occasional bleeding, our iron needs are minimal. If a man takes a woman's vitamin *plus iron* they can accumulate dangerous levels of iron, and suffer from *hemochromatosis* a severe health condition that damages internal organs due to excess accumulated iron in the blood. This condition in humans is analogous to excess copper usage in many aquatic plants and animals.. The more exposure, the greater chance the chemical will *bio-amplify* cellular membranes increasing the chances for toxicity

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[1] **National Pesticide Information Center of Oregon State University**
http://npic.orst.edu/factsheets/cuso4gen.html

and thereby decreasing immunity with future diseases.

COPPER SULFATE DOES NOT LEAVE THE WATER:

Copper lingers in the environment. If you use copper sulfate to kill algae one year it settles in the sediments with the dead algae. Using copper sulfate the next year adds more copper to the sediments, and the net result is more accumulated copper that will have a negative impact on new generations of plants and animals. Copper does not dissolve in the water, it settles on the bottom, and re-circulates during spring or fall turnover events when water temperatures drop. Note the warning from Cornell University:

> Copper sulfate is very toxic to fish. Its toxicity to fish varies with the species and the physical and chemical characteristics of the water. Even at recommended rates of application, this material may be poisonous to trout and other fish, especially in soft or acid waters. Its toxicity to fish generally decreases as water hardness increases. Fish eggs are more resistant than young fish fry to the toxic effects of copper sulfate. Very small amounts of this material can have damaging effects on fish. Permits are being required in some situations for application of copper sulfate to water bodies. Further field studies have been required by the EPA. Direct application of copper sulfate to water may cause a significant decrease in populations of aquatic invertebrates, plants and fish. Copper sulfate is toxic to aquatic invertebrates, such as crab, shrimp and oysters. Bees are endangered by strong, water-based copper compounds, such as a Bordeaux mixture of copper sulfate, lime and water. Copper sulfate and similar fungicides have been poisonous to sheep and chickens on farms at normal application rates. Most animal life in soil, including large earthworms, have been eliminated by the extensive use of copper-containing fungicides in orchards. Frogs died after being given intravenous doses of 25 mg/kg of copper sulfate. The lethal concentration fifty, or LC50, is that concentration of a chemical in air or water that kills half of the experimental animals exposed to it for a set time period. The 96-hour LC50 of copper sulfate to pond snails is 0.39 mg/l, at 20 degrees C. Higher concentrations of the material caused some behavioral changes, such as secretion of mucous, and discharge of eggs and embryos. [2]

COPPER SULFATE AND INVERTEBRATES:

In Wisconsin, state regulators are particularly concerned with the general high levels of toxicity found in invertebrates (water fleas, crustaceans, mollusks, mayflies, snails, and crayfish).[3] Part of the general concern is the how excess copper moves through the food chain. For example, target algae absorb the copper sulfate and become the food for small zooplankton. Larger zooplankton feed on the copper rich small zooplankton. Fish consume the larger zooplankton and the copper levels also

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[2] Cornell University
http://pmep.cce.cornell.edu/profiles/extoxnet/carbaryl-dicrotophos/copper-sulfate-ext.html

[3] Wisconsin Department of Natural Resources
http://dnr.wi.gov/lakes/plants/factsheets/CopperFactsheet.pdf

accumulate reaching toxic proportions, contributing to fish-kills in two ways. First, copper sulfate applications contribute to the demise and subsequent decomposition of algal populations, thereby lowering dissolved oxygen. The second way occurs when fish accumulate excess copper in their muscle tissue, gills, and the liver.[4] It's no wonder that many states are heavily restricting the use of copper sulfate to treat blooms of algae.

