Copper Sulfate and Other Copper Products

Crops

For Use as Plant Disease Control and For Use as Algicide and Invertebrate Pest Control

Identification of Petitioned Substance

Chemical Name: Copper sulfate

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

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

Other Copper Products:
Copper hydroxide. Cuprous oxide. Copper carbonate. Copper ammonium carbonate. Copper oxychloride. Copper octanoate. More copper compounds are given below and listed in "Status."

CAS Number:
Listed below.

Other Codes:
Listed below.

CAS Number and U.S. EPA PC Code[1]

Copper Product	Formula	CAS Number	EPA PC Code	EPA Registered
	Copper Compounds Listed in 40 CFR 180.1021			
Basic copper carbonate	$Cu(OH)_2 \cdot CuCO_3$	1184-64-1	022901	Yes
Copper ammonium complex	$Cu(NH_3)_4^{2+}$	16828-95-8	022702	Yes
Copper ethylenediamine	$C_2H_8N_2Cu$	13426-91-0	024407	Yes
Copper hydroxide	$Cu(OH)_2$	20427-59-2	023401	Yes
Copper octanoate	$C_{16}H_{30}CuO_4$	20543-04-8	023306	Yes
Copper oxychloride	$Cu_2Cl(OH)_3$	1332-65-6	023501	Yes
Copper oxychloride sulfate	$3Cu(OH)_2 \cdot CuCl_2 + 3Cu(OH)_2 \cdot CuSO_4$	8012-69-9	023503	Yes
Copper salts of fatty and rosin acids		9007-39-0	023104	Yes
Copper sulfate basic	$3Cu(OH)_2 \cdot CuSO_4$	1344-73-6	008101	Yes
Copper sulfate pentahydrate	$CuSO_4 \cdot 5H_2O$	7758-99-8	024401	Yes
Copper oxide (cuprous)	Cu_2O	1317-39-1	025601	Yes
Cu-triethanolamine complex	$C_6H_{15}O_3NCu^{2+}$	82027-59-6	024403	Yes
Copper ethanolamine complex	$C_2H_7ONCu^{2+}$	14215-52-2	024409	Yes
	Other Copper Compounds			
Copper oxide(cupric)	CuO	1317-38-0	042401	Yes
Copper ammonium carbonate	$Cu(NH_3)(HCO_3)_2$	33113-08-5	022703	Yes
Copper chloride basic	$3Cu(OH)_2 \cdot CuCl_2$	1332-40-7	008001	No
Copper sulfate (anhydrous)	$CuSO_4$	7758-98-7	024408	No
Copper sulfate (monohydrate)	$CuSO_4 \cdot H_2O$	1332-14-5	024402	No

[1] U.S. EPA PC Code: The Office of Pesticide Programs, U.S. Environmental Protection Agency, assigns a unique six-digit number to a particular pesticide active ingredient or mixture of active ingredients. The U.S. EPA PC (Pesticide Chemical) Code is sometimes referred to as the Shaughnessy Code.

Copper Sulfate and Other Copper Products:

The Federal Insecticide, Fungicide and Rodenticide Act (FIFRA) was amended in 1988 to accelerate the reregistration of products with active ingredients registered prior to November 1, 1984. On August 3, 1996, the Food Quality Protection Act of 1996 (FQPA) was signed into law. This Act amends FIFRA and the Federal Food, Drug and Cosmetic Act (FFDCA) to require reassessment of all existing tolerances for pesticides in food. FQPA also requires EPA to review all tolerances in effect on August 2, 1996, by August 3, 2006.

The U.S. Environmental Protection Agency (U.S. EPA) completed the "Coppers Reregistration Eligibility Decision (RED)" in July 2006 and published it in August 2006. This 2006 version was revised and published in May 2009 as the "Reregistration Eligibility Decision (RED) for Coppers – Revised May 2009" (hereafter referred to in this document as RED-Cu, 2009). RED-Cu (2009) incorporated public comments received after its 2006 version was published, reflected the latest status of the Office of Pesticide Programs initiatives (namely, the Endangered Species Program), updated the list of copper compounds technical registrants to reflect the latest companies which regain copper-containing technical registrations, and considered other decisions that occurred after the 2006 version was published.

This 176-page RED-Cu (2009) included chemical overview; copper risk assessments; risk management, reregistration, and tolerance reassessment decision; and registrant's responsibilities. RED-Cu (2009) assessed human health effects resulted from both agricultural and antimicrobial applications of copper-containing products. RED-Cu (2009) assessed ecological effects resulted from agricultural applications only but not from antimicrobial applications of copper products.

Copper sulfate and other copper products given above actually are examples of copper products listed in RED-Cu (2009). As given in Table 3 (Copper compounds subject to reregistration) of RED-Cu (2009), more than 30 copper compounds were addressed, in the categories of copper sulfates, group II copper compounds, copper and oxides, copper salts, and other copper compounds. RED-Cu (2009) indicated that "agricultural copper pesticides are formulated using various forms of copper, which ultimately dissociates into the cupric ion, the active component of concern," and "although there are several forms of copper-containing active ingredients under review, the active component of toxicological interest is the cupric ion." For simplicity, copper sulfate will be used to represent copper sulfate and other copper products in this technical report, unless specifically noted.

Previous Technical Reports:

1995 Technical Advisory Panel (TAP) Review - #5 Coppers, Fixed.
2001 Crops – For use as algicide and invertebrate pest control (Copper Sulfate, 2001).

Characterization of Petitioned Substance

Composition of the Substance:

Copper sulfate, or cupric sulfate, exists as compounds with a different degree of hydration: $CuSO_4 \cdot nH_2O$. Copper oxide (CuO), or Cu(II), differs from cuprous oxide (Cu_2O), or Cu(I), by copper's oxidation status. Copper oxychloride is a compound with the chemical formula of $CuCl_2 \cdot 3Cu(OH)_2$. Copper octanoate is the copper salt of octanoic acid which is an eight-carbon saturated fatty acid known by a common name of caprylic acid.

Properties of the Substance:

The anhydrous form of copper sulfate ($CuSO_4$) is gray-white to pale green-white granules or powder or just white rhombic crystals, odorless, air sensitive, very water soluble, slightly soluble in methanol, insoluble in ethanol, and nonvolatile. The commonly encountered copper sulfate is the pentahydrate form

($CuSO_4 \cdot 5H_2O$) granules, or powder, or crystals with bright blue color, and is hygroscopic[2] (Merck, 1960; MSDS-Copper Sulfate 1; Hebert, 1993). A common natural mineral of pentahydrate copper sulfate is chalcanthite.

Copper hydroxide, $Cu(OH)_2$, is a pale blue, gelatinous solid.

Copper oxide (CuO), or cupric oxide, is a black solid. Cuprous oxide (Cu_2O) is a red-colored solid or powder and quickly changes to copper oxide in moist air. A natural mineral of cuprous oxide is the reddish mineral cuprite.

Copper oxychloride, $CuCl_2 \cdot 3Cu(OH)_2$, is a blue to green odorless powder (MSDS-Copper Oxychloride).

The commercial product of copper octanoate is a liquid (MSDS-Copper Octanoate). "Copper octanoate degrades to form free copper and the organic ligand octanoic acid. The free copper and native copper are indistinguishable and behave similarly in the natural copper cycle" (US EPA-Copper Octanoate).

Table 4 (Copper chemical properties) of RED-Cu (2009) described the chemical properties of other copper compounds.

Specific Uses of the Substance:

Copper compounds are used as fungicides, algicides, herbicides, a source of copper in animal nutrition, and as fertilizers. They are also used to kill slugs and snails in irrigation and municipal water treatment systems (Kamrin, 1997). In 2001, an additional petition to expand the use of copper sulfate for use as an algicide and to control invertebrates, specifically tadpole shrimp[3] in rice production was submitted to the National Organic Program (McElroy, 2001). This petition was approved by the National Organic Standards Board (NOSB).

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.

---

[2] Hygroscopy is the ability of a substance to attract water molecules from the surrounding environment through either absorption or adsorption.

[3] The following is quoted from Godfrey and Espino (1999): "Tadpole shrimp: Although they are crustaceans, tadpole shrimp resemble tadpoles in size, shape, color, and mobility. …… Adults deposit eggs singly on soil or on plants at the bottom of the field. They are highly resistant to drying and remain viable for several years in unflooded soil. Most of the eggs hatch 1 to 3 days after spring flooding of the rice fields, but hatching may continue for 1 to 2 weeks. The young develop rapidly by a series of molts and resemble the adults in less than 24 hours. They feed on a variety of small animals and plants commensurate with their size as they grow and molt. The somewhat transparent molt skins may be mistaken for dead shrimp. …… Tadpole shrimp cause losses in seedling rice stands in two ways. First, they may chew off the coleoptiles, roots, and leaves of the seedling, and uproot seedlings with their digging and feeding activity, all of which may kill the plants. Second, their digging activities associated with egg laying muddy the water, reducing light penetration and thereby slow the growth of the submerged seedlings. Tadpole shrimp cause no injury to rice once leaves have reached the water surface and roots are well established in the soil."

Detailed description of use profile was provided from p. 18 to p. 21 and in Appendix A (Copper refined actual use rates for crops) of RED-Cu (2009). "Copper is a broad-spectrum fungicide, bactericide, aquatic herbicide, algaecide and molluscicide for use on a variety of agricultural crops, ornamentals and turf," (RED-Cu, 2009). The maximum annual application rate for tree fruit and tree nuts was less than 20 lb Cu^{2+} A^{-1} except the application rates for papaya (21.2 lb A^{-1}), filbert (24 lb A^{-1}), walnut (32 lb A^{-1}) and mongo (48.0 lb A^{-1}). The maximum annual application rates were also listed for "field crops," "small fruits," "vegetable", "vines," "ornamentals," and "miscellaneous." The maximum rate per application was from 0.4 to 2.5 ppm for direct aquatic uses.

