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Resistance & Susceptibility of Algae to

CUPRICIDE®

Sensitivity of Algae to Copper Algicides

The genera of algae listed in Table 1 are commonly found in irrigation waters and dams in Australia.

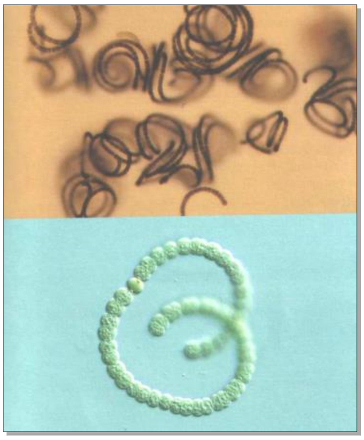
Free floating algae such as Anabaena and Oscillatoria are controlled using 0.2 to 0.5 ppm copper, depending on severity of growth. Filamentous and mat-forming algae such as Spirogyra and Coelastrum are controlled using 0.2 to 0.5 ppm copper.

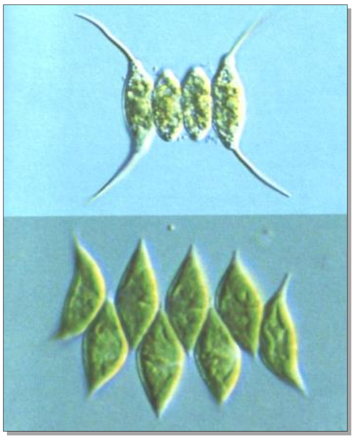
More resistant non-motile green algae such as Cosmarium, Scenedesmus and Kirchnieriella are controlled at the higher concentration of 0.5 – 1.0 ppm copper.

For optimum results, CUPRICIDE® should be applied at the first signs of an algal bloom. Apply CUPRICIDE® early in the day when conditions are calm. Water temperature should be greater than 15^0 C.

***Table 1.* Copper Concentrations Required for the Control of Susceptible (S) and Resistant (R) Algae.**

Organism	Susceptible (0.2-0.5 ppm Cu)		Resistant (0.5-1.0 ppm Cu)	
Cyanophyceae (Blue-green)	Anabaena Aphanizomenon Cylindrospermum Gloeotrichia Gomphosphaeria	Microcystis Oscillatoria Plectonema Polycystis	Calothrix Nostoc Phormidium Symploca	
Chlorophyceae (Green)	Botryococcus Closterium Coelastrum Drapamaldia Enteromorpha Gloecystis	Hydrodictyon Microspora Spirogyra Tribonema Ulothrix Zygnema	Ankistrodesmus Chara Chlorella Cladophora Crucigenia Desmidium Golenkinia	Nitella Oocystis Palmella Pithophora Scenedesmus Staurastrum Tetraedron
Diatomaceae (Diatoms)	Asterionella Fragilaria Gomphonema Melosira Navicula	Nitzchia Stephanodiscus Synedra Tabellaria	Achnanthes Cymbella Neidium	
Protozoa (Flagellates)	Ceratium Cryptomonas Dinobryon Euglena Glenodinium	Mallomonas Synura Uroglena Volvox	Chlamydomonas Eudorina Hawmatococcus Pandorina Peridinium	





Far Left: Anabaena is the most common toxic bloom-forming blue-green algae throughout Australia.
(Pictured Top x 100, Bottom x 450).

Left: Scenedesmus is common in standing water, ponds, lakes and also on damp soil .
(Pictured Top x 1500, Bottom x 2000).

Compatibility of Cupricide® with Herbicides

CUPRICIDE® has been tested for physical and chemical compatibility with selected herbicides commonly used.

Tank Mixes were prepared in proportions recommended for 100 Litres of spray solution. These solutions are based on the highest concentrations of herbicides recommended by the manufacturer and can be used for aerial spray application at the rate of 10 Litres per Hectare.

Typically, 20 Litres of CUPRICIDE® is added to 100 Litres total tank mix and this solution will be sufficient to treat 10 Hectares when the water depth is 5 – 10 cm. More dilute solutions in water can be prepared by following the instructions on the label.

CUPRICIDE® was found to be compatible with Molinate, Londax®, Saturn® and Taipan®. CUPRICIDE® is **not** compatible with the insecticide Chlorpyrifos. Further details of the Tank Mix proportions are shown in Table 2.