GENERAL TOXICITY IN BIRDS:

Birds are often called *Apex* predators in lakes, ponds and coastal bays which means these animals are at the top of the food chain. This means they will consume the higher aquatic organisms like fish. Since fish have higher accumulated levels of $CuSO_4$ they are at risk for the *bioaccumulation* of the toxin.[5]

TOXICITY IN PROTECTED WILDLIFE SUCH AS FALCONS, BALD EAGLES, PERGRINE FALCOMS, TURTLES & FROGS:

> When pesticides enter aquatic systems, the environmental costs can be high. Unintentional pesticide-related fish kills occur throughout the United States. Some of these kills have been large, involving thousands of fishes, as well as frogs, turtles, mussels, water birds, and other wildlife. Fish and other wildlife species, including rare and endangered ones like the peregrine falcon, bald eagle, and osprey, have been victims of pesticide poisoning. Pesticide use is one of many factors contributing to the decline of fish and other aquatic species.[6]

TOXICITY IN DOMESTIC ANIMALS:

Family pets such as dogs and cats exposed to $CuSO_4$ after an algal bloom are likely to suffer skin damage if they enter the water or parish if they inadvertently drink the water for two reasons. The first reason is that algae, such as cyanobacteria, emit toxics that damage vital organs such as the liver, lungs, the kidneys and the brain. Secondly, algae treated with in higher $CuSO_4$ doses increase the chances for the animal poisoning. The same deleterious effects have been shown with sheep, cattle and other farms animals' drinking water from agricultural chance for the animal poisoning. The same deleterious effects have been shown with sheep, cattle and other farms animals' drinking water from agricultural ponds.

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[4] **Wisconsin Department of Natural Resources**
http://dnr.wi.gov/lakes/plants/factsheets/CopperFactsheet.pdf

[5] **Oregon State University**
http://npic.orst.edu/factsheets/cuso4gen.html#wildlife

[6] **Virginia Tech University**
https://pubs.ext.vt.edu/420/420-013/420-013.html

RESEARCH STUDIES ON $CuSO_4$ LONG-TERM EXPOSURE HUMAN IS LACKING:

> Copper is an essential element and it is required to support proper health. The human body adjusts its internal environment to maintain copper equilibrium. Copper sulfate is absorbed into the body if eaten or inhaled. It then rapidly enters the bloodstream. Once inside, copper moves throughout the body. It then binds to proteins and enters different organs. Excess copper is excreted and not often stored in the body. Copper can be collected in the liver but it can also be found in stomach secretions, bone, brain, hair, heart, intestine, kidneys, muscle, nails, skin, and spleen. Copper is mainly excreted in the feces. Small amounts can also be eliminated in hair and nails. In one study, researchers found it takes 13 to 33 days for half of a large copper dose to be eliminated from the body. Whether copper sulfate causes cancer in animals is uncertain. The U.S. Environmental Protection Agency (U.S. EPA) has not published a cancer rating for copper sulfate. This is due to a lack of evidence linking copper or copper salts to cancer development in animals that can normally regulate copper in their bodies. One study looked at long-term work-related exposures to copper sulfate. They found an increased risk of kidney cancer. Another study found that decreasing copper can inhibit cancer growth. Animal studies have provided conflicting results.[7]

With few studies on long-term effects on humans, it is no wonder that the use of $CuSO_4$ will continue to be the main algaecide used in freshwater management. Trained and dedicated chemical applicators will likely constitute the population with the greatest risk to long-term health consequences. Homeowners living near or on lakes and ponds could also suffer adverse long-term health consequences. Public health researchers and state environmental regulators should consider long-term exposure on at-risk populations for the well being of public safety. It would make sense for epidemiologists to consider spending more time studying the health consequences of groups of people at greater risk for organ damage, disease, and cancer at a result of exposure to copper sulfate.

ALTERNATIVES TO COPPER SULFATE:

There are alternatives to using copper sulfate for the elimination of unwanted algae. New compounds using hydrogen peroxide are showing promise in reducing algal populations and these compounds break down into the non-toxic elements of hydrogen and oxygen. WEEDOO[INC] has introduced a skimming attachment to the front end harvesting assembly. The mesh screen collects aggregated algal cells and gathers surface algae for disposal on land. This process not only eliminates the excess surface algae, but also reduces the nutrient levels of nitrogen and phosphorus stored within the algal cells.[8]

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[7] **National Pesticide Information Information Center**
http://npic.orst.edu/factsheets/cuso4gen.html

[8] **WEEDOO[INC]** http://www.weedooboats.com/

WEEDOO^{INC} Conveyor System and Skimmer for Surface Algae


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