RED-Cu (2009) also provided estimated usage of copper pesticides. The EPA's Screening Level Usage Analysis (SLUA) for copper hydroxide on 55 crops, and for copper sulfate pentahydrate on 47 crops was listed (p. 21 of RED-Cu, 2009). "The CSTF[4] estimated that 9-11 million pounds of elemental copper in the form of copper sulfate pentahydrate are applied each year solely for algae and weed control. Applied Biochemists Company estimates that 300,000 pounds of elemental copper in various forms of complexed copper compounds are applied annually for algae and weed control," (RED-Cu, 2009). Several largest applications were oranges, walnuts, and grapefruit, almonds, tomatoes and grapes.

Approved Legal Uses of the Substance:

See below in "Status".

Action of the Substance:

The toxic action of copper is attributed to its ability to denature cellular proteins and to deactivate enzyme systems in fungi and algae. The mode of action might be that cupric ions bind to various groups including sulfidal groups, imidazoles, carboxyls, phosphate groups and thiol groups, and this binding causes non-specific denaturing of proteins and cell leakage (Caldwell et al., 2006; RED-Cu, 2009). With respect to mollusks, copper might disrupt peroxidase enzymes and affect the functioning of the surface epithelia (RED-Cu, 2009).

Status

Historic Use by Organic Growers:

Copper sulfate historically has been widely used for plant disease control, and permitted by U.S. certifiers.

U.S. Department of Agriculture:

Copper sulfate and copper products are listed in several sections of the National Organic Standards as given below:

7 CFR § 205.601 Synthetic substances allowed for use in organic crop production.

(a) As algicide, disinfectants, and sanitizer, including irrigation system cleaning systems.

(3) Copper sulfate—for use as an algicide in aquatic rice systems, is limited to one application per field during any 24-month period. Application rates are limited to those which do not increase

[4] CSTF: In support of the agricultural uses of copper, the Copper Sulfate Task Force (CSTF) was formed in 1986 to represent the interest of several registrants. There were 17 members in CSTF, as given in RED-Cu (2009).

baseline soil test values for copper over a timeframe agreed upon by the producer and accredited certifying agent.

(e) As insecticides (including acaricides or mite control).

(3) Copper sulfate—for use as tadpole shrimp control in aquatic rice production, is limited to one application per field during any 24-month period. Application rates are limited to levels which do not increase baseline soil test values for copper over a timeframe agreed upon by the producer and accredited certifying agent.

(i) As plant disease control.

(1) Coppers, fixed—copper hydroxide, copper oxide, copper oxychloride, includes products exempted from EPA tolerance, *Provided*, That, copper-based materials must be used in a manner that minimizes accumulation in the soil and shall not be used as herbicides.

(2) Copper sulfate—Substance must be used in a manner that minimizes accumulation of copper in the soil.

(j) As plant or soil amendments.

(6) Micronutrients—not to be used as a defoliant, herbicide, or desiccant. Those made from nitrates or chlorides are not allowed. Soil deficiency must be documented by testing.

(ii) Sulfates, carbonates, oxides, or silicates of zinc, copper, iron, manganese, molybdenum, selenium, and cobalt.

7 CFR § 205.603 Synthetic substances allowed for use in organic livestock production.

(b) As topical treatment, external parasiticide or local anesthetic as applicable.

(6) Copper sulfate.

U.S. Environmental Protection Agency:

Copper sulfate and other copper compounds are registered as pesticides. As given above in "Copper Sulfate and Other Copper Products," US EPA evaluated the use of copper compounds as pesticides and published "Reregistration Eligibility Decision (RED) for Coppers – Revised May 2009" (RED-Cu, 2009).

In "IV Risk Management, Reregistration, and Tolerance Reassessment Decision" of RED-Cu (2009), EPA concluded that EPA had sufficient information on the human health and ecological effects (agricultural uses only) and determined the reregistration eligibility for copper-containing products to be used for agricultural uses, provided that the risk mitigation measures outlined in RED-Cu (2009) were adopted and label amendments were made to reflect those measures. The "agricultural uses" include terrestrial and aquatic crops, direct aquatic uses, and urban uses of copper products.

In "C. Regulatory Position" of "IV Risk Management, Reregistration, and Tolerance Reassessment Decision," RED-Cu (2009) provided decisions on the following items:

1. FQPA (Food Quality Protection Act) Findings
    a. Risk Determination
    b. Determination of Safety to U.S. Population
    c. Determination of Safety to Infants and Children
2. Endocrine Disruptor Effects
3. Cumulative Risks
4. Endangered Species

Overall, the relevant risks of copper compounds are low (Hebert, 1993). In fact, two old tolerance regulations are revoked. Old regulation "40 CFR 180.136" was about the "3 ppm tolerance" for residues of basic copper carbonate in or on pears of combined copper from post-harvest, and old regulation "40 CFR 180.538" was about the "1 ppm tolerance for copper residues in potable water."

More copper compounds are added to "Table 25. List of Copper Compounds to Address under 40 CFR §180.1021(4)(b)" as it is given below. Details are given in RED-Cu (2009).

"Table 25. List of Copper Compounds to Address under 40 CFR §180.1021(4)(b)"

Chemical Name	EPA PC Code	C.A.S. Number	Comments
Basic Copper Sulfate	008101	1344-73-6	No change
Copper Sulfate Pentahydrate	024401	7758-99-8	Needs to be added
Copper Chloride	008001	1332-40-7	No change
Copper Ammonium Carbonate	022703	33113-08-5	Needs to be added
Basic Copper Carbonate (malachite)	022901	1184-64-1	No change
Copper Hydroxide	023401	20427-59-2	No change
Copper Oxychloride	023501	1332-65-6	Needs to be added
Copper Oxychloride Sulfate	023503	8012-69-9	Needs to be added
Copper Ammonia Complex	022702	16828-95-8	Needs to be added
Copper in the form of chelates of citrate and gluconate	024405	10402-15-0	Needs to be added
Cuprous Oxide	025601	1317-39-1	No change
Copper Salts of Fatty and Rosin Acids	023104	9007-39-0	Needs to be added
Copper Ethylenediamine Complex	024407	13426-91-0	No change
Copper Octanoate	023306	20543-04-8	No change
		Copper Compounds to Remove	
Cupric Oxide	042401	1317-38-0	Remove; no currently registered food uses.
Copper oleate	023304	10402-16-1	Remove; this compound was cancelled.
Copper linoleate	023303	7721-15-5	Remove; this compound was cancelled.
Bordeaux Mixture	None	None	Remove; active ingredient is copper sulfate, which is already included.
Copper Lime Mixtures	None	None	Remove; active ingredient is copper sulfate, which is already included.

After the two old tolerance regulations are revoked, several copper compounds are added, and several other copper compounds are removed, as given above in "Table 25," tolerance exemptions for residues of copper in/on plant, animal and processed commodities are established under 40 CFR180.1021. The latest 40 CFR 180.1021 is presented below.

40 CFR 180.1021 (Copper; exemption from the requirement of a tolerance

(a) Copper is exempted from the requirement of a tolerance in cattle, meat; goat, meat; hog, meat; horse, meat; sheep, meat; milk, poultry, fat; poultry, meat; poultry, meat byproducts; egg, fish, shellfish, and irrigated crops when it results from the use of:

(1) Copper sulfate as an algicide or herbicide in irrigation conveyance systems and lakes, ponds, reservoirs, or bodies of water in which fish or shellfish are cultivated.
(2) Basic copper carbonate (malachite) as an algicide or herbicide in impounded and stagnant bodies of water.
(3) Copper triethanolamine and copper monoethanolamine as an algicide or herbicide in fish hatcheries, lakes, ponds, and reservoirs.
(4) Cuprous oxide bearing antifouling coatings for control of algae or other coatings for control of algae or other organisms on submerged concrete or other (irrigation) structures.

(b) The following, copper compounds are exempt from the requirement of a tolerance when applied (primarily) as a fungicide to growing crops using good agricultural practices:

Copper compounds	**CAS Reg. No.**
Basic copper carbonate (malachite)	1184–64–1
Copper ammonia complex	16828–95–8
Copper ethylenediamine complex	13426–91–0
Copper hydroxide	20427–59–2
Copper octanoate	20543–04–8
Copper oxychloride	1332–65–6
Copper oxychloride sulfate	8012–69–9
Copper salts of fatty and rosin acids	9007–39–0
Copper sulfate basic	1344–73–6
Copper sulfate pentahydrate	7758–99–8
Cuprous oxide	1317–19–1

(c) Copper sulfate pentahydrate (CAS Reg. No. 7758–99–8) is exempt from the requirement of a tolerance when applied as a fungicide to growing crops or to raw agricultural commodities after harvest, and as a bactericide/fungicide in or on meat, fat and meat by-products of cattle, sheep, hogs, goats, horses and poultry, milk and eggs when applied as a bactericide/fungicide to animal premises and bedding.

(d) Copper (II) hydroxide (CAS Reg. No. 20427–59–2) is exempt from the requirement of a tolerance when applied to growing crops or to raw agricultural commodities as an inert ingredient (for pH control) in pesticide products.

U.S. Food and Drug Administration:

There are a number of copper compounds listed in the code of federal regulations, Title 21, Food and Drugs, which are regulated by the U.S. Food and Drug Administration. The allowable level of copper in drinking water is 1.0 mg L^{-1} (21 CFR 165.110). Copper sulfate is also a direct food substance affirmed as generally recognized as safe (GRAS) (21 CFR 184.1261).

