Copper Sulfate

Crops

for use as algicide and invertebrate pest control

September 21, 2001

Executive Summary

Copper sulfate is listed as allowed for use in crop systems in 7CFR 205 for plant disease control, with a restriction that it be used in a manner that minimizes copper accumulation in the soil. It is also listed for use as a micronutrient with a testing requirement for documented deficiency. The petition is for use as an algicide and to control invertebrates, specifically tadpole shrimp in rice production. This material has been historically widely used for organic crop disease control in the US and internationally, but the EU has proposed a complete ban on all copper use scheduled to take effect in May 2002.

Reviewers were concerned primarily about effects of this use on the aquatic environment, impact on aquatic organisms, and soil accumulation. Reviewers cited concerns about negative effect on mosquito fish, pond snails, and amphibians at the requested rate of use. The literature indicates that while copper sulfate is relatively immobile in soil and becomes quickly bound or adsorbed to organic or clay fractions in the soil, it is also highly water soluble. Some research indicates this may be of concern in marshland ecosystems subject to flooding and drying conditions.

While all three reviewer shared concerns about impact on aquatic organisms, one felt that the use of the material should be permitted with strict limitations. Two reviewers found this material not compatible with sustainable systems and recommended against this use. The petitioner proposes listing for this use, with possible restrictions to limit the use to one application per year not to exceed rates of 10 lbs /acre (copper pentahydrate form).

Identification

Chemical Name: copper sulfate

Other Generic Names:
copper (II) sulfate, cupric sulfate. Copper sulfate pentahydrate form is also called bluestone, blue vitriol, and blue copperas.

Trade Names: Agritox, Basicap BSC Copper Fungicide, CP Basic Sulfate, TriBasic Copper Sulfate, Triangle Brand Copper Sulfate Crystal, Diamond Copper Sulphate (Bluestone), plus many others.

CAS Numbers:
copper sulfate: 7758-98-7
copper sulfate pentahydrate: 7758-99-8

Other Codes:
copper sulfate pentahydrate:
EPA PC code 024401, NIOSH: GL8900000
copper sulfate (anhydrous): EPA PC 024408,
NIOSH No.: GL8800000 DOT NA 9109

Summary of TAP Reviewer Analysis [1]

Synthetic / Non-Synthetic:	Allowed or Prohibited:	Suggested Annotation:
Synthetic (3-0)	*Prohibited for this use (2)* *Allowed as algicide and for invertebrate pest control with restrictions (1)*	*Reviewers 1 and 2:* no annotation, no change in current listing. *Reviewer 3:* for emergency use in aquatic crop systems, requires monitoring of soil and water levels. Not to exceed one application per twelve-month period.

[1] *This Technical Advisory Panel (TAP) review is based on the information available as of the date of this review. This review addresses the requirements of the Organic Foods Production Act (OFPA) to the best of the investigator's ability, and has been reviewed by experts on the TAP. The substance is evaluated against the criteria found in section 2119(m) of the OFPA [7 USC 6517(m)]. The information and advice presented to the NOSB is based on the technical evaluation against that criteria, and does not incorporate commercial availability, socio-economic impact or other factors that the NOSB and the USDA may want to consider in making decisions.*

Characterization

Composition:
copper sulfate (anhydrous salt) $CuSO_4$
copper sulfate pentahydrate $CuSO_4 \cdot 5H_20$

Properties: The anhydrous form is gray white to green-white crystalline granules or powder or just white rhombic crystals, odorless, air sensitive and is very water soluble, slightly soluble in methanol, insoluble in ethanol, and nonvolatile. The pentahydrate form is blue crystalline granules or powder or when crystallized slowly, large, blue, ultramarine, triclinic crystals. It is hygroscopic. (Merck, 1960, NTP 2001)

How Made:
Copper sulfate pentahydrate is the most widely used form. In nature it is found as the mineral chalcanthite. The pentahydrate can be dehydrated to intermediate hydrates and the anhydrous salt. The anhydrous salt also occurs naturally as the mineral hydrocyanite (Kirk-Othmer, 1982). Copper sulfate solutions are derived from the processing of copper ores, which are electrorefined or electrolytically processed to produce copper metal. The pentahydrate is made by dissolving scrap copper in hot concentrated sulfuric acid (generating sulfur dioxide) or by air oxidation of scrap copper in dilute sulfuric acid (Pimentel, 1981).

Specific Uses:
Used as a fungicide, algicide, a source of copper in animal nutrition, and as fertilizer and herbicide. Also used to kill slugs and snails in irrigation and municipal water treatment systems (Kamrin, 1997; NTP, 2001). The petition is for use as an algicide and to control invertebrates, specifically tadpole shrimp in rice production (CCOF, 2001).

Non- agricultural uses include germicide; textile mordant; leather industry; pigments; electric batteries; electroplating coatings; copper salts; reagent in analytical chemistry; medicine; wood preservative; process engraving and lithography; ore flotation; petroleum industry; synthetic rubber; steel manufacture; and treatment of natural asphalts.

Action: The toxic action of copper is attributed to its ability to denature cellular proteins and to deactivate enzyme systems in fungi and algae.

Combinations: For fungicidal use, more effective when either mixed with liming agents or placed in a basic solution.

Status

Historic Use by Organic Growers: Copper sulfate has been historically widely used for plant disease control, and permitted by U.S. certifiers.

OFPA, USDA Final Rule: OFPA, at 6517(c)(1)(B)(i), provides an exemption for synthetic copper and sulfur compounds to appear on the National List. The USDA final rule lists copper sulfate for plant disease control at 205.601(i)(2), with a restriction that "substance must be used in a manner that minimizes copper accumulation in the soil." It is not listed under algicides or insecticides. It is also listed for use as plant or soil amendment at 205.601(j)(6)(ii) as a micronutrient with restrictions: "Not to be used as a defoliant, herbicide, or desiccant. Soil deficiency must be documented by testing." Also listed at 205.603(b)(6) for topical (healthcare) treatment of livestock, and at 205.603d)(1)(i) as a trace mineral feed additive.