Table 2. **Compatibility Tests with CUPRICIDE® and Selected Herbicide/Insecticides.**

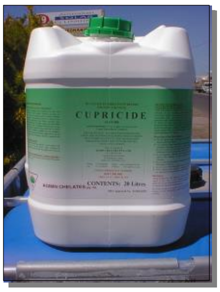
Herbicide	Group	Trade Names	Tank Mix* 100 Litres	pH	Test Results
Molinate 960g/L	E	Ordram EC Molinate 960	37L Herbicide 20L CUPRICIDE®	8.7	Compatible
Thiobencarb 800g/L	H	Saturn EC	37L Herbicide 20L CUPRICIDE®	8.7	Compatible
Clomazone 480g/L	F	Magister	6L Herbicide 20L CUPRICIDE®	8.6	Compatible
Benzofenap 300g/Kg	F	Taipan	20Kg Herbicide 20L CUPRICIDE®	8.6	Compatible
Bensulfuron Methyl 600g/Kg	B	Londax DF	1Kg Herbicide 20L CUPRICIDE®	8.6	Compatible
MCPA 250g/L	I	MCPA 250	25L Herbicide 20L CUPRICIDE®	9.1	Compatible
Fibronil 500g/L	1	Cosmos	0.25L Insecticide 20L CUPRICIDE®	8.6	Compatible
Prodione	B	Rovral	0.1L Herbicide 20L CUPRICIDE®	8.6	Compatible
Chlorpyrifos 500g/L	3	Lorsban Chlorfos Iban	1.5L Insecticide 20L CUPRICIDE®	8.4	Incompatible

**Tank Mix is designed for Aerial Spray at 10L per Hectare*

Right: 20Lt Drum of CUPRICIDE®.

Far Right: 200Lt Drum of CUPRICIDE®.

CUPRICIDE® is also available in other sizes of 1Lt, 5Lt & 1000Lt



Cupricide® – Environmental Chemistry and Fate

Environmental Transport and Transformation

Copper compounds such as CUPRICIDE® are intentionally applied to water to kill algae. Several processes influence the fate of copper in the aqueous environment. These include complex formation, sorption to hydrous metal oxides, clays and organic materials, and bioaccumulation.

Information on the physicochemical forms of copper (speciation) is more informative than total copper concentrations. Much of the copper discharged to water is in particulate form and tends to settle out, precipitate out or be adsorbed by organic matter, hydrous iron, manganese oxides and clay in the sediment or water column.

In the aquatic environment the concentration of copper and its bioavailability depend on factors such as water hardness and alkalinity, ionic strength, pH and redox potential, complexing ligands, suspended particulate matter and carbon, and the interaction between sediments and water.

Most copper deposited in soil is strongly adsorbed and remains in the upper few centimetres of soil. Copper adsorbs to organic matter, carbonate minerals, clay minerals, hydrous iron and manganese oxides. The greatest amount of leaching occurs from sandy acidic soils. In the terrestrial environment a number of important factors influence the fate of copper in soil. These include the nature of the soil itself, pH, presence of oxides, redox potential, charged surfaces, organic matter and cation exchange.

Bioaccumulation of copper form the environment occurs if the copper is biologically available. Accumulation factors vary greatly between different organisms, but tend to be higher at lower exposure concentrations. Accumulation may lead to exceptionally high body burdens in certain animals (such as bivalves) and terrestrial plants (such as those growing on contaminated soils). However, many organisms are capable of regulating their body copper concentration.

Environmental Levels of Copper

Copper levels in seawater of 0.15 µg/litre and in fresh water of 1-20 µg/litre are found in uncontaminated areas. Sediment is an important sink and reservoir for copper. Background levels of copper in natural freshwater sediments range from 16 to 5000 mg/kg (dry weight). Copper levels in marine sediments range from 2 to 740 mg/kg (dry weight). In anoxic sediments copper is bound strongly by sulphide and therefore not bioavailable.

Median copper concentrations in uncontaminated soil were reported to be 30 mg/kg (range 2 – 250 mg/kg). Copper is accumulated by plants, invertebrates and fish. Higher concentrations of copper have been reported in organisms from copper-contaminated sites than in those from non-contaminated sites.