International:

CODEX – Copper in the form of copper hydroxide, copper oxychloride, (tribasic) copper sulfate, cuprous oxide, Bordeaux mixture and Burgundy mixture are listed in Annex 2 (Permitted substances for the production of organic foods), Table 2 (Substances for plant pest and disease control) of “Guidelines for the production, processing, labeling and marketing of organically produced foods” (CODEX-GL 32, 1999).

CODEX – The proposed addition of copper octanoate to Table 2 in Annex 2 of “Guidelines for the production, processing, labeling and marketing of organically produced foods” (CODEX-GL 32, 1999) was assessed by the Food and Agriculture Organization of the United Nations in May 2010 (CODEX-CX/FL 10/38/1, 2010).

Annex II.
Copper in the form of copper hydroxide, copper oxychloride, (tribasic) copper sulphate, cuprous oxide, copper octanoate: Fungicide. Up to 6 kg copper per ha per year. For perennial crops, Member States may, by derogation from the previous paragraph, provide that the 6 kg copper limit can be exceeded in a given year provided that the average quantity actually used over a 5-year period consisting of that year and of the four preceding years does not exceed 6 kg.

European Union: European Union's regulation on organic production and labeling of organic products was published (EU-834/2007). The detailed rules for organic production and labeling were revised in September 2008 (EU-889/2008).

European Union: Copper octanoate (cupric salt of fatty acid) for organic food production was amended into Annex II of Commission Regulation (EEC) No 2092/91 (EU-404/2008).

Canada: Health Canada published a 47-page report of "Proposed re-evaluation decision – Copper pesticides" in 2009 (Copper Pesticides). Its primary status is very similar to US EPA's RED-Cu (2009), as it is stated in the document: "This program relies as much as possible on foreign reviews, typically United States Environmental Protection Agency (USEPA) Reregistration Eligibility Decision (RED) documents," and "Copper is unlikely to affect non-target organisms when used according to the revised label directions."

Evaluation Questions for Substances to be used in Organic Crop or Livestock Production

<u>Evaluation Question #1:</u> (A) Does the substance contain an active ingredient in either of the following categories: copper and sulfur compounds, toxins derived from bacteria; pheromones, soaps, horticultural oils, fish emulsions, treated seed, vitamins and minerals; livestock parasiticides and medicines and production aids including netting, tree warps and seals, insect traps, sticky barriers, row covers, and equipment cleansers? (B) Does the substance contain synthetic inert ingredients that are not classified by the EPA as inerts of toxicological concern (i.e., EPA List 4 inerts)? (7 U.S.C. § 6517(c)(1)(B)(i)). Does the synthetic substance contain inert ingredients which are not on EPA List 4, but are exempt from a requirement of a tolerance, per 40 CFR part 180?

The substance copper, addressed in RED-Cu (2009), consists of copper sulfate and its relevant hydrates, group II copper compounds (such as copper chloride, copper hydroxide, and copper oxychloride), copper oxides (such as cuprous oxide), copper metal (for antimicrobial uses only), copper salts (such as copper salts of fatty and rosin acids), and other copper compounds (such as copper octanoate). Octanoate actually is one of the copper salts of fatty acids.

Copper sulfate, $CuSO_4$, contains sulfur. A common natural mineral of pentahydrate copper sulfate is chalcanthite. Copper octanoate is also considered a "soap".

These copper compounds may be used "as is" without additional synthetic inert ingredients. Some formulated pesticide products may contain inert ingredients, in addition to copper as the active ingredient.

<u>Evaluation</u> <u>Question #2:</u> Discuss whether the petitioned substance is formulated or manufactured by a chemical process, or created by naturally occurring biological processes. (7 U.S.C. § 6502 (21)

As a pesticide, the substance copper refers to a group of copper compounds which could be manufactured or created in different ways from different sources.

Commercially, copper sulfate may be manufactured by dissolving scrap copper in hot concentrated sulfuric acid (Pimentel, 1981). It is not a simple dissolution like sugar dissolving in water. This "dissolving" is a chemical reaction in which copper metal is oxidized to cupric ions. Copper sulfate may also be the by-products from processing copper ores, which are electro-refined or electrolytically processed to produce copper metal.

Copper (II) hydroxide may be produced by mixing copper sulfate with sodium hydroxide. The solubility of copper hydroxide is much less than that of copper sulfate. When copper sulfate and sodium hydroxide are mixed, copper hydroxide is preferentially produced and precipitated out of solution. The copper in copper sulfate and in copper hydroxide is still cupric copper. Alternatively, copper hydroxide is manufactured by the electrolysis of water where copper metal is used as the anode. In this case, copper metal is converted to cupric ions in an electrochemical reaction.

Natural mineral chalcanthite is pentahydrate copper sulfate, and natural mineral hydrocyanite (Kirk-Othmer, 1982) is anhydrous copper sulfate. Copper (II) hydroxide is found in several natural minerals: azurite, malachite, antlerite, and brochantite. These naturally-occurring minerals potentially may be made into algicide or similar after proper processing such as breaking and grounding. However, natural minerals apparently contain more materials, such as several other heavy metals, than just copper compounds.

The pentahydrate salt can be dehydrated to the intermediate hydrates and the anhydrous salt. After dehydration, the chemical properties of anhydrous copper sulfate are not different from that of pentahydrate salt. Dehydration is not necessarily a chemical process.

Copper octanoate commercially is made into two copper soaps. These copper soaps are manufactured by combining a soluble copper fertilizer with a naturally-occurring fatty acid (US EPA-Copper Octanoate). Octanoic acid is readily found in coconut oils.

Evaluation Question #3: Describe the most prevalent processes used to manufacture or formulate the petitioned substance. Further, describe any chemical change that may occur during manufacture or formulation of the petitioned substance when this substance is extracted from naturally occurring plant, animal, or mineral sources. (7 U.S.C. § 6502 (21))

As mentioned in Question #2, copper sulfate pentahydrate is the most widely used form. Copper sulfate is often "the starting raw material for the production of many of the other copper salts. Today in the world there are more than 100 manufacturers and the world's consumption is around 200,000 tons per annum of which it is estimated that approximately three-quarters is used in agriculture, principally as a fungicide," according to the Copper Development Association Inc[5] (Copper.ORG, 2010).

According to (Copper.ORG, 2010), "in the production of copper sulphate virgin copper is seldom, if ever, used as the starting raw material. Copper ores are used in countries where these are mined. For the bulk of the world's production nonferrous scrap is the general source. The scrap is refined and the molten metal poured into water to produce roughly spherical porous pieces about the size of marbles which are termed 'shot'. This shot is dissolved in dilute sulphuric acid in the presence of air to produce a hot saturated liquor which, if the traditional large crystals of copper sulphate are required, is allowed to cool slowly in large cooling vats into which strips of lead are hung to provide a surface for the crystals to grow on. If the granulated (snow) crystal grades are desired, the cooling process is accelerated by agitating the liquor in water cooled vessels." In this process, the main chemical change is the oxidation of copper metal (the shot), Cu(0), to cupric ions, Cu(II).

[5] Copper.ORG (2010) claims that the Copper Development Association Inc. is "the market development, engineering and information services arm of the copper industry, chartered to enhance and expand markets for copper and its alloys in North America."

Alternatively, "other methods of production are: by heating copper scrap with sulphur to produce copper sulphide which is then oxidised to form copper sulphate, by heating copper sulphide ores to produce copper oxide which is then treated with sulphuric acid to form copper sulphate, and by slow leaching in air of piles of low grade ore (Bacterial action is sometimes employed to hasten the process. A solution of copper sulphate drains away from such heaps)" (Copper.ORG, 2010). These processes are common chemical changes of inorganic oxidations and reductions.

Evaluation Question #4: Describe the persistence or concentration of the petitioned substance and/or its by-products in the environment. (7 U.S.C. § 6518 (m) (2))

Concentration of Copper in Soil

Total Copper and Bio-available Copper: Copper is one of the minor elements found ubiquitously in natural environments. Its average concentration in the earth's crust is 58 mg kg^{-1} (Frank et al., 2005). Since copper held within aluminum-silicate minerals is not available to plants or not toxic to microorganisms, the leachable or bio-available copper[6] is pertinent to environmental issues such as toxicity or other ecological effects. The bio-available copper is one fraction of total copper in soil, but is referred as the "copper in soil."

Operationally Defined Copper in Soil: Total copper in a soil sample is not variable. Its concentration is the same, no matter how or where the soil sample is analyzed, at least conceptually. This bio-available copper is variable. The concentration of "copper in soil" depends on how copper is leached out of soil and measured, since the leaching solutions can be water only, 1 mol L^{-1} potassium acetate, concentrated nitric acid, or other leaching solutions (e.g. Bogomolov et al., 1996; Gremion et al., 2004). A "water extraction at room temperature" is a weak extraction while an "extraction with concentrated nitric acid at raised temperature" is a strong extraction.

Concentration of Copper in Soil: In Europe, copper in soil has been reported at 5-30 mg kg^{-1} in general cropland, and 100-1,500 mg kg^{-1} in vineyards (Besnard et al., 2001). US soils contain 6 to 65 mg kg^{-1} of copper (Besnard et al., 2001). The average concentration of copper is 37 mg kg^{-1} in California and about 16 mg kg^{-1} in the US soils (Holmgren et al., 1993). At the Pike Hill Copper Mine Superfund site (Orange Country, Vermont, USA) where copper ore was mined, concentrations of copper in surrounding areas were as high as 559 mg kg^{-1} (Piatak et al., 2007). The background concentrations of copper in Ontario soils commonly average less than 25 mg kg^{-1}, but can contain copper levels as high as 85 mg kg^{-1} (Ontario, 2001)

Persistence of Copper in Soil

Because copper sulfate is highly water soluble, it is considered one of the more mobile metals in soils. However, because of its binding character, its leaching potential is low in all but sandy soils. In anoxic environment where sulfide exists, copper may precipitate as copper sulfide which is very insoluble and fixed to sediment.