Regulatory: EPA/NIEHS/Other Sources
EPA: Copper sulfate is classified as a General Use Pesticide (GUP) by the U.S. Environmental Protection Agency (EPA). It is rated as toxicity class I - highly toxic, requiring signal words "Danger-Poison". Because of its potentially harmful effects on some endangered aquatic species, surface water use may require a permit in some places (Extoxnet).

EPA Guidelines for Biosolids applications (21CFR 503.13): set a ceiling concentration of copper that can be found in bulk or bagged sludge as 4300 mg/kg (or ppm). The maximum cumulative loading rate for copper in soils is established at 1500 kg/ha. Annual pollutant loading rates are set at 75 kg/ha (67 lb/ac).

EU limits for soil application are set at 12 kg/ha/year (cited in Gimeno-Garcia 1996). Total concentrations permitted in soil under Directive 86/278/EEC are in the range of 50-140 mg/kg dry soil at soil pH of 6-7. The UK standard permits a range depending on soil ph, from 80 mg/kg at ph less the 5.5, to 200 mg/kg for soil ph over 7.0 (Obbard, 2001).

NIEHS National Toxicity Program database includes the following regulatory limits for copper sulfate pentahydrate:
OSHA: Federal Register (1/19/89) and 29 CFR 1910.1000 Subpart Z

Transitional Limit: PEL-TWA 1 mg (Cu)/m3 (dusts and mists) [610]
Final Limit: PEL-TWA 1 mg (Cu)/m3 (dusts and mists) [610]
Transitional Limit: PEL-TWA 0.1 mg (Cu)/m3 (fume) [610]
Final Limit: PEL-TWA 0.1 mg (Cu)/m3 (fume) [610]
ACGIH: TLV-TWA 1 mg (Cu)/m3 (dusts or mists) [610]
TLV-TWA 0.2 mg (Cu)/m3 (fume) [610]
NIOSH Criteria Document: None
NFPA Hazard Rating: Health (H): None
Flammability (F): None
Reactivity (R): None

<u>Status Among U.S. Certifiers</u>

US certifiers permit as bactericides, fungicides, micronutrients and livestock uses (OTCO, TDA, WSDA). A number also include the use as invertebrate pest controls or wood treatments, including CCOF, OCIA (2001) and this was the listing in the January 2001 *OMRI Generic Materials List.*

<u>International</u>

CODEX – lists in Annex II, Table 2. Substances For Plant Pest And Disease Control: copper salts - Need recognized by certification body or authority.

EU 2092/91 (#1488/97) – Lists in Annex II. Products for plant protection. Copper in the form of copper hydroxide, copper oxychloride, (tribasic) copper sulphate, cuprous oxide. Conditions for use: Fungicide; only during a period expiring on 31 March 2002; need recognized by the inspection body or inspection authority.

IFOAM Basic Standards 2000 – included in Annex 2, Products for Plant Pest and Disease Control, Weed Management and Growth Regulation: Copper salts (e.g., sulphate, hydroxide, oxychloride, octanoate) - Restricted. Copper usage will be reduced after 2002 to max 8 kg/ha per year (on a rolling average basis), or less according to national laws or private label standards. IFOAM has petitioned the EU to consider this rate restriction rather than the planned total phase-out of copper use in 2002; however, the EU is reportedly firm in plans to prohibit copper use, due to environmental concerns about excessive copper buildup particularly in vineyards (Schmidt, 2001).

Canada – permitted for disease management, not listed as a soil amendment, listed for livestock mineral products lists as "vitamins and trace elements"

Japanese Agricultural Standard – lists as permitted; copper sulfate "limited to be used for preparing Bordeaux mix."

Other International Certifiers –
Biological Farmers of Australia: Allows as algicides, bactericides, fungicides, molluscicides, for arthropod control, wood treatment, or as micronutrients. Cannot be used as an herbicide. Shall be used in a manner that prevents excessive copper accumulation in the soil. Build-up of copper in soil may prohibit future use. Use with caution. No visible residue allowed on harvested crops. Copper oxychloride is prohibited.

Soil Association Certification, UK: Restricted-for disease control, - approval must be obtained from the Certification Department <u>before use</u>: 1) Copper Sulphate; Copper oxychloride; Copper ammonium carbonate (max. application of 25g/l).

KRAV, Sweden: Products containing copper may be used as fungicides in fruit production but only within the framework of the limits stated in the standards for heavy metals.

<u>Section 2119 OFPA U.S.C. 6518(m)(1-7) Criteria</u>

1. *The potential of the substance for detrimental chemical interactions with other materials used in organic farming systems.*
   Incompatible with strong oxidizers and magnesium. It is also incompatible with finely powdered metals and can corrode steel. It can also corrode iron. It can react with alkalies, phosphates, acetylene gas, hydrazine, or nitromethane. A reaction may occur if mixed with beta-naphthol, propylene glycol, sul-phathiazole and triethanolamine; however, the pH usually needs to be >7 before a reaction will proceed (NTP, 2001).

2. *The toxicity and mode of action of the substance and of its breakdown products or any contaminants, and their persistence and areas of concentration in the environment.*
   Toxicity:

Acute toxicity: The oral LD50 of copper is 472 mg/kg in rats. Copper sulfate is caustic and acute toxicity is largely due to this property. The lowest dose of copper sulfate that has been toxic when ingested by humans is 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. Some of the signs of poisoning which occurred after 1 to 12 g of copper sulfate was swallowed. 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. Examination of copper sulfate-poisoned animals showed signs of acute toxicity in the spleen, liver, and kidneys. Injury may also occur to the brain, liver, kidneys, and gastrointestinal tract in response to overexposure to this material. Some of the signs of poisoning that occurred after 1-12 g of copper sulfate was swallowed include: a metallic taste in the mouth, burning pain in the chest and abdomen, intense nausea, repeated vomiting, diarrhea, headache, sweating, shock, and discontinued urination leading to yellowing of the skin. Injury to the brain, liver, kidneys, stomach, and intestinal linings may also occur in copper sulfate poisoning. It is readily absorbed through the skin and will give the above symptoms. Contact with skin causes burns and also acts as a sensitizer. Later exposure can cause allergic reactions (Kamrin 1997; Extoxnet).

