

# MATERIAL FACT SHEET

## COPPER PRODUCTS

**MATERIAL NAME:** Copper products

**MATERIAL TYPE:** Mineral based fungicide/bactericide

**U.S. EPA TOXICITY CATEGORY:** varies by form. Copper hydroxide and copper sulfate are Category I, "Danger." Basic copper sulfate and copper oxychloride are Category II, "Warning." Copper oxide is Category III, "Caution."

**USDA-NOP:** considered synthetic, allowed with restrictions. The following forms are permitted for use in plant disease control:

- 1) Coppers, fixed - copper hydroxide, copper oxide, copper oxychloride, includes products exempted from EPA tolerance, provided that copper-based materials are used in a manner that minimizes accumulation in the soil. Use as an herbicide is not permitted (NOP: 7CFR 205.601(i)(1)).
- 2) Copper sulfate - substance must be used in a manner that minimizes accumulation of copper in the soil. (7CFR 205.601(i)(2)).
- 3) Copper sulfate is also permitted for use as an aquatic algicide and for tadpole shrimp control in rice production. (7CFR 205.601(a)(4) and (e)(3)).

**MATERIAL DESCRIPTION:**

Copper fungicides can be described as insoluble compounds, yet their action as fungicides and bactericides is due to the release of small quantities of copper ( $\text{Cu}^{++}$ ) ions when in contact with water. Copper hydroxide is more water soluble at low pH (high acidity). It is important that this product be applied in a spray solution (such as water) at a pH above 6.0. If the solution is more acidic, phytotoxicity could occur. Bordeaux mixes are preparations of copper sulfate and calcium hydroxide (hydrated lime), working in much the same way as the newer copper fungicides, which are effective at lower rates of application.

**HOW IT WORKS:** Following absorption into the fungus or bacterium, the copper ions will link to various chemical groups (imidazoles, phos-

phates, sulfhydryls, hydroxyls) present in many proteins and disrupt the function of these proteins. Thus, the mode-of-action of copper hydroxide (or any other copper fungicide) is the nonspecific denaturation (disruption) of cellular proteins. The toxic copper ion is absorbed by the germinating fungal spore and thus for best results copper must be reapplied as plants grow to maintain coverage and prevent disease establishment.

**OMRI LISTED PRODUCTS** (not including copper fertilizers):

Champion WP® (NuFarm Americas, Inc.)  
 Crop Clean COCS® (copper and sulfur product) (Platte Chemical Company)  
 Britz Copper Sulfur 15-25 Dust® (Britz Fertilizers, Inc.)  
 Nordox 75WG® (Monterey Chemical Co.)  
 Concern® Copper Soap Fungicide Ready to Use (Woodstream Corporation)  
 Cueva Fungicide Concentrate® (W Neudorff GmbH KG)  
 Cueva Fungicide Ready to Use® (W Neudorff GmbH KG)  
 Copper Sulfate Crystals® (Chem One Ltd.) aquatic use only.  
 Lilly Miller Ready to Use Cueva Copper Soap Fungicide® (W Neudorff GmbH KG)

**NON-OMRI LISTED PRODUCTS:**

Kocide®, Champ®, Blue Shield®, Cuprofix®

**FORMULATION AND APPLICATION GUIDELINES:**

See labels for application guidelines. Champion WP is 77% copper hydroxide. It is generally applied to vegetables at a rate of 0.5 – 5.0 lbs/acre depending on the crop, with a common rate of 2 lbs./acre (Champion WP product label). This wide range of allowable rates is in part due to the phytotoxic effects copper can have on some plants. The higher rates will provide more control, but will also increase chances for phytotoxicity. It is crucial to read the product label and follow the recommended rate for each crop.

Some mixtures, such as oil and copper products, are strongly phytotoxic to some crops. For instance, citrus and apples have little tolerance, while this combination is sometimes used on tomatoes without damage.

**HANDLE COPPER PRODUCTS WITH CARE.** The re-entry interval (REI) is 24 hours for Champion WP®.

**AVAILABILITY AND SOURCES:**

OMRI-approved copper products are not widely available in the Northeast. Champion WP® (Nufarm Americas Inc ) is carried by a few distributors and mail-order companies, but shipping costs may be high.

**EFFECTS ON THE ENVIRONMENT AND HUMAN HEALTH:**

Small amounts of copper are necessary for the life and health of both plants and animals. The following discussion is centered on the effects of excessive doses.

## LEAF PERSISTENCE

Copper will generally remain on leaf surfaces for 1-2 weeks, or until it is washed off by rain or overhead irrigation.

## FATE IN WATER AND SOIL

Copper is bound, or adsorbed, to organic materials, and to clay and mineral surfaces. The degree of adsorption to soils depends on the acidity or alkalinity of the soil. Because copper sulfate is highly water soluble, it is considered one of the more mobile metals in soils. However, because of its binding capacity, its leaching potential is low in all but sandy soils (Exttoxnet 1996).