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).

Copper may be chelated by soil organic substances, 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 et al., 2001). Soil pH affects the availability of copper, which decreases at higher pH in calcareous soils (Andreu and Gimeno-Garcia, 1999).

[6] Bio-available copper, within this context, is the portion of copper which can be taken up into plants or affect microorganisms.

Soil erosion in hilly vineyard situations created a potential for contamination of water quality (Besnard et al., 2001).

Copper is a metal that has a potential to build up and decrease the productivity, filtering capacity, and buffering capacity of soil (Andreu and Gimeno-Garcia, 1999). This may be more of a concern in fragile ecosystems such as marsh or wetlands than rice crops. When metals such as copper are applied to 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 and Gimeno-Garcia, 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 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 and Gimeno-Garcia, 1999). Copper is found in the upper levels of the soil profile, and decreases with depth.

The environment fate of copper is further discussed in Question 9.

Factors Affecting Copper in Soil

Copper in a specific location greatly depends on the bedrock composition, weathering extent, and agricultural operations (crop rotation, fertilizer application, pesticide application, irrigation, crop harvest, etc). Copper levels in soils studied in Italy were found to be closely correlated to agricultural use (Facchinelli et al., 2000). An application of 10 lb A^{-1} of copper sulfate pentahydrate, which is 25% copper as the active ingredient, would add 2.5 lb A^{-1} of copper (Besnard et al., 2001; Gimeno-Garcia et al., 1996). Grape producers may apply 3-10 application per year of Bordeaux mix. Vineyard soils in Europe, which have seen intensive use of copper sulfate containing Bordeaux mixtures for 100 years, have concentrations ranging from 100-1,500 mg/kg in soil (Besnard et al., 2001).

<u>Evaluation Question #5:</u> Describe the toxicity, mode of action and breakdown products of the petitioned substance any known toxic or other adverse action of the substance and/or its breakdown products. (7 U.S.C. § 6518 (m) (2))

Copper is an element, it cannot break down any further via hydrolysis, metabolism, or any other degradation processes (RED-Cu, 2009).

"Products containing certain copper compounds can cause severe eye, dermal, or inhalation irritation if exposed to the handler and/or applicator of that product," according to U.S. EPA (RED-Cu, 2009). U.S. EPA "has reviewed all toxicity studies submitted for copper and has determined that the toxicological database is sufficient to assess the hazard from pesticides containing copper" (RED-Cu, 2009).

Acute Toxicity

The previous technical report (Copper Sulfate, 2001) discussed the acute toxicity of copper products.

The section "Toxicity Summary for Copper" in "III Summary of Coppers Risk Assessment" of RED-Cu (2009) indicated that humans have homeostatic capabilities to regulate copper in the system, "copper generally has low acute toxicity," and "there is no evidence of copper or its salts being carcinogenic." Endpoints were not established to quantify any potential risks from exposure to copper (RED-Cu, 2009).

Table 5 of RED-Cu (2009) listed the "Available Acute Toxicity Studies on Copper-Containing Compounds". Twenty-two copper containing compounds were listed against the items of "Acute Oral LD_{50}", "Acute Dermal LD_{50}", "Acute Inhalation", "Primary Eye Irritation", "Dermal Irritation", and "Dermal Sensitization". For example, the values for copper sulfate pentahydrate are: 450-790 mg kg^{-1} (Acute Oral

LD_{50}), > 2000 mg kg^{-1} (Acute Dermal LD_{50}), none available (Acute Inhalation), severe eye irritation day 1 to day 21 (Primary Eye Irritation), and non-irritating (Dermal Irritation). Nothing is listed for "Dermal Sensitization". Table 5 was summarized in RED-Cu (2009) as:

> "Copper generally has moderate to low toxicity (Toxicity Category II, III and IV)[7] based on acute oral, dermal and inhalation studies in animals. However, available studies indicate that some copper species may cause severe irritation (Toxicity Category I), such as copper sulfate pentahydrate, cuprous oxide, and copper 8-quinolinolate."

> "All effects resulting from acute exposure to these copper-containing pesticides are due to acute body responses to minimize excessive absorption or exposure to copper. Given the role copper plays as an essential element to the human body, its ubiquitous nature in food and drinking water, the long-standing tolerance exemptions for the pesticidal use of copper on growing crops, as well as on meat, milk, poultry, eggs, fish, shellfish, and irrigated crops, and the lack of systemic toxicity resulting from copper, a quantitative acute toxicity assessment was not conducted for acute dietary, dermal, oral or inhalation exposures. Current available data in animals do not show any evidence of upper limit toxicity level that warrant determining acute toxicity endpoints."

Sub-chronic and Chronic Toxicity

The previous technical report (Copper Sulfate, 2001) discussed the sub-chronic and chronic toxicity of copper products.

RED-Cu (2009) concluded that "based on available data, there is no evidence that warrants determining any dietary, oral, dermal or inhalation endpoints to quantify sub-chronic and chronic toxicity." Further, after providing some rational, RED-Cu (2009) indicated that "available reproductive and developmental studies by the oral route of exposure generally indicate that the main concern in animals for reproductive and teratogenic effects of copper has usually been associated with the deficiency rather than the excess of copper. Current available data in animals do not show any evidence of upper limit toxicity level that warrant determining chronic toxicity endpoints for any potential routes of exposure."

<u>Evaluation Question #6:</u> Describe any environmental contamination that could result from the petitioned substance's manufacture, use, misuse, or disposal. (7 U.S.C. § 6518 (m) (3))

As given Question #4, copper exists ubiquitously in natural environment. "Although copper pesticides have been used for over one hundred years and several million pounds of copper are applied each year, there are relatively few reported incidents associated with copper compounds," (RED-Cu, 2009). The section of "Ecological Incidents" in "III Summary of Coppers Pesticides" of RED-Cu (2009) discussed 24 incidents related to copper pesticide applications recorded in U.S. EPA's "Ecological Incident Information Systems." The most severe incident was the death of over one million fish in New York.

The event of fish kills in New York was reported by Preddice (2009) in the New York State Department of Environmental Conservation. The event occurred in the Hoosic River of Rensselaer County, New York, in 2001. Over one million of fish were killed by acidic copper sulfate solution. Details were not given in the report. According to a local news paper, about 2,000 gallons of acidic copper sulfate, used to electroplate circuit boards, was accidentally spilled from a storage building at the Oak-Mitsui plant into the Hoosic River before 3:30 am, June 28, 2001. A seven-mile stretch of the river was contaminated. Most of the aquatic life, including brown and rainbow trout, was killed (Albany Times Union, 2001).

[7] As listed in 40 CFR 156.62, U.S. EPA establishes the four toxicity categories: I, II, III and IV. Toxicity category I is highly toxic and severely irritating, category II moderately toxic and moderately irritating, category III slightly toxic and slightly irritating, and category IV practically non-toxic and not an irritant. Toxicity category III substances cause eye irritation effects but the irritation effects are reversible within seven days. Toxicity category IV substances do not cause eye irritation effects.

The report (Preddice, 2009) described the nine main causes of fish death in New York in the last ten years (2000 – 2009). Chlorine, manure, and pesticides were the leading three causes. The most significant fish kill, occurred 2001 in the Hoosic River, was not caused by a regulated use of copper sulfate as algicide or invertebrate pest control but was an accidental release of industry material to the environment, according to the local news paper.

A 23-page review on the effect of copper on freshwater food chains and salmon was given by Woody (2007).

<u>Evaluation Question #7:</u> Describe any known chemical interactions between the petitioned substance and other substances used in organic crop or livestock production or handling. Describe any environmental or human health effects from these chemical interactions. (7 U.S.C. § 6518 (m) (1))

Chemically, copper sulfate is incompatible with strong reducing reagents and incompatible with finely powdered metals. It is very corrosive to steel and iron. It can react with magnesium, phosphates, hydroxylamine, acetylene gas, hydrazine, or nitromethane. A reaction may occur if mixed with beta-naphthol, propylene glycol, sulphathiazole and triethanolamine. The pH usually needs to be greater than pH 7 before a reaction will proceed (MSDS-Copper Sulfate 1; MSDS-Copper Sulfate 2; MSDS-Copper Sulfate 3). However, these are general chemical reactions and are not specific to organic farming.

Copper is a naturally occurring substance with several oxidation states. Cupric copper has an oxidation state of +2 and is the most stable form under most environmental conditions, which is demonstrated by the natural existence of copper sulfate minerals such as chalcanthite.

Specific to agricultural applications, copper has been used as a fungicide as early as the mid-1700s, and has been used as fungicide, bactericide, aquatic herbicide, algaecide and molluscicide for use on a variety of agricultural crops, ornamentals and turf for several hundreds of years. "Unlike other pesticides for which EPA has followed a cumulative risk approach based on a common mechanism of toxicity, EPA has not made a common mechanism of toxicity finding as to the copper ion and any other substances, and the copper ion does not produce toxic metabolites produced by other substances. For the purposes of this tolerance action; therefore, EPA has not assumed that the copper ion has a common mechanism of toxicity with other substances," (RED-Cu, 2009).

<u>Evaluation Question #8:</u> Describe any effects of the petitioned substance on biological or chemical interactions in the agro-ecosystem, including physiological effects on soil organisms, crops, and/or livestock. (7 U.S.C. § 6518 (m) (5))

As noted in the 2001 petition for copper sulfate used as algicide and for tadpole shrimp control (McElroy, 2001), 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 mg kg^{-1} in California (Johnson and Grant, 1977; Fry and Mulla, 1992).