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. Sheep given oral doses of 20 mg/kg/day showed blood cell and kidney damage. They also showed an absence of appetite, anemia, and degenerative changes.

Reproductive effects: Copper sulfate has been shown to cause reproductive effects in test animals. Reproduction and fertility was affected in pregnant rats given this material on day 3 of pregnancy.

Teratogenic effects: There is very limited evidence about the teratogenic effects of copper sulfate; unlikely to be teratogenic in humans at expected exposure levels.

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.

Considered an experimental equivocal tumorigenic agent (NTP, 2001). It has systemic and gastrointestinal effects in humans. HIGH via intraperitoneal route. MODERATE via oral and inhalation routes.

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

Organ toxicity: Long-term animal studies indicate that the testes and endocrine glands have been affected.

Fate in humans and animals: 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 bioaccumulated. It is stored primarily in the liver, brain, heart, kidney, and muscles.

Ecological Effects:

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 (Extoxnet, Kamrin 1997).

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 fry to the toxic effects of copper sulfate. Copper sulfate is toxic to aquatic invertebrates, such as crab, shrimp, and oysters. 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.

Effects on other organisms: Bees are endangered by Bordeaux mixture. Copper sulfate may be poisonous to sheep and chickens 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 (Pimental, 1971, cited in Kamrin, 1997).

Environmental Fate:

Breakdown in soil and groundwater: Since copper is an element it will persist indefinitely. 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 it binding capacity, its leaching potential is low in all but sandy soils. When applied with irrigation water, copper sulfate does not accumulate in the surrounding soils. Some (60%) is deposited in the sediments at the bottom of the irrigation ditch, where it becomes adsorbed to clay, mineral, and organic particles. Copper compounds also settle out of solution. (Kamrin, 1997)

Breakdown in water: As an element, copper can persist indefinitely. However, it will bind to water particulates and sediment (Extoxnet, 1996).

Toxicity to Plants

One of the limiting factors in the use of copper compounds is their serious potential for phytotoxicity. Copper sulfate can kill plants by disrupting photosynthesis. Blue-green algae in some copper sulfate treated Minnesota lakes became increasingly resistant to the algacide after 26 years of use (Extoxnet, Kamrin, 1997). Copper is more available for plant uptake from soil when soil is acidic. Toxic plant levels could be reached at soil levels of 25-140 ppm in acidic mineral soils. It is less available in soils rich in organic matter. Levels in soil with high organic matter could reach 1000 ppm before phytotoxicity would occur (Erich 1994). In Europe, general cropland has 5-30 mg/kg soil, and vineyards in Europe 100 to 1500 mg Cu/kg soil (Besnard 2001). Each addition of 10 lbs/acre of copper sulfate could increase the concentration in the top 2 inches of soil by 6 mg/kg or 6ppm.

Normal concentration of copper in plants is 5-20 ppm. More than 30 ppm could cause phytotoxic effects. Copper sulfate at 15 lb/acre on rice fields caused an accumulation of 3.5 to 5.7 ppm (3.5-5.7 mg/kg) in the rice seed (Dunigan and Hill 1978). Apparently, copper sulfate treatment of rice would not be phytotoxic, at least after one treatment.

3. *The probability of environmental contamination during manufacture, use, misuse, or disposal of the substance.*

Copper mining and refining cause pollution through runoff from spoils and emissions associated from acid rain. Production of copper sulfate recycles water used in the crystallization vats and wastewater is limited to some sludge form the softening process plus boiler blowdown (Sittig, 1980).

4. *The effects of the substance on human health.*

Direct hazards to applicators are the major concern; see response to question two. Exempt from EPA tolerance for residues on food. Copper is also a nutrient and levels found on food are not of concern for residues.

5. *The effects of the substance on biological and chemical interactions in the agroecosystem, including the physiological effects of the substance on soil organisms (including the salt index and solubility of the soil), crops and livestock.*

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. It is normally found at soil concentrations ranging between 5 and 30 mg/kg soil in Europe (Besnard, 2001) and 6- 65 ppm in the US, with average US level found to be 15.5 ppm. The California reported average is 37.3 ppm (Holmgren, 1993). Vineyard soils in Europe, which have seen intensive use of copper sulfate containing Bordeaux mixtures for 100 years, have concentrations ranging from 100 - 1500 mg Cu/kg soil. Soil erosion in hilly vineyard situations creates a potential for contamination of water quality (Besnard, 2001). Copper levels in soils studied in Italy were found to be closely correlated to agricultural use (Facchinelli, 2000).

One single application of Bordeaux mixture adds 3-5 kg of Cu /ha annually. An application of 10 lbs/a of copper sulfate pentahydrate, which is 25% copper as the active ingredient, would add 2.5 lbs/acre (2.8 kg/ha) (Besnard, 2001; Gimeno-Garcia, 1995). Grape producers may apply 3 - 10 application per year of Bordeaux mix. Fixed coppers are applied at lower rates.

Copper has an affinity to organic substances in the soil, and becomes less available to crops when organic matter is increased. Addition of organic matter has been shown to prevent erosion, and retain copper in vineyard soils (Besnard, 2001). Soil pH affects availability, which decreases at higher pH in calcareous soils (Andreu, 1999). Rice growing regions in California are reportedly in high pH conditions. In high soil copper situations (600-900 ppm), while corn roots take up copper, it is not translocated to the aerial parts of the plant or the crop (Brun, 2001). Copper concentration in corn roots was shown to be as high in calcareous soils as low pH soil, showing that soil pH did not influence root uptake. Copper did increase in aerial plant parts at a lower pH. Cu was thought to be retained in root cell walls and not really taken up; however, high levels of copper inhibits root growth and damages root cells before affecting shoot growth (Brun, 2001).