Copper is a necessary plant and animal nutrient, but it is toxic to plants and other organisms at high levels. It is always present at a background level, but can be of concern in situations of heavy agronomic use of copper compounds. Agricultural soils are reported to have average background levels of 20-30 ppm (Baker 1990), with average overall US level found to be 15.5 ppm (Holmgren, 1993). Some vineyard soils in Europe, which have seen intensive use of copper sulfate containing Bordeaux mixtures for 100 years, have soil Cu concentrations ranging from 100 - 1500 ppm (Besnard, 2001).

Maximum soil concentration rates for copper in New York soils have been recommended based on soil type, from 40 ppm (sandy soils) to 60 ppm (silt loam) to 100 ppm (clay soils) in order to protect against phytotoxicity and negative impacts on soil life (Harrison et al. 1999). Typically, each spray with a copper-based fungicide results in an application of 1 to 4 lb. of copper per acre (raising the topsoil concentration from 0.5 to 2 ppm), and often several copper sprays are made per season. Thus, under a heavy copper spray program, toxic topsoil levels could be reached in a matter of decades. Some certifiers recommend that growers include copper in their soil testing in order to determine a background level and track any changes in that level as a consequence of repeated copper spraying.

## WILDLIFE:

**Effects on birds:** Copper sulfate is practically nontoxic to birds. It poses less of a threat to birds than to other animals. The lowest lethal dose (LDLo) is 1000 mg/kg in pigeons and 600 mg/kg in ducks. The oral LD50 for Bordeaux mixture in young mallards is 2000 mg/kg (Exttoxnet 1996).

**Effects on aquatic organisms:** Copper sulfate is highly toxic to fish. 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 to the toxic effects of copper sulfate. Copper sulfate is toxic to aquatic invertebrates, such as crab, shrimp, and oysters. It is used as a pesticide to control tadpole shrimp in rice production. The 96-hour LC50 of copper sulfate to pond snails is 0.39 mg/L at 20 C. Higher concentrations of the material caused some behavioral changes, such as secretion of mucous, and discharge of eggs and embryos (Exttoxnet 1996).

**Effects on other organisms:** Bees are endangered by Bordeaux mixture. Copper sulfate may be poisonous to sheep and chickens at normal application rates. In some orchards, most animal life in soil, including large earthworms, has been eliminated by the past extensive use of copper containing fungicides (Exttoxnet 1996). Copper has been found to suppress rates of nitrogen fixation by the bacteria *Rhizobium* under some situations at relatively high copper levels of 235 ppm (OMRI 2001). Earthworms are sensitive to several heavy metals and may accumulate them in their tissues.

#### **NATURAL ENEMIES:**

Copper is a relatively non-specific bactericide and fungicide and can kill naturally occurring microorganisms on leaves as well as those that have been applied as biocontrols including *Bacillus* sp., *Trichoderma* and others.

#### **EFFECT ON HUMAN HEALTH:**

**Acute toxicity.** The oral LD50 of copper sulfate is 472 mg/kg in rats. Toxic response in humans has been observed at 11 mg/kg. Ingestion of copper sulfate is often not toxic because vomiting is automatically triggered by its irritating effect on the gastrointestinal tract. Symptoms are severe, however, if copper sulfate is retained in the stomach, as in the unconscious victim. Injury to the brain, liver, kidneys, and stomach and intestinal linings may occur in copper sulfate poisoning. Copper sulfate can be corrosive to the skin and eyes. It is readily absorbed through the skin and can produce a burning pain, as well as the other symptoms of poisoning resulting from ingestion. Skin contact may result in itching or eczema. It is a skin sensitizer and can cause allergic reactions in some individuals. Eye contact with this material can cause conjunctivitis, inflammation of the eyelid lining, cornea tissue deterioration, and clouding of the cornea (Exttoxnet 1996).

Copper hydroxide is less acutely toxic, with an oral LD50 in rats of 833 mg/kg. It is also not readily absorbed through the skin, with a dermal LD50 of over 5000 mg/kg in rats (Nufarm Americas Inc. 2004).

**Metabolism:** Absorption of copper sulfate into the blood occurs primarily under the acidic conditions of the stomach. The mucous membrane lining of the intestines acts as a barrier to absorption of ingested copper. After ingestion, more than 99% of copper is excreted in the feces. However, residual copper is an essential trace element that is strongly bio-accumulated. It is stored primarily in the liver, brain, heart, kidney, and muscles (Exttoxnet 1996).

**Chronic Toxicity:** Vineyard sprayers experienced liver disease after 3 to 15 years of exposure to copper sulfate solution in Bordeaux mixture. Long-term effects are more likely in individuals with Wilson's disease, a condition that causes excessive absorption and storage of copper. Chronic exposure to low levels of copper can lead to anemia. The growth of rats was retarded when given dietary doses of 25 mg/kg/day

of copper sulfate. Dietary doses of 200 mg/kg/day caused starvation and death (Exttoxnet1996).