Effects on Soil Microorganisms

Copper is intended to be used as fungicides, algicides, and herbicides. The detrimental effects of copper on soil microorganisms including fungi are documented (Van-Zwieten et al., 2004; Norgrove, 2007; Lejon et al., 2008; and references cited therein). Copper was found to suppress rates of nitrogen fixation by Rhizobium under some situations at copper levels of 235 mg kg^{-1} (Obbard and Jones, 2001; Mhatre et al., 1997). 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 mg kg^{-1}) with no reduction noted up to a medium level (140 mg kg^{-1}) (Mhatre et al., 1997).

The tolerance and adaptation of soil microorganisms to heavy metals such as copper is the subject of numerous researches (Blaszak and Plewake, 2008; Leano and Pang, 2010; and the references cited therein).

Different mechanisms might explain the tolerance of soil microorganisms to copper: "the ability to passively extract metals from the cell, active transport of metal ions outside the cell, ability to mask metals by chelating them, enzymatic transformation of metal ions, creating vacuoles in which metal ions are gathered and immobilized in the form of polyphosphates, increased production of melanin and other pigments, ability to produce specific metal binding compounds inside the cell," (Blaszak and Plewake, 2008). Microorganism "community tolerance to specific metals increased the most when the same metal was added to the soil; for example, tolerance to Cu increased most in Cu-polluted treatments," (Baath et al., 1998).

The effects of copper on soil microorganisms depend on the soil (e.g. organic material content, and pH) (Lejon et al., 2008), the concentration of copper, and the species of microorganisms (Hashem, 1997; Ezzouhri et al., 2009). As in a general case, a substance's "toxic" effect depends on its application dose. Soil microorganisms are under the influence of copper already. Soil contains copper, as discussed in Question 4, in the range of tens of mg kg^{-1}. Numerous researches used much higher concentrations of copper, on the order of hundreds of mg kg^{-1}, in order to observe the expected detrimental effects of copper on soil microorganisms. For example, copper was 18 mg kg^{-1} in control soil, 125 mg kg^{-1} in treated low-Cu soil and 282 mg kg^{-1} in treated high-Cu soil in investigating the effect of metal-rich sludge amendments on the soil microbial community (Baath et al., 1998). The interpretation of experiment results was complicated by the soil moisture content, but no significant differences were observed in the microorganism activities between the control soil and the low-Cu soil.

A soil containing 6.1 mg kg^{-1} of copper was augmented to a weak soil containing 80 mg kg^{-1} of copper and a strong soil containing 500 mg kg^{-1} of copper in order to confirm the resistance of soil fungi to copper contamination (Blaszak and Plewako, 2008). A soil containing 60 mg kg^{-1} of copper was treated to contain 250 mg kg^{-1} of copper in order for confirming the copper dynamics and impact on microbial communities in soils of variable organic status (Lejon et al., 2008). A soil was treated with copper acetate to contain 770 mg kg^{-1} of copper to see the effect of copper on microorganisms in soil (Lugauskas et al., 2005).

A soil was treated with $CuSO_4$ to contain copper at following concentrations: 0 (control), 50, 100, 200, 400, and 800 mg kg^{-1}. The copper contamination in laboratory soil microcosms was investigated. "SIR (substrate-induced respiration) was the most sensitive of the parameters measured with significant effects observed at Cu concentrations as low as 50 mg kg^{-1}. Microbial biomass N and earthworm growth showed intermediate sensitivity with effects at 200 mg kg^{-1} Cu. The least sensitive organism-level parameters were soil urease activity and nematode abundance, both showing significant effects only at 800 mg kg^{-1} Cu. At the process-level, there was an inhibition of litter decomposition starting at 100 mg kg^{-1} Cu, and a sharp increase in net N mineralization at 800 mg kg^{-1} Cu," (Bogomolov et al., 1996).

Van-Zwieten et al. (2004) reviewed the copper impacts on soil biota. Significant impacts were observed when soil copper concentrations were greater than 150 mg kg^{-1}.

Soil microorganisms are most active in the surface soil and an "active" depth of top six-inch (0-15 cm) might be a fair estimate. For example, soil microorganisms were most active in the top 0-25 cm (0-9.8 inch) depth (Lugauskas et al., 2005). As discussed in Question 9, the increment of copper resulting from the application of copper at a yearly rate of 10 lb A^{-1}, is 5.3 mg kg^{-1} to the top six-inch soil. Assuming the active depth is the top 3-inch of soil, the increment of copper is 10.6 mg kg^{-1}. The application of copper to mongo trees is 48 lb A^{-1}.

Earthworms

Earthworms might be susceptible to heavy metals such as copper (Reinecke et al., 1997; Helling et al., 2000; Valenzuela, 2010). 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 (Mahrtre, 2001). In that work (Mahrtre, 2001), soil copper levels were not given, but earthworm copper contents in the low and medium sites were 90-160 mg kg^{-1} (Mahrtre, 2001).

In the experiment by Helling et al. (2000), earthworms (*Eisenia fetida*) were exposed to urine-free cattle manure substrate containing 4.02 (control), 8.92, 15.92, 39.47, 108.72, and 346.85 mg kg^{-1} of copper. The growth of earthworms at exposures between 8.92 and 108.72 mg kg^{-1} of copper, in terms of earthworm weight and mature worm percentage, was 70-80% of the growth of earthworms in the control substrate. The mature worm percentage was zero when the copper exposure was 346.85 mg kg^{-1}.

Norgrove (2007) investigated the effects of copper fungicide on earthworm activity and impacts on cocoa yield over four years. The applications rates were high (about 2.8 lb Cu A^{-1} $year^{-1}$), low (0.93 lb A^{-1} $year^{-1}$) and zero, respectively. Actually, "cocoa yields were 2.5 times greater in the high spray treatment than in the low spray treatment. There were no significant differences in cast production between cacao spray treatments in the first 3 years. In year 4 only, cast production was significantly lower in the high spray treatment than in the no-spray control," (Norgrove, 2007).

Effects on Crops

Soils contain tens of mg kg^{-1} of copper. As discussed in Question 4, copper is bound to organic materials and clay minerals, and the availability of copper to crops depends on the soil acidity. Therefore, 25-140 mg kg^{-1} of copper in acidic soils might be toxic to plants, but copper could reach 1,000 mg kg^{-1} in soil with high organic matter before phytotoxicity[8] would occur (Erich, 1994).

Rehm and Schimitt (2009) stated that "copper (Cu) is an essential nutrient for plant growth, but because only a small amount is needed, it is classified as a micronutrient. …… The amount of Cu available to plants varies widely by soils. Available Cu can vary from 1 to 200 ppm (parts per million) in both mineral and organic soils as a function of soil pH and soil texture. The finer-textured mineral soils generally contain the highest amounts of Cu. The lowest concentrations are associated with the organic or peat soils. Availability of Cu is related to soil pH. As soil pH increases, the availability of this nutrient decreases. Copper is not mobile in soils. It is attracted to soil organic matter and clay minerals."

For crops of alfalfa, corn, soybeans, and wheat, the amount of copper is "deficient" at concentrations less than 2-5 mg kg^{-1}, "low" at concentrations of 2-9 mg kg^{-1}, "sufficient" at concentrations of 5-30 mg kg^{-1}, "high" at concentrations of 20-50 mg kg^{-1}, and "excessive" at concentrations greater than 50 mg kg^{-1} (Rehm and Schimitt, 2009).

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 et al., 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. Copper 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 et al., 2001).

<u>Evaluation Question #9:</u> Discuss and summarize findings on whether the petitioned substance may be harmful to the environment. (7 U.S.C. § 6517 (c) (1) (A) (i) and 7 U.S.C. § 6517 (c) (2) (A) (i))

US EPA's RED-Cu (2009) discussed the harmful effects on human being, terrestrial organisms, and aquatic organisms (as detailed below in "Ecological Exposure and Risk"), but it indicated that "the antimicrobial ecological assessment of copper compounds will be conducted at a later date." The effects of copper on soil microorganisms including fungi were discussed in Question 8.

---

[8] Phytotoxicity: is a term used to describe the degree of toxic effect by a compound on plant growth. Such damage may be caused by a wide variety of compounds, including trace metals, pesticides, salinity, phytotoxin or allelopthy.

Copper in Soil

As given in Question #4, copper, at concentrations of tens of mg kg^{-1}, exits ubiquitously in natural environment, and is one of the minor to trace components in soil.

Addition of Copper to Soil

Copper used as a fungicide is applied as a foliar spray. Eventually, the applied copper ends up in the surface soil if not assimilated by plants and removed as crops. The application rate of copper to crops is expressed as pound of cupric ions per acre (lb $Cu^{2+}A^{-1}$) which is 454 g $Cu^{2+}A^{-1}$ (or 1.12 mg dm^{-2}). The soil cultivation depth is typically considered as six inches (or 1.52 dm)[9]. Assuming a soil density of 1400 g dm^{-3}, an application rate of 1 lb A^{-1} is equivalent to an addition of 0.526 mg kg^{-1} to the top six-inch soil.

Most of the maximum annual application rates, as given in Appendix A of RED-Cu (2009), are less than 5 lbs A^{-1} for field crops and vegetable (clover, corn, soybean, asparagus, bean, carrot, etc), less than 10 lbs A^{-1} for small fruits (blueberry, strawberry), and less than 5-10 lbs A^{-1} for other crops. The equivalent addition of copper to soil, at an application rate of 10 lbs A^{-1}, is 5.3 mg kg^{-1} to the top six-inch soil.

The application rates are 10-20 lbs A^{-1} for tree nuts (avocado, olive, coffee, etc). The highest rate, 48 lbs A^{-1}, is applied to mango. Tree roots extend much deeper in soil than other crop roots such as carrot, in terms of taking nutrients (or toxic substance) from soil. The corresponding addition of copper to soil is on the order of several mg kg^{-1}.

Removal of Copper from Soil by Crops

Normal concentration of copper in plants is 5-20 mg kg^{-1}. For a quick estimation, the crop yields and copper concentrations from a paper about copper uptake by Reddy et al. (1989) are used here.