Copper is a heavy metal that has a potential to build up in soil and decrease the productivity and filter and buffer capacity (Andreu, 1999). This may be more of a concern in fragile ecosystems such as marsh or wetlands than rice crops. When heavy metals enter the soil they may: (a) remain in soil solution and run off in drainage water, (b) be taken up by plants, or (c) be retained by soil in soluble or insoluble forms. In a system that is seasonally wet and dry, there is continuous change in the availability of metals due to cycles of aerobic and anaerobic conditions affecting the soil redox potential. This may make such soils more vulnerable to enhanced solubility and toxicity of metals (Andreu, 1999). Of the metals, copper is relatively more mobile (extractable) than cadmium, lead, zinc, nickel, or cobalt, but even so is retained in the soil for a very long time periods. In a study that sampled the same site over a five-year period in a rice growing region of Spain, it was found that copper does, however, gradually decrease over time, unlike cadmium that has shown a tendency to increase (Andreu, 1999). Copper is found in the upper levels of the soil profile, and decreases with depth.

Effect on soil microorganisms: Copper has been found to suppress rates of nitrogen fixation by Rhizobium under some situations at copper levels of 235 ppm (Obbard, 2001; Mhatre, 2001). Microbial biomass carbon is reduced in metal contaminated soils, and these effects may last many years. A measure of soil enzyme activity indicated a large reduction of activity at high levels of copper (900 ppm) with no reduction noted up to a medium level (140 ppm) (Mhatre, 1997). Earthworms are sensitive to several heavy metals and may accumulate them in their tissues. A reduction of abundance and biomass of two species of earthworms was found at low and medium levels of copper, and no earthworms present at high concentrations. Soil levels were not cited, but earthworm copper content in the low and medium sites were 90-160 ppm (Yeates, cited in Mahrtre, 2001).

As noted in the petition, copper sulfate does kill algae and crustaceans. It also causes mortality of adult mosquito fish (Gambusia affinis) and three spined sticklebacks (Gasterosteus aculeatus) at levels of 8-10 ppm in California (Johnson, 1977; Fry, 1992).

Copper sulfate does not have a salt index rating (Meister, 2000).

6. *The alternatives to using the substance in terms of practices or other available materials.*

The petition notes that occasional use of copper sulfate is needed in situations where rice is direct seeded into flooded fields. This is common in the Americas, southern Europe, Australia, India, Sri Lanka, Malaysia and Thailand (Luh, 1991). It is done where production is highly mechanized, and where labor is not available or economically justified for direct transplanting. Tadpole shrimp are not a problem in transplanted rice, and are in fact encouraged as a method of biological weed control. Japanese literature has many references to efficacy and use of tadpole shrimp (Igarashi, 1995; Yonekura, 1979; Matsunaka, 1975).

Cultural control: In addition to transplanting rice, direct seeding by drilling seed before flooding is practiced in some areas. This does not seem to be the practice in California, and has limitations regarding weed control and soil type (Luh, 1991).

Most tadpole shrimp eggs hatch within 2 days after contact with water. Immediate seeding reduces the potential for plant injury. Extension publications recommend seeding basins in sequence as they fill with water. Windy weather conditions can prevent the seeding operation from happening in a timely way.

Since tadpole shrimp are aquatic in their damaging stage, draining is an alternative to chemical control. The draining should not take place until 4 to 5 days after initial flood so the maximum egg hatch would have occurred. The draining time will vary due to soil type and weather but should continue for at least 24 hours after all standing water is gone. Shrimp will gather in standing water in low areas and will re-infest the field if the drain period is too short. Reflooding may result in some shrimp from previously unhatched eggs, but they would be in noneconomic numbers and less likely to damage the older, firmer rooted seedlings.

Flooding and draining before planting will expose hatched tadpole shrimp to desiccation if adequate time is allowed. Any soil cultivation following the drain period may bring viable, unhatched shrimp eggs to the soil surface for possible infestation upon reflooding, however.

Draining as a control measure has negative aspects such as fertilizer loss, encouragement of weeds, or interruption of weed control procedures, interruption of pesticide holding requirements, and the economics of irrigation (UC Davis, 1999).

Tadpole shrimp eggs are adapted to alternate periods of drying and wetting, and will not hatch if they do not receive a drying period. Suppression of tadpole shrimp hatch was very high when soil moisture levels did not drop below 25% and resulted in egg mortality (Fry, 1992). It seems possible, though it may not be practical, to manipulate soil water levels on a cyclical basis to reduce populations.

Algae growth is also aggravated by delayed seeding and warm temperatures that encourage algae growth before rice seedlings emerge. Water management strategies can be manipulated, and shallow water (0 to 2 inches) promotes the growth of all rice weeds. Intermittent draining, particularly early in the season to control algae, may allow other weed seedlings to establish that would not have survived a continuous flood. Nitrogen and phosphate fertilizers can affect algae growth. Algae grows more vigorously and may become well-established when high rates of nitrogen and phosphorous are left on the soil surface (UC Davis, 1999b).

7. *Its compatibility with a system of sustainable agriculture.*

Copper compounds have historically been used in organic agriculture, and are widely used to control bacterial and fungal diseases of fruit, vegetable, nuts, and field crops (Kamrin, Boyer, 1994). Increasing concern about long-term build up in soil is particularly evident in Europe, where a history of high application rates has occurred. Copper is very limited in mobility and availability in the soil, particularly in higher pH soils and in association with higher organic content of soils. Application rates used in rice production (a once yearly use, usually in a rotation of once every three years) does not appear to pose as high an environmental impact as levels applied for foliar disease control. However, use in aquatic systems presents additional concerns about impact on fish and other aquatic wildlife, and potential for water contamination.