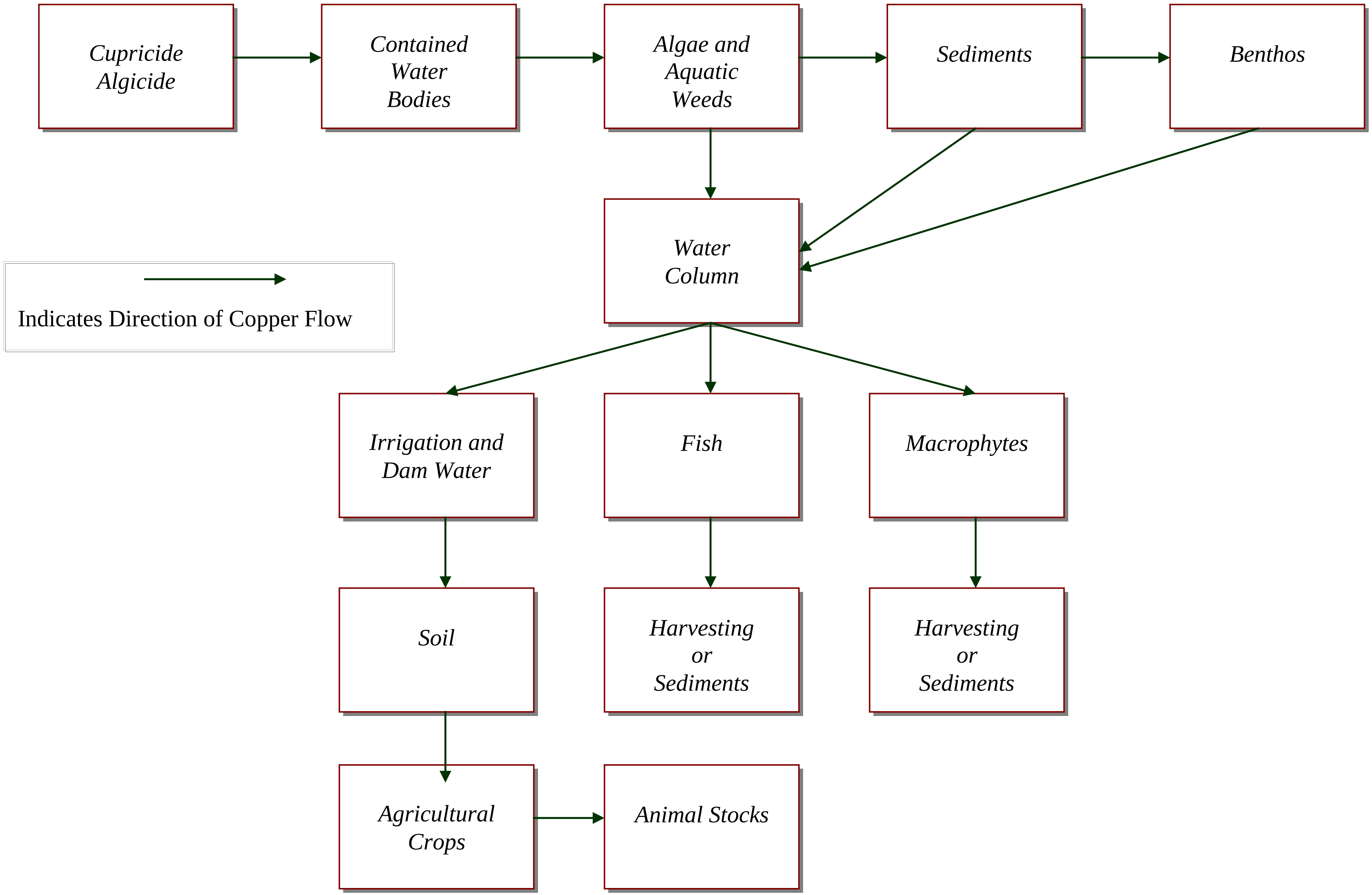
Effects of Copper on Humans

Copper is an essential element and adverse health effects are related to deficiency as well as excess. Copper deficiency is associated with anaemia, neutropenia and bone abnormalities but clinically evident deficiency is relatively infrequent in humans. Balance data may be used to anticipate clinical effects, whereas serum copper and ceruloplasmin levels are useful measures of moderate to severe deficiency but less sensitive measures of marginal deficiency.

For healthy, non-occupationally-exposed humans the major route of exposure to copper is oral. The mean daily dietary intake of copper in adults ranges between 0.9 and 2.2 mg. A majority of studies have found intakes to be at the lower end of that range.

The variation reflects different dietary habits as well as different agricultural and food processing practices used worldwide. In general, total daily oral intakes of copper (food plus drinking water) are between 1 and 2 mg/day, although they may occasionally exceed 5 mg/day.

Biogeochemical Cycle of Copper from Cupricide® Algicide



Effects of Copper on Biota

The adverse effects of copper must be balanced against its essentially. Copper is an essential element for all biota, and care must be taken to ensure the copper nutritional needs of organisms are met. At least 12 major proteins require copper as an integral part of their structure.

It is essential for the utilization of iron in the formation of haemoglobin, and most crustaceans and molluscs possess the copper-containing haemocyanin as their main oxygen-carrying blood protein. In plants copper is a component of several enzymes involved in carbohydrate, nitrogen and cell wall metabolism.