	Grain yield (kg ha^{-1})	Leaf Cu (mg kg^{-1})	Stem Cu (mg kg^{-1})	Grain Cu (mg kg^{-1})
Soybeans	2988	14.4	11.4	19.9
Corn	3407	13.0	5.0	1.0

One acre is 0.404 hectares. The removal of copper was 24 g A^{-1} by soybean grains or 1.4 g A^{-1} by corn grains. The total removal of copper by soybean grain, leaf, and stem might not be greater than 300 g A^{-1} (or 0.5 lbs A^{-1}). The total removal of copper by corn might also not likely to be greater than 300 g A^{-1} (or 0.5 lbs A^{-1}).

Environmental Fate – Crop and Soil Application

The mobility of copper in soil depends on soil pH, soil composition (e.g. organic material, clay minerals), and agricultural operations (e.g. crop rotation, irrigation), as discussed in Question 4. "Because copper is an element, it cannot break down any further via hydrolysis, metabolism, or any other degradation processes. The free cupric ion has a high sorption affinity for soil, sediments and organic matter, and copper applied to the surface is not expected to readily move into groundwater" (RED-Cu, 2009).

[9] A certain soil depth is needed to correlate an application value which is mass per area (lb A^{-1}) to a concentration which is mass per volume (or mass per mass, mg kg^{-1}). Relevant to issues of plant nutrient or toxicity, a 6-inch (or 1-foot) depth is used for discussion simplicity and is assumed as the soil depth most (crop) plant roots would extend to (take nutrients or toxic from). Tree roots extend much deeper than 6 inches.

As given above, the majority of applied copper as a pesticide would remain in soil, resulting in an increase of copper concentration in soil over time with continued applications. Furthermore, "since copper is a naturally occurring element, there are always background concentrations of copper from which point and non-point sources cannot easily be distinguished. Aside from natural environmental releases of copper, there are other sources, such as pesticides, anti-foulants and wood preservatives, leaching from mining operations, industrial runoff, architectural uses, and brake pads. Therefore, concentrations of copper measured in soil or water can also reflect other point or non-point sources of copper besides pesticides," (RED-Cu, 2009).

"Copper is an essential nutrient required for proper homeostasis in all organisms. Most organisms have homeostatic mechanisms to process excess copper or to manage the deficiency of copper levels" (RED-Cu 2009). Copper toxicity to crops might be possible if copper use is unregulated (Stehouwer and Roth, 2004). "Copper deficiencies are rare in Wisconsin. Most verified cases have involved small grains, lettuce, or onion grown in acid organic soils. Copper toxicity in some sandy soils has resulted from repeated use of copper-containing fungicides over many years," (Schulte and Kelling, 1999).

Environmental Fate – Water Application

An application rate of one pound per acre (1 lb Cu^{2+} A^{-1}, or 1.12 mg dm^{-2}) is equivalent to an addition of one mg kg^{-1} (one ppm) of copper to 0.112 m-deep water. An application rate of 18 lb A^{-1} is needed to add one ppm of copper to a 2-meter deep pond. The target concentrations of copper are 0.1-1 ppm for algae and aquatic weeds control, and 1-2.5 ppm for snails, leeches, and other similar organism's control. Appendix A of RED-Cu (2009) listed several direct aquatic application rates.

The average concentration of dissolved copper in several hundreds of surface water samples collected nationwide was 2.61 μg L^{-1} (ppb) (Table 7 of RED-Cu, 2009). Therefore, a direct aquatic application of copper, at ppm level, could cause a great disturbance to natural ecology in terms of copper concentration if released without further treatment.

The fate of copper applied to water bodies could be quite complicated. Affecting factors could include copper compound (salts, oxides, hydroxides, and organic complexes), water pH, water redox potential (surface water is usually oxic, but deep water, or water containing high concentrations of dissolved organic materials, could be anoxic or even contain sulfide), concentration of suspended material, concentration of dissolved organic carbon and competing ligands, and other factors such as water movement. The fate of copper would become very mobile, stay as dissolved or be fixed to bottom sediment. In a no-outlet pond, the applied copper might eventually be deposited to the bottom sediment. Depending on the applied amount (proportional to targeted concentration and water depth), the accumulation of copper to bottom sediment could be significant, especially since the deposition of copper would be limited to the very top layer of sediment. For example, an application rate of 17 lb A^{-1} would be equivalent to an addition of 27 mg kg^{-1} of copper to the top 5-cm (about two inches) of sediment.

"Copper is an essential nutrient required for proper homeostasis in all organisms. Most organisms have homeostatic mechanisms to process excess copper or to manage the deficiency of copper levels. However, aquatic animals are exposed to copper by more than just dietary routes, and are more sensitive to copper than terrestrial animals. The mode of toxicity for aquatic organisms is different than for terrestrial animals in that copper rapidly binds and causes damage to the gill membranes, and interferes with osmoregulatory processes. Aquatic plants, which are target organisms for most direct aquatic uses of copper, are also more sensitive to copper than terrestrial plants," (RED-Cu, 2009). With a direct aquatic application, all are affected, including fish, invertebrates, and plants. A 23-page review on the effect of copper on freshwater food chains and salmon was given by Woody (2007).

The tolerances of these organisms to copper may vary, and some non-target species may be eliminated while targeted species are controlled. "The potential risk to aquatic organisms must be considered in conjunction with the environmental benefit intended for some uses of copper. Excessive algal growth in lakes or ponds caused by high nutrient input can damage aquatic life by causing high oxygen demand, in some cases leading to eutrophication. In other cases, copper is used to control invasive aquatic plants which can out-compete and replace native plants, changing the ecosystem and reducing food sources for aquatic and terrestrial animals in or near the water. The use of copper for control of parasites (through snail control) benefits swimmers in recreational waters and fish that can be infected" (RED-Cu, 2009).

Ecological Exposure and Risk

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 (Copper Sulfate, 2001; 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 mg kg^{-1} in acidic mineral soils. It is less available in soils rich in organic matter. Levels in soil with high organic matter could reach 1000 mg kg^{-1} before phytotoxicity would occur (Erich 1994).

Effects on Birds: Copper sulfate is considered to be nontoxic to birds. It poses less of a threat to birds than to other animals. The lowest lethal dose is 1000 mg kg^{-1} in pigeons and 600 mg kg^{-1} in ducks. The oral LD_{50} for Bordeaux mixture in young mallards is 2000 mg kg^{-1} (Copper Sulfate, 2001; 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. Wurts provided the application rate of copper sulfate with respect to fish species and water alkalinity (Wurts). 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 LC_{50} of copper sulfate to pond snails is 0.39 mg L^{-1} (ppm) at 20°C. Higher concentrations of the material caused some behavioral changes, such as secretion of mucous, and discharge of eggs and embryos.

The previous Technical Advisory Panel (TAP) Review for Copper Sulfate, as an algicide and invertebrate pest control, indicated that bees might be endangered by Bordeaux mixture (Copper Sulfate, 2001). However, RED-Cu (2009) indicated that "available data from a honey bee acute toxicity study indicated that copper is practically nontoxic to honey bees, with an acute LD_{50} > 100 µg/bee."

As it was given in Question #6, copper pesticides have been used for over one hundred years, but there were relatively few reported incidents associated with copper compounds.

Models were used by U.S. EPA to assess the ecological exposure and risk of copper application. The contents covered are:

a. Aquatic organisms
    1. Freshwater fish and invertebrates (Agricultural uses, exposure via spray drift, uncertainties in freshwater animal risk assessment, aquatic uses, and urban uses)
    2. Freshwater plants
    3. Estuarine/marine fish and invertebrates
    4. Estuarine/marine plants
b. Terrestrial Organisms
    1. Birds and mammals (Copper exposure to birds and mammals, toxicity to birds and mammals, risk to birds and mammals, birds-orchard applications, birds-row crop applications, mammals-orchard applications, and mammals-row crop applications)
    2. Nontarget insects
    3. Terrestrial plants
c. Endangered species
    1. Terrestrial organisms (Mammals, and birds)
    2. Aquatic organisms (Freshwater animals, estuarine/marine, and plants)

Selection of models, parameters of models, interpretation of modeling results, and limitations of models are discussed in p. 35-59 of RED-Cu (2009).

Evaluation Question #10: Describe and summarize any reported effects upon human health from use of the petitioned substance. (7 U.S.C. § 6517 (c) (1) (A) (i), 7 U.S.C. § 6517 (c) (2) (A) (i)) and 7 U.S.C. § 6518 (m) (4))

In "III Summary of Coppers Risk Assessments" of RED-Cu (2009), human health risk, after aggregate or combined exposure to copper compounds, was adequately assessed. The basic considerations are that copper is naturally-occurring, ubiquitous in environment, copper itself is a nutrient, copper deficiency is more of a problem than copper over-exposure, the active assimilation of copper through routes of food, drink, air, non-occupational sources, and other exposure is efficiently modulated, excessively available copper is not assimilated but instead is actively excreted, and no systematic and carcinogenic effects are observed/confirmed. The overall conclusion is that copper, when used as pesticide following the label, would not cause toxic effects.

Humans are exposed to copper primarily from food (organ meats, seafood, beans, nuts, and whole grains), and drinking water sources, as well as in the air. The estimated total daily oral intake of copper is between 1 and 2 mg day^{-1}. These values are higher than the recommended dietary allowance (RDA) of copper, as established by the National Academy of Science, ranging from 0.34 mg day^{-1} in young children to 1.3 mg day^{-1} for pregnant and lactating females. In a number of clinical trials, copper doses of 2-10 milligrams by mouth were safely used in patients (Hopkins Technology).