TAP Reviewer Discussion[2]

Reviewer 1 *(Ph.D. chemistry. Research entomologist advising growers about pesticides and alternative pest control methods. Western U.S.)*

[The reviewer submitted corrections and additions to the database information regarding physical properties and an omission of reference to use as soil amendments in 7CFR 205. These changes have been added to the appropriate sections. The reviewer submitted the following additional information and corrections regarding evaluation under the OFPA criteria and supplied additional references cited.]

OFPA Criteria Evaluation

(1*) The potential of such substances for detrimental chemical interactions with other materials used in organic farming systems;*

I agree with the criteria evaluation. Additional comments:

The [investigator] has listed various chemical incompatibilities of copper sulfate. Many of these will not be encountered in organic farming.

(2) *The toxicity and mode of action of the substance and of its breakdown products or any contaminants, and their persistence and areas of concentration in the environment;*

[Reviewer suggested additional points regarding acute toxicity and environmental fate -toxicity to plants. These have been added to the preceding review under criterion 2.]

(3) The probability of environmental contamination during manufacture, use, misuse or disposal of such substance;

From 1987 to 1993, about 450 million pounds of copper were released to the environment in the U.S., mainly through copper smelting operations. About 1.5 million pounds were released into water from various industrial operations (EPA, 2001). So it looks like the probability of environmental contamination from copper mining and smelting is high.

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2 *OMRI's information is enclosed is square brackets in italics. Where a reviewer corrected a technical point (e.g., the word should be "intravenous" rather than "subcutaneous"), these corrections were made in this document and are not listed here in the Reviewer Comments. The rest of the TAP Reviewer's comments are edited for any identifying comments, redundant statements, and typographical errors. Additions to the TAP review text were incorporated into the review. Text removed is identified by ellipses […]. Statements expressed by reviewers are their own and do not reflect the opinions of any other individual or organizations.*

Care must also be taken to trap the sulfur oxides produced during manufacture of copper sulfate from copper and sulfuric acid, or these could cause acid rain and air contamination.

(4) The effect of the substance on human health;

The reviewer covered most of this under [criterion] 2. One thing left out is that there is an excess of cancer cases in the copper smelting industry (Sax 1979). Of significance is the tendency to bioaccumulation, the problem with skin absorption, and the liver damage of vineyard workers after 3-15 years exposure. Chronic exposures to animals caused problems at 20mg/kg/day (Kamrin 1997).

Copper sulfate pentahydrate applied at 15 lb/acre of rice led to accumulation of 3.5 to 5.7 mg/kg in rice seed. Daily copper consumption of treated rice for one person should be no greater than 6 mg (Dunnigan and Hill 1978). Daily copper intake from rice in China is reported to be 1.4 mg/person (Herawati et al. 1998). Exposures of 1.3 mg/liter are permitted in drinking water (EPA 2001).

Use of copper sulfate on rice at 10lbs/acre does not seem to pose a human health risk from ingested food.

(5) The effects of the substance on biological and chemical interactions in the agroecosystem, including the physiological effects of the substance on soil organisms (including the salt index and solubility of the soil), crops and livestock;

Addition of copper sulfate to kill algae can cause the algae to release toxins that can poison water. Problems of this kind are worse after algae populations have become large (Kenefick et al., 1993). Copper sulfate in water can also be poisonous to fish. Catfish are stressed by 1.7 mg/liter (Griffin et al., 1999). Enzyme activity in fish is increased due to stress at 2 mg/liter. Negative effects on fish health were still seen after 2 weeks in clean water (Karan et al., 1998).

The reviewer notes that earthworms are killed at 90-160 ppm. Nitrogen fixation is suppressed at 235 ppm. Application of 10 lb/acre of copper sulfate pentahydrate is 2.5 lbs/acre (2.8 kg/ha) of copper ion. Concentration of copper in water 6 inches deep would be 1.8 mg/liter (1.8 ppm). This amount would stress fish and must kill algae, but only slightly exceeds drinking water standards (EPA, 2001).

(6) The alternatives to using the substance in terms of practices or other available materials; and

There are alternatives to copper sulfate for managing algae. Other than chemicals that kill the algae, nutrient management and biological controls have been used. Dissolved iron, phosphate, nitrate, or humic materials can trigger growth of algae, and removal of phosphate by adding calcium carbonate or lime can stop algal growth (King, 1996; Kenefick et al., 1993). Some fish species preferentially graze on algae (King, 1996), but stocking fish in a rice paddy may be impractical.

Addition of bacteria to the system could suppress the algae. A commercial product called Pond Saver is available from Plant Health Care (see BIRC, 2001). The bacteria stop algae by competing for nutrients (King, 1996). A possibly less expensive method of using bacteria to stop algae involves inoculation of the water with bales of barley straw (Gibson et al., 1990). The microbes on the straw remove phosphorous from water, and encourage populations of algae-feeding invertebrates (Welch et al., 1990). The exact mechanism has not been determined. Based on laboratory tests, Newman and Barrett (1993) calculated that three 40-lb bales would provide 95% reduction of Microcystis aeruginosa over two acres of water. Mechanical harvesters that vacuum the surface of the water to remove algae are commercially available (Koopman and Oswald, 1977; BIRC, 2001).

Alternatives for the tadpole shrimp have been given by the TAP reviewer.

(7) Its compatibility with a system of sustainable agriculture.

Copper sulfate's compatibility with sustainable agriculture rests on the probability of soil and water contamination by copper sulfate. Also important is whether or not the material is toxic to the plant, and whether pest resistance is possible or likely. From a number of references cited by the TAP reviewer, it is clear that copper sulfate can build up in soil. A simple comparison of vineyard soils, where copper has been used for long periods, with other soils shows accumulation can occur (Narimanidze and Bruckner, 1999).