A critical factor in assessing the hazard of copper is its bioavailability. Adsorption of copper to particles and complexation by organic matter can greatly limit the degree to which copper will be accumulated and elicit effects. Other cations and pH can also significantly affect bioavailability.

In natural phytoplankton communities, chlorophyll and nitrogen fixation were significantly reduced at copper concentrations of 20 µg/litre and carbon fixation was significantly reduced at 10 µg/litre. ED_{50}s (72 hrs) for algae, based on growth inhibition range from 47 to 120 µg Cu/litre.

For freshwater invertebrates, 48 hrs LC_{50}s range from 5 µg Cu/litre for a daphnid species to 5300 µg Cu/litre for an ostracod. For marine invertebrates 96 hrs LC_{50}s range from 29 µg Cu/litre for a bay scallop to 9400 µg Cu/litre for the fiddler crab. The acute toxicity of copper of freshwater and marine fish is highly variable. For freshwater fish 96 hrs LC_{50}s range from 3 µg Cu/litre (Arctic grayling) to 7340 µg Cu/litre (bluegill). For marine fish 96 hrs LC_{50}s range from 60 µg Cu/litre for Chinook salmon to 1400 µg Cu/litre for grey mullet.

Tolerance to copper has been demonstrated in the environment for phytoplankton, aquatic and terrestrial invertebrates, fish and terrestrial plants. Tolerance mechanisms which have been proposed in plants include binding of metal to cell wall material, presence of metal-tolerant enzymes, complex formation with organic acids with subsequent removal to the vacuole, and binding to specialized thiol-rich proteins or phytochelatins.

Environmental Effects

Protection of aquatic life in water with high bioavailability will require limiting total dissolved copper to some concentration less than 10 µg/litre; however, the appropriate concentration limit will depend on the biota and exposure conditions at sites of concern and should be set based on further evaluation of all relevant data.

At many sites, physicochemical factors limiting bioavailability will warrant higher copper limits. Regulatory criteria should take into account the speciation of copper if dischargers can demonstrate that the bioavailability of copper in the receiving water can be measured reliably.

Because copper is an essential element, procedures to prevent toxic levels of copper should not incorporate safety factors that result in recommended concentrations being below natural levels.

Cupricide® Safety Directions and Toxicological Data

CUPRICIDE® has been registered by the NRA for use as an algicide in lakes, potable water reservoirs, farms, fish and industrial ponds, fish hatcheries, rice paddies, raceways and irrigation systems. The product is designed to be diluted at 1:5 in water, and applied to the water surface of the area to be treated.

Safety Directions

The safety directions on the label have been developed based on current standards issued by TGA and NOHSC and known hazards of copper sulphate and its chelate compounds. These standard hazard statements are:

Harmful if swallowed. Will irritate eyes, nose, throat and skin.
Avoid contact with eyes and skin.
If product on skin, immediately wash area with soap and water.
If product in eyes, wash it out immediately with water.
Wash hands after use.

Toxicology

Copper sulphate is currently on the NRA TGAC exempt list. It is included in Schedule 5 of the SUSDP for concentrations less than 15%, except in preparations for internal use, or in other preparations containing 5% or less copper sulphate. It is included in Schedule 6 of the SUSDP, except when in Schedule 5, in preparations for internal use or in other preparations containing 5% or less copper sulphate. No Allowable Daily Intake has been established for copper sulphate.

The toxicity of copper sulphate has been considered previously. It has an oral LD_{50} of 300 mg/kg body weight in the rat, while in the mouse the LD_{50} is 50 mg/kg body weight. Clinical signs observed included salivation, vomiting, diarrhoea, gastric haemorrhage, tachycardia, hypotension, haemolytic crisis, convulsions and paralysis.

Copper sulphate is a severe skin and eye irritant, and can cause allergic contact dermatitis in susceptible individuals. Long term dosing with copper sulphate in a range of species produced effects relating to irritation of the stomach, decreased body weight gain, liver effects and anaemia.

No toxicological data relating to CUPRICIDE® have been established. No allowable Daily Intake has been established for copper, however it is ubiquitous in the environment and forms part of the normal diet.

The proposed use pattern of CUPRICIDE® should result in copper levels at the time of application of up to 1 mg/L in the treated water. This is equal to the National Water Quality Management Strategy Australian Drinking Water Guidelines recommended levels for aesthetic quality (1 mg/L), and half the Drinking Water Guidelines recommended level for health (2 mg/L). As reapplication is only recommended at a minimum of 14 day intervals, use of CUPRICIDE® is unlikely to produce copper levels of concern in drinking water.