However, copper deficiency seems a more consistent problem. RED-Cu (2009) stated that "the mechanisms for regulating total copper in the body appear to be efficient in maintaining a generally consistent level of copper needed for homeostasis. The efficiency of copper absorption varies greatly, depending on dietary intake. When dietary copper is high and more copper is absorbed, mainly through the gastrointestinal tract, excretion of copper from the body increases, protecting against excess accumulation of copper in the body. Depending on the copper status in the body at the time, approximately 20 to 60% of dietary copper may be absorbed. Copper absorption is also affected by other factors such as species, age, chemical form, and pregnancy. When copper intake is low, little copper is excreted from the body, protecting against copper depletion. Generally, current available data and literature studies indicate that there is a greater risk from the deficiency of copper intake than from excess intake. A deficiency of copper or a defect in copper carrying proteins may result in symptoms such as anemia, defective blood vessel development, or connective tissue symptoms."

Evaluation Question #11: Describe all natural (non-synthetic) substances or products which may be used in place of a petitioned substance. (7 U.S.C. § 6517 (c) (1) (A) (ii)) Provide a list of allowed substances that may be used in place of the petitioned substance. (7 U.S.C. § 6518 (m) (6))

Elemental sulfur and liquid lime sulfur, as well as copper compounds, are used as standard fungicides for many years in organic production systems (Organic Production 1; Organic Production 2). Copper sulfate and copper hydroxide exist as natural minerals, as discussed in Question #2. Copper and sulfur products have different degrees of effectiveness for specific diseases on various crops (Caldwell et al., 2006). As given below, the use of copper sulfate still possesses several advantages.

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, 1997; Boyer et al., 1994). Increasing concern about long-term build up in soil is particularly evident in Europe, where a history of high application rates has occurred. EU was supposed to propose a complete ban on all copper use, scheduled to take effect in May 2002 (Copper Sulfate, 2001). Instead, Commission Regulation (EC) No. 889/2008 was published in September 2008, setting maximum limits for copper accumulation as 6 kg Cu/ha per year (5.36 lb A^{-1}), and added copper octanoate (cupric salt of fatty acid) for organic food production in 2009. This adjustment was assessed by the Food and Agriculture Organization of the United Nations in May 2010 (CODEX-CX/FL 10/38/1, 2010).

Copper is very limited in mobility and availability in the soil, particularly in high pH soils and in association with high 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.

U.S. EPA recognized the advantages of using copper pesticides (RED-Cu, 2009):

> "Through extensive outreach to the public as well as additional comments and refined information provided by the user community, the Agency has determined that there are many benefits that support the significance and continued agricultural uses of copper pesticides. A significant benefit is that copper exposure from all sources, including use as a pesticide in agricultural settings, does not pose any human health concerns. Although there is still potential for ecological effects to non-target organisms, there are many benefits to retain agricultural uses of copper pesticides."

One of the benefits, for example, is that "based on its history of use for many centuries, there is little evidence to indicate any significant pest-resistance problems. … …. Coppers are used in some Integrated Pest Management (IPM) systems, alternated with some systemic fungicides that have a high risk of developing resistance or have shown early indications of some pesticide resistance," (RED-Cu, 2009).

The specific areas where the benefits of coppers are significant were given by (RED-Cu, 2009) (p. 69-p. 72):

a. Benefits of Copper Pesticides
   1. Terrestrial Uses
   2. Aquatic Weeds and Algae: Aquaculture, drinking water, irrigation/conveyance systems, and quiescent water bodies (recreational, ornamental). Alternatives
   3. Aquatic Invertebrate Control (Leech, tadpole shrimp, and freshwater snails)

Evaluation Question #12: Describe any alternative practices that would make the use of the petitioned substance unnecessary. (7 U.S.C. § 6518 (m) (6))

Several strategies for organic crops are rotating crops, selecting resistant plants and cultivars, keeping out any materials that are contaminated with pathogens or diseased plants, finding disease suppressive soils, managing nutrients, and controlling diseases, such as given in "Plant disease management for organic crops" by Koike et al. (2000), "Sustainable management of soil-borne plant diseases" by Sullivan (2004), and "Pesticides and organic farming – a last resort" by Soil Association – Organic Standard (Soil Association-Information Sheet).

Plant diseases may be managed by the "Strategies of Integrated Pest Management" (IPM). IPM "is an effective and environmentally sensitive approach to pest management that relies on a combination of common-sense practices. IPM programs use current, comprehensive information on the life cycles of pests and their interaction with the environment. This information, in combination with available pest control methods, is used to manage pest damage by the most economical means, and with the least possible hazard to people, property, and the environment. The IPM approach can be applied to both agricultural and non-agricultural settings, such as the home, garden, and workplace. IPM takes advantage of all appropriate pest management options including, but not limited to, the judicious use of pesticides. In contrast, *organic* food production applies many of the same concepts as IPM but limits the use of pesticides to those that are produced from natural sources, as opposed to synthetic chemicals," (US EPA–IPM).

A "Database of IPM Resources (DIR)" (Vegetable-IPM) is provided by the Integrated Plant Protection Center – Oregon State University, including sources of information for vegetable disease control methods.

Crop rotation

Crop rotation is that the succeeding crops are of a different genus, species, subspecies, or variety than the previous crop on a field. Some benefits of crop rotation are the reduced insect and disease problems, and beneficial residual herbicide carryover (Peel, 1998; Ashley, 1994.)

The initial petition (McElroy, 2001) submitted to National Organic Program to expand the use of copper sulfate notes that occasional use of copper sulfate is needed in situations where rice is directly seeded into flooded fields. Direct-seeding is common in the Americas, southern Europe, Australia, India, Sri Lanka, Malaysia and Thailand (Luh, 1991). It is done where production is highly mechanized, but labor is not available or economically justified for direct transplanting.

Cultural Control

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).

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 after flooding reduces the potential for plant injury. Extension publications recommend seeding basins in sequence as they fill with water. However, windy weather conditions can prevent the seeding operation from happening in a timely way.

Draining Control

Since tadpole shrimp are aquatic in their damaging stage, draining is an alternative to chemical control. The draining should not take place until four to five 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. Tadpole 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 tadpole shrimp from previously unhatched eggs, but they would be in noneconomic numbers and less likely to damage the older, firmer rooted seedlings.

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 (Godfrey and Espino, 1999).

Alternate Flooding and Draining

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.

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 and Mulla, 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.

Organic Apple Project

REPCO was a project conducted in EU to contribute to the replacement of copper fungicides in organic agriculture by new measures for control of downy mildew in grapevine and scab in apple. A 70-page report was produced (Kohl, 2007). The report covered the project from November 1, 2003 to October 31, 2007. It suggested that the project results "strongly support EU policies to replace the use of copper fungicides in organic agriculture in near future." The REPCO project resulted in finding "a number of potential new compounds, Yucca extracts, and a formulated antagonist with high potentials for future scab control," (Heijne et al., 2008). However, as given above in "International" status, copper sulfate is still accepted by CODEX and European Union.

Primary disease organisms of concern in Michigan are apple scab and fire blight. Farmers have options in managing these diseases including: "1) varieties of apples that have varying degrees of resistance to the pathogens; 2) hygienic practices and scouting that limit that quantity of inoculum in and around the orchard; 3) a system of forecasting when cumulative environmental factors favor an infection by the pathogen; and 4) once such conditions are forecasted, spray applications may reduce infection," (Schwaillier, 2006). The four approved spray products are lime-sulfur, copper, Serenade, and compost tea. Copper is used for very high risk of the disease infection.

The document of "Disease management guidelines for organic apple production in Ohio" (Ellis, 2008) provided excellent contents such as "Disease that need to be considered within the IPM program," "Disease management options for organic production systems," and "Approaches toward reducing the use of fungicides for scab control." It also provided links for additional information about "Organic insect and disease management." The documents of "Organic small fruit disease management guidelines" (Organic Production 1) and "Integrated management of grape diseases" (Organic Production 2) provided information about fungicides for use in organic production systems. For example, ten "alternative disease control products" were discussed in these documents.

Additional information about tree fruits are available from "Backyard orchard: apples and pears," (Swift et al., 2007), "Using common pesticides on backyard tree fruits," (Longstroth, 2007), "Home tree & small fruit pest management guide," (Faubert et al., 2000), and "Disease management for fruit trees after crop loss," (Beckerman, 2010).

References

Albany Times Union. **2001**. Article: Spill was plant's second shock to Hoosic River. (Main). *Albany Times Union (Albany, NY)*. July 3, 2001. http://www.highbeam.com/doc/1G1-157494824.html

Andreu V and Gimeno-Garcia E. **1999**. Evolution of heavy metals in marsh areas under rice farming. *Environmental Pollution*, 104, 271-282.

Ashley RA. **1994**. Having problems controlling vegetable crop diseases – Try rotation. *University of Connecticut*. http://www.hort.uconn.edu/ipm/veg/htms/rotate.htm

Baath E, Diaz-Ravina M, Frostegard A and Campbell C. **1998**. Effect of metal-rich sludge amendments on the soil microbial community. *Appl. Environ. Micro.*, 64, 238-245.

Beckerman J. **2010**. Disease management for fruit trees after crop loss. *Perdue University – Extension*. http://www.extension.purdue.edu/extmedia/BP/BP-179-W.pdf

Besnard E, Chenu C and Robert M. **2001**. Influence of organic amendments on copper distribution among particle-size and density fractions in Champagne vineyard soils. *Environmental Pollution*, 112, 329-337.

Blaszak M and Plewako M. **2008**. Resistance of soil fungi to copper contamination. *Polish J. Natural Sci.,* 23, 635-644.

Bogomolov DM, Chen SK, Parmelee RW, Subler S and Edwards CA. **1996**. An ecosystem approach to soil toxicity testing: a study of copper contamination in laboratory soil microcosms. *Appl. Soil Ecol*., 4, 95-105.