Experiments in Hawaii showed that 98% or more of copper ion added to wetland soil was absorbed within an hour by the soil. More was absorbed if the soil had lots of organic matter (Hue et al., 1997). Most of the copper binds to organic matter and accumulates near the surface (Ma, 1988; Andreu et al., 1999). So, each application of 10 lb/acre could increase the concentration of copper in the upper 2 inches of soil by 6 mg/kg or 6 ppm.

Although copper does build up in soil, a number of crops have shown limited uptake of copper after soil amendments of swine manure containing large concentrations of copper. Apparently, organic matter can bind with copper, making it biologically unavailable (Miller et al., 1987).

Copper seems more capable of causing plant damage as a foliar spray. Some wheat crop damage was noticed after two sprays of 375 g/ha (0.33 lb/acre) of copper sulfate (Brennan, 1990). For control of algae and tadpole shrimp about 10 lb/acre is applied to water. Apparently, this does not cause phytoxicity to rice.

Another question is whether the copper will concentrate in the crop. A Chinese researcher has found that addition of copper sulfate to rice crops increases rice yields by about 8%. Increased yields were seen with as little as 1 kg of copper sulfate (probably per hectare). Copper was taken up by the rice plant. Plant copper contents were highest at maturity, and the copper content of unhulled rice seed was several times that present in rice plants. Total concentrations were not listed in the abstract that I have (Guan, 1991).

Another reference shows that copper sulfate at 15 lb/acre on rice fields caused an accumulation of 3.5 to 5.7 ppm (3.5-5.7 mg/kg) in the rice seed. I believe that this result was from one application (Dunigan and Hill, 1978).

Another key point is the possibility of resistance development in algae and in tadpole shrimp. According to Kamrin (1997), algae can become resistant to copper sulfate. If resistance builds, application of copper sulfate is inconsistent with sustainable agriculture as it would become ineffective, and would not be a sustainable approach.

Conclusion-Reviewer 1

Clearly copper sulfate is a synthetic. The Final Rule allows the use of synthetic copper sulfate for plant diseases with an annotation "must be used in a manner that minimizes copper accumulation in the soil." In case of documented deficiency copper sulfate is allowed as a micronutrient with the annotation "not to be used as a defoliant, herbicide, or desiccant."

Clearly, the intent of the NOSB and the annotation is that copper sulfate should not be deliberately applied to soil unless there is a documented deficiency of copper. Some of the concerns that led to this annotation were concerns for soil and water quality.

Using copper sulfate at the rate of 10 lbs/acre for control of algae and tadpole shrimp in rice crops once each year would not seriously degrade drinking water quality, since water concentrations with each application would be about 2 ppm (2 mg/liter), and drinking water standards are 1.3 mg/liter. By the time the million treated liters from each ha reached a water treatment plant, it would be diluted. Possibly, there could be a toxic plume where the field water ran off into surface water. However, most of the copper in the water would probably be bound to the soil before the irrigation water was released anyway.

Most of the articles supplied to me and that I have found show that copper will bind to the soil and accumulate near the surface (Andreu et al., 1988; Ma, 1988). Each application of 10 lbs per acre could increase the copper concentration in the top 2 inches of soil by 6 mg/kg or 6 ppm. Over a period of years, applications could lead to a buildup in soil similar to the vineyards of Europe. Deliberate application of copper to soil in the absence of documented deficiency would seem to violate the spirit if not the letter of sustainable farming principles.

Also, there are alternatives to copper sulfate use for algae and tadpole shrimp pointed out under question 6. However, the alternatives for algae have apparently not been tested in rice paddies.

I do not believe copper sulfate should be allowed in organic production for management of algae and tadpole shrimp in rice crops at this time. Perhaps the applicant could reapply, if good faith assessments of alternate methods prove fruitless.

Reviewer 1 - Recommendation Advised to the NOSB:

a. The substance is
___X_Synthetic ______Not Synthetic

b. For Crops and Livestock, the substance should be
______Added _____X_Not Added to the National List for this new use.

Suggested Annotation, including justification:
(none)

Reviewer 1 response to additional questions:
(Similar questions were posted to the OMRI web site.)

1. Do you have any more information about residual copper levels in rice soils in CA, or impacts/fate of copper in irrigation water discharge?

If you assume that copper is bound to the organic layer and accumulates near the surface (Andreu et al., 1999; Ma, 1988), then each application of 10 lbs/acre of the pentahydrate leads to an increased copper ion concentration of about 6mg/kg (6 ppm) in the top 2 inches of soil. This is a rough calculation that assumes soil density is the same as water.

Copper in water should be quickly bound to soil, so that water contamination is unlikely. However, if a 10 lb/acre application stayed in 6 inches of water, drainage into surface water would result in the release of about a million liters of water with a concentration of 2 ppm of copper.

2. Can you provide any information on water quality regulations downstream from rice fields?

The EPA has set drinking water standards at 1.3 mg/liter (EPA, 2001). Simple calculations show that concentration of copper in the treated rice paddies should be no greater than about twice the drinking water standards. If released, it should not be a problem for drinking water quality after dilution, unless we are talking about huge acreages. However, surface water coming out of the Sacramento Valley could drain to the San Francisco Bay.

Water quality criteria and standards for Bay waters have been developed by the US EPA, the state of California Water Resources Control Board, and the San Francisco Regional Water Quality Control Board. It has been found that the concentrations of total recoverable copper and, for that matter, dissolved copper in San Francisco Bay waters exceed the water quality standard adopted for these waters. In accord with current US EPA policy, this situation requires that a wasteload allocation be developed in which the various sources of copper are assigned a TMDL (total maximum daily load). At this time the San Francisco Regional Water Quality Control Board has developed a highly arbitrary set of TMDL"s for various point and non-point source discharges-sources of copper for San Francisco Bay. It is estimated that based on current regulatory approaches over $1 billion will have to be spent to try to control copper inputs to San Francisco Bay from urban stormwater runoff sources (Lee and Lee 1996).