**Reproductive effects:** Copper sulfate has been shown to cause reproductive effects in test animals. Testicular atrophy increased in birds as they were fed larger amounts of copper sulfate. Sperm production was also interrupted to varying degrees. Reproduction and fertility was affected in pregnant rats given this material on day 3 of pregnancy (Exttoxnet 1996).

**Teratogenic effects:** There is very limited evidence about the teratogenic effects of copper sulfate.

**Mutagenic effects:** Copper sulfate may cause mutagenic effects at high doses. At 400 and 1000 ppm, copper sulfate caused mutations in two types of microorganisms. Such effects are not expected in humans under normal conditions (Exttoxnet 1996).

**Carcinogenic effects:** Copper sulfate at 10 mg/kg/day caused endocrine tumors in chickens given the material outside of the gastrointestinal tract through an intravenous or intramuscular injection. However, the relevance of these results to mammals, including humans, is not known (Exttoxnet 1996).

**Organ toxicity:** Long-term animal studies indicate that the testes and endocrine glands have been affected (Exttoxnet 1996). Heart disease occurred in the surviving offspring of pregnant hamsters given intravenous copper salts on day 8 of gestation.

#### **EFFICACY:**

Copper is labeled for use on over 100 crop plants to control fungal and bacterial diseases. It is important to read the label and use the product according to the labeled instructions for your specific crop. In general, copper is more effective against bacterial than fungal pathogens, however it is widely used to control both bacterial and fungal diseases on tomato.

#### **PEST SPECIFIC OBSERVATIONS**

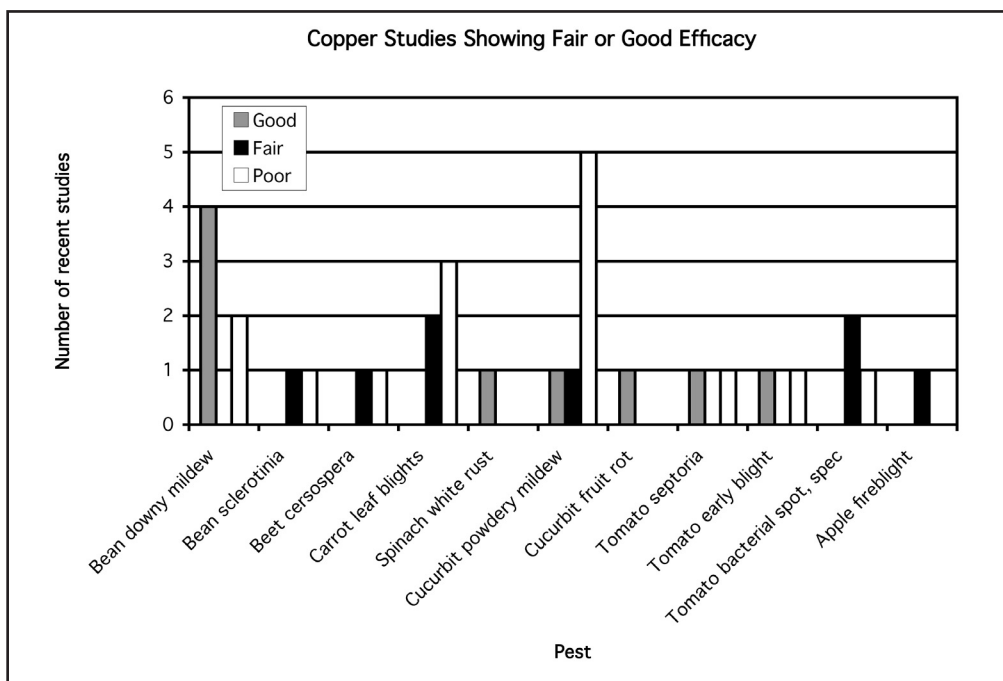
A summary of recent university field trials of copper hydroxide and copper sulfate products on fruit and vegetable crops commonly grown in the Northeast was compiled for this fact sheet. These university-based trials typically test products with untreated buffer rows and other conditions that create unusually severe pest pressure. The level of pest control is likely to be higher on treated fields in which a good program of cultural controls has also been implemented.

Recent copper product trials demonstrated only poor results for:

- Bean—Botrytis
- Spinach—Stemphylium leaf spot; downy mildew
- Brassicas—black rot; bacterial spot; Alternaria
- Cucurbits—Phytophthora; downy mildew; anthracnose
- Lettuce—bacterial leaf spot
- Onion—purple blotch
- Tomato—anthracnose

In the table below, only pest species which responded to copper products at a “good” or “fair” level are included. “Good control” means statistically significant reductions in disease severity or damage of 75% or more, compared to an untreated control. “Fair control” includes those with significant reductions of 50-74%, and any non-significant reductions of over 50%. The “poor control” group includes any results with less than 50% reduction.

Unfortunately, we found no trials with OMRI-listed copper products. The products included in the database have approved active ingredients, but may contain prohibited inerts. They were Kocide®, Champ®, Blue Shield®, and Cuprofix® formulations.



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