Boyer J, Christup J, Trusty G. and Uddameri V. **1994**. Copper fungicides and certifiable organic produce - A report to the Maine Organic Farmers and Growers Association (part of petition and original 1995 TAP review).

Brun LA, Maillet J, Hinsinger P. and Pepin M. **2001**. Evaluation of copper availability to plants in copper-contaminated vineyard soils. *Environmental Pollution,* 111, 293-302.

Caldwell B, Brown Rosen E, Sideman E, Shelton AM and Smart CD. **2006**. Resource guide for organic insect and disease management. *Cornell University NYS Agricultural Experiment Station*. http://www.nysaes.cornell.edu/pp/resourceguide/index.php

CODEX-GL 32. **1999**. Guidelines for the production, processing, labeling and marketing of organically produced foods. *CODEX. Joint FAO/WHO Food Standards Programme*. GL 32-1999. Adopted 1999. Revisions 2001, 2003, 2004 and 2007. Amendments 2008, 2009 and 2010. http://www.codexalimentarius.net/download/standards/360/cxg_032e.pdf

CODEX-CX/FL 10/38/1, **2010**. Joint FAO/WHO food standards programme – CODEX Committee on food labeling. *CODEX. Joint FAO/WHO Food Standards Programme*. CODEX. 38th Session. CX/FL 10/38/1

Copper.ORG. **2010**. Uses of copper compounds: Copper sulphate. *Copper Development Association Inc.* http://www.copper.org/applications/compounds/copper_sulfate01.html

Copper Pesticides. **2009**. Proposed Re-evaluation Decision – Copper Pesticides - PRVD2009-04. Canada. Health Canada. February 2009. http://www.hc-sc.gc.ca/cps-spc/pest/part/consultations/_prvd2009-04/copper-cuivre-eng.php

Copper Sulfate. **2001**. Copper sulfate, as algicide and invertebrate pest control. NOSB TAP Review *Compiled by OMRI* (http://www.ams.usda.gov/AMSv1.0/getfile?dDocName=STELPRDC5067070).

Ellis MA. **2008**. Disease management guidelines for organic apple production in Ohio. *Ohio State University.* Department of Plant Pathology. http://www.caf.wvu.edu/kearneysville/organic-apple.html#Links

Erich S. **1994**. Copper fungicides and certifiable organic produce: a report to the Maine organic farmers and growers association. In the petition to NOSB: McElroy, 2001. p. 27 – 53.

EU-404/2008. **2008**. Commission regulation (EC) No 404/2008 of 6 May 2008 amending Annex II to Council Regulation (EEC) No 2092/91 on organic production of agricultural products as concerns the authorization of spinosad, potassium bicarbonate and copper octanoate and the use of ethylene. *Official Journal of the European Union*. OJ L 120/8. 7.5.2008.

EU-834/2007. **2007**. Regulations – Council regulation (EC) No 834/2007 of 28 June 2007 on organic production and labeling of organic products and repealing regulation (EEC No 2092/91. *Official Journal of the European Union*. OJ L 189/1. 20.7.2007

EU-889/2008. **2008**. Regulations – Council regulation (EC) No 889/2008 of 5 September 2008 laying down detailed rules for the implementation of Council Regulation (EC) no 834/2007 on organic production and labeling of organic products with regard to organic production, labeling and control. *Official Journal of the European Union*. OJ L 250/1. 18.9.2008.

Ezzouhri L, Castro E, Moya M, Espinola F andLairini K. **2009**. Heavy metal tolerance of filamentous fungi isolated from polluted sites in Tangier, Morocco. *African J. Microbiol. Res*., 3, 35-48.

Facchinelli A, Sacchi E and Mallen L. **2001**. Multivariate statistical and GIS - based approach to identify heavy metal sources in soils. *Environmental Pollution*, 114, 313-324.

Faubert HH, Alm SR, Wallace DB, Casagrande RA and Tewksbury L. **2000**. Home tree & small fruit pest management guide. *University of Rhode Island.* http://www.uri.edu/ce/factsheets/sheets/fruitsprayguide.html

Frank D, Galloway J and Assmus K. **2005**. The life cycle of a mineral deposit – A teacher's guide for hands on mineral education activities. *U.S. Department of the Interior, U.S. Geological Survey.* General Information Product 17.

Fry L and Mulla MS. **1992**. Effect of drying period and soil moisture on egg hatch of the tadpole shrimp (Notostraca: Tripdisidae). *Journal of Economic Entomology,* 85, 65-69.

Gimeno-Garcia E, Andreu V. and Boluda R. **1996**. Heavy metals incidence in the application of inorganic fertilizers and pesticides to rice farming soils. *Environmental Pollution*, 92, 19-25.

Godfrey LD and Espino LA. **1999**. Rice – Tadpole shrimp. *UC IPM Online. US-Davis* http://www.ipm.ucdavis.edu/PMG/r682500111.html

Gremion F, Chatzinotas A, Kaufmann K, Von Sigler V and Harms H. **2004**. Impacts of heavy metal contamination and phytoremediation on a microbial community during a twelve-month microcosm experiment. *FEMS Micro. Ecolo*., 48, 273-283.

Hashem AR. **1997**. Effect of heavy metal ions on the mycelia growth of some fungi isolated from the soil of Al-Jubail Industrial City, Saudi Arabia. *J. King Saud. Univ*., 9, 119-124.

Hebert C. **1993**. NTP Technical report on toxicity studies of cupric sulfate (CAs no. 7758-99-8) administered in drinking water and feed to F344/N rats and BGC3F mice. *Toxic Rep. Ser*., 29, 1-D3.

Heijne B, de Jong PF, Trapman M, Lindhard Pdeersen H, Paaske K, Bengtsson M, Hockenhull J, Eiben U and Kohl J. **2008**. EU-Project replacement of copper fungicides in organic production of apple (REPCO): Strategy against apple scab and results. *International Society for Horticultural Science Commission.* Organic Fruit Conference. June 16^{th} – 17^{th}, 2008. Vignola. http://www.ifoam.org/events/ifoam_conferences/owc/modules/abstracts_pdfs/heijne_fruit_pap.doc-FC.pdf

Helling B, Reinecke SA and Reinecke AJ. **2000**. Effects of the fungicide copper oxychloride on the growth and reproduction of *Eisenia fetida* (Oligochaeta). *Ecotoxicol. Environ. Saf*., 46, 108-116.

Holmgren, G.G.S., Meyer, M.W., Chaney, R.L. and Daniesl, R.B. **1993**. Cadmium, lead, zinc, copper, and nickel in agricultural soils of the United States of America. *Journal Environmental Quality,* 22, 335-348.

Hopkins Technology. Copper. *Hopkins Technology LLC*. http://www.hoptechno.com/book29m.htm

Igarashi, K. **1985**. Ecological studies on Triops cancriformis (Bosc) inhabiting Shonai district, Japan. VI. Oscillation of biomass and biological control of weeds in paddy. *Journal-of-the-Yamagata-Agriculture-and-Forestry-Society*., No.42, 35-42.

Johnson, C.R. and Grant, C.D. **1977**. The effects of copper sulphate exposure on thermal tolerance, orientation and survival in adult mosquitofish, *Gambusia affinis*, and juvenile threespined sticklebacks, *Gasterosteus aculeatus*. Proceedings and papers of the Forty-fifth Annual Conferenc of the Californian Mosquito and Vector Control Association Inc. February 13-16 1977. pp. 66-68.

Kamrin, M.A. **1997**. Pesticide profiles - Toxicity environmental impact, and fate. *CRC-Lewis Publishers, Boca Raton FL*. pp. 421-578.

Kirk-Othmer. **1982**. Encyclopedia of Chemical Technology, 3rd Ed. *John Wiley and Sons NY* (included in the petition by McElroy, 2001).

Kohl J. **2007**. REPCO – Replacement of copper fungicides in organic production of grapevine and apple in Europe. REPCO. http://www.pri.wur.nl/NR/rdonlyres/2A128277-9900-436F-85FD-C82998B022C2/69863/REPCOFinal_executive_summaryJ%C3%BCrgenK%C3%B6hl.pdf

Koike, S.T., Gaskell, M., Fouche, C., Smith, R. and Mitchell, J. **2002**. Plant disease management for organic crops. *University of California*. http://ucanr.org/freepubs/docs/7252.pdf

Leano EM and Pang KL. **2010**. Effect of copper(II), lead(II), and Zn(II) on growth and sporulation of Halophytophthora from Taiwan Mangrove. *Water Air Soil Pollut*., 213, 85-93.

Lejon DPH, Martins JMF, Leveque J, Spadini L, Pascault N, Landry D, Milloux M, Nowak V, Chaussod R and Ranjard L. **2008**. Copper dynamics and impact on microbial communities in soils of variable organic stutus. *Environ. Sci. Technol*., 42, 2819-2825.

Longstroth M. **2009**. Using common pesticides on backyard tree fruits. *Michigan University – Extension*. http://www.canr.msu.edu/vanburen/fhtrespry1.htm

Lugauskas A, Levinskaite L, Peeiulyte D, Repeekiene J, Motuzas A, Vaisvalavieius R and Prosyeevas I. **2005**. Effect of copper, zinc and lead acetates on microorganisms in soil. *Ekologija*, 1, 61-69.

Luh, B.S. Ed. **1991**. Rice. Volume I, Production. *Van Nostrand Reinhold, NY* pp. 155 – 179.

Matsunaka, S. **1976**. Tadpole shrimp: a biological tool of weed control in transplanted rice fields. *Proceedings-of-5th- Asian-Pacific-Weed-Science-Society-Conference-Tokyo-Japan-1975*. p. 439-443.

McElroy B. **2001**. Petition for copper sulfate in crop production – To add another annotation. California Certified Organic