3.Can you provide any more information about alternative methods for algae or tadpole shrimp control?

This information is contained in the answer to criteria question 6.

Reviewer 2 *(Ph.D. plant pathology, M.S. soil science. Project development, research, consulting, and administrative activities related to waste treatment and reuse of waste as soil amendments and fertilizers. Eastern US.)*

[The reviewer submitted corrections and additions to the database information as follows regarding evaluation under the OFPA criteria and supplied additional references cited.]

OFPA Criteria Evaluation

(1) *The potential of such substances for detrimental chemical interactions with other materials used in organic farming systems;*

I agree with the criteria evaluation.

(2) *The toxicity and mode of action of the substance and of its breakdown products or any contaminants, and their persistence and areas of concentration in the environment*;

Under environmental fate, in the first paragraph, the 3rd to last sentence says that copper sulfate does not accumulate in soils when applied with irrigation water. [requests reference to be cited, this was added] There are various ways to irrigate. This appears to refer to a gravity flow method where water is released from irrigation ditches to flood fields. The water in the ditches generally flows from a river to the ditches then to fields, back to ditches, and sometimes back to the river. I feel skeptical that there is no accumulation of copper in the field soil. If the copper accumulates in the ditch sediments, it may be moving back to the river in silt carried by the irrigation water.

In the rice production system it appears that the copper is applied once the field is flooded. That water is held on the field for weeks as the rice grows. During that growth period there is time for copper to precipitate to the field soil. The use of water in this system is more than just irrigation water, it has a much longer residence time. The system is more analogous to a catfish pond than an irrigated field in terms of how copper might precipitate.

It would have been helpful to have information on copper's impact on frogs and a greater variety of aquatic organisms. The following website summarizes some European research done on the presence and toxicity of copper in frogs and toads. One of the sites sampled was an area of intensive agriculture. Copper and other heavy metals were at levels of acute toxicity to some aquatic predators (DATP, 1998).

(3) *the probability of environmental contamination during manufacture, use, misuse or disposal of such substance;*

More information is needed on the fate of water from the rice paddies after it leaves the fields. This is quite important in terms of environmental impact. If this water flushes directly to natural water bodies the copper most likely would have impacts on aquatic life. The information [supplied] on rice production indicated that California did not require irrigation water treated with copper to be held before returning to the irrigation channels. I am not familiar with how used irrigation water is channeled in California but in Idaho some of that water returns to the rivers.

Data on copper concentrations and sediment content in the water at the time it leaves the field would be useful. Most of the copper will probably be in the sediment when water is drawn down. Any research addressing the issue of copper impacts on aquatic systems would be useful. Research by Otero et al. (2000) indicates that copper is variably bioaccumulated by marine polychaete [worms] in some marine systems. The variation is linked to the presence of metal sulfides and their oxidation.

(5) the effects of the substance on biological and chemical interactions in the agroecosystem, including the physiological effects of the substance on soil organisms (including the salt index and solubility of the soil), crops and livestock;

[Reviewer notes the Andreu, 1999 study regarding decreasing levels of copper in soil] conflicts with information I have read that indicates is does not decrease with time (see Extoxnet 1996).

This section needs more information on the accumulation of Cu in sediments of aquatic systems and the effects of oxidation and reduction on its bioavailabilty. Han et al. (2001) show copper accumulation of Cu in catfish pond sediments when these ponds are amended with copper sulfate for algae control. They suggest further avenues of research to evaluate bioavailabilty and toxicity of Cu in sediments to benthic organisms.

Research references on copper in aquatic agricultural systems do not need to be limited to rice. Other systems can provide valuable information.

(6) the alternatives to using the substance in terms of practices or other available materials;

More information should be included on planting mechanisms as an alternative to copper sulfate. The reference on rice by Bor S. Luh mentions that there are machines available for drilling pre-germinated rice onto puddled soils. If pre-germinated seed were drilled and allowed to grow for a short while before flooding the fields, the rice most likely would escape the impacts of the shrimp and algae that only bother seedlings or rice that have not emerged above the water level.

The author also mentions that combines on oversized pneumatic tires for floatation are used effectively in drained fields. No mention is made though of seedling transplanting equipment. The literature provided with this review does indicate that tadpole shrimp and algae are not a problem in systems where rice seedlings are transplanted. Transplanting equipment does exist for other agricultural crops. If rice transplanting equipment exists it would be an possible solution to the problem of shrimp and algae. If it does not exist it appears to be a machine worth developing to deal with this problem.

The question also arises in this reviewer's mind whether there are any native fish that eat tadpole shrimp and/or algae that could be introduced to rice fields.

(7) its compatibility with a system of sustainable agriculture.

Although copper sulfate is used in organic agriculture, it is not a practice to be encouraged because of its toxicity and residence time. This petition would expand the accepted uses of copper sulfate in US organic agriculture. The EU plans to phase out the use of copper.

Because copper sulfate is being petitioned for use in rice production as an algicide and to control crustaceans it is a more delicate situation. A rice paddy is a wetland and as such attracts aquatic organisms. Some rice fields were natural wetlands previously converted to rice production and others are manmade. In addition water and silt from paddies may or may not return to natural water bodies after the field is drained. Copper is toxic to many aquatic organisms. A sustainable system of agriculture needs to strive to reduce its negative impact on the biology of the area. Copper sulfate is not compatible with aquatic agricultural systems.

Conclusion – Reviewer 2

The use of copper sulfate to control shrimp and as an algaecide in aquatic systems such as rice production in organic agriculture should be prohibited. Aquatic systems are very susceptible to copper toxicity and flooded rice fields act as an attractive nuisance to aquatic organisms such as frogs and others. In gravity flow irrigation systems, water is often brought from a river and may return to that river downstream after it leaves a field carrying sediment. California water quality requirements do not regulate copper. Other states may be the same.

Reveiwer 2 Recommendation Advised to the NOSB:

The substance is
__X__Synthetic _____Not Synthetic

For Crops, the substance should be
_____Added __X__ Not Added to the National List.

Suggested Annotation, including justification:
Prohibited. Copper sulfate should not be used in aquatic systems due to its toxicity to many aquatic organisms.

Reveiwer 2 response to additional questions:

1) *Do you have any more information about residual copper levels in rice soils in California, or impacts/fate of copper in irrigation water discharge?*
The article listed above by Han et al. discusses the use of copper sulfate as an algaecide in catfish ponds. It shows accumulation of copper in the pond sediment. This system has similarities with rice production in that the fields and the ponds remain flooded for long periods of time.

2) *Any information on water quality regulations downstream from rice fields?*
I do not have any information on water quality regulations downstream from rice fields. [The investigator reported] that California exempts copper from water quality regulations. If copper sulfate is accepted as an algicide it will be used in more areas than California.

3) *Any more information about alternative methods for algae or tadpole shrimp control?*
As suggested in 6 above equipment for drilling pre-germinated rice seed should be used. Machines that can transplant rice seedlings would also alleviate the shrimp/algae problem.

Reviewer 3 (*Analytical lab technician with extensive experience in organic production. Western US.)*

[The reviewer found the database Characterization and Status to be reasonably complete and accurate, and submitted the following additional information regarding evaluation under the OFPA criteria.]

Comments on OFPA Criteria Evaluation
(3) *the probability of environmental contamination during manufacture, use, misuse or disposal of such substance*
[evaluation needs amendment or correction] Needs evaluation of fate in solution; how much copper sulfate travels in the water when paddies are drained, is there a potential of biota kills in marshes and steams?

General Discussion of OFPA Criteria

COPPER SULFATE IN RICE GROWING SYSTEMS
Most of the studies on Copper sulfate seem to be based on soil accumulation, and plant uptake. Copper itself is quite mobile, and goes into solution readily when there are acid conditions. $CuSO_4$ is very soluble. As conditions approach neutral, or basic, the Cu would adhere to organic particles in the water, and surface sediment. If copper is mobile, changes in pH would free it up again to go into solution.

Most studies dealing with copper accumulation in soils are looking at rates that are far higher in both rate and frequency of application than in rice culture. Also, much of the copper applied is done in alkaline conditions such as vineyards. Because of its mobility, copper appears to be metabolized by plants, and the actual levels of copper in the soil do lessen over time. Also, it seems to adsorb mostly to surface soil. In a soil ecology, this is good, as the copper does not travel far and thus contaminate groundwater. It remains at or near the soil surface, the area with the most biological activity, and thus can be available to plants.

Copper can change the soil biota profile, and it is toxic at fairly low levels to such organisms as earthworms (approx 30 ppm). Plant toxicity can occur as well, but it depends on a variety of conditions (higher levels in alkaline soils can be less toxic than lower levels in acid soils)

Typical application rates in paddies to control algae appear to range from 0.25 ppm to 2.0 ppm. For treating tadpole shrimp, application rates appear to be "less than 10 ppm". With aquatic organisms showing detrimental effects at levels of about 0.4 ppm and above, this means that the application of $CuSO_4$ to rice paddies could kill mosquito fish, pond snails, and other organisms that could have beneficial properties.

What is the fate of $CuSO_4$ in the paddy waters? Does it stay in solution for some period of time, continuing its effects on algae, tadpole shrimp, and other organisms? Does it cleave to organic matter in the water and settle quickly to the bottom? Do pH changes due to other chemical additions, evaporation, and plant breakdown cause the $CuSO_4$ to go back into solution? How much copper heads downstream when the ponds are drained? What is the fate of susceptible organisms downstream when the paddies are drained?

Because of copper's mobility, and because of the unique water ecology in which this substance is being applied, use of this product should be approached with caution. In soil environments, the copper can be bound and made less available. And, although long-term heavy use of such products can cause phytotoxicity and complete cessation of soil microflora and –fauna activity, I suspect that there is a wider "default" zone than in water ecologies.

My understanding is that organic rice management systems seek to control both algae and tadpole shrimp by practices such as draining and flushing. They seek to avoid chemical inputs whenever possible. $CuSO_4$ would come into use only when weather makes these practices impossible. Since both algae and tadpole shrimp seem to be problems during the very beginning of the rice growing cycle, I assume that once the rice is established, there would be no more need for $CuSO_4$ as a control. Would this mean a maximum of a once a year application? Or are there some areas in which more than one rice crop is grown per year? And if weather conditions were right, it would not be necessary to use $CuSO_4$ at all during the entire growing cycle?

Reviewer 3 Conclusion

Because synthetic copper products are allowed in other organic agricultural systems, and because this use of $CuSO_4$ seems to be a fairly rare occurrence in rice growing systems, it should be allowed as an algicide and a means to control tadpole shrimp. However copper levels in soil and water should be monitored, and use should be tightly restricted. It should never be considered as a routine and convenient treatment to handle these problems. I believe that because of copper's higher mobility in a water situation, the vulnerability of aquatic life both in the paddies and downstream, and the periodic flushing of the paddies, that restrictions on its uses should be more stringent than on land-based agricultural systems.

Reviewer 3 Recommendation Advised to the NOSB:

The substance is

__X__Synthetic ______Not Synthetic

For Crops, the substance should be

___X__Added ___Not Added to the National List.

Suggested Annotation:

Copper sulfate should be listed under 205.601(a) as algicide and 205.610(e) as insecticide, (including acaracides or mite control, and invertebrate control).

Both listings should have the following annotation:

For emergency use in aquatic crop systems, requires monitoring of soil and water levels. No more than one application per 12 months.

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This TAP Review was completed pursuant to United States Department of Agriculture Purchase Order 40-6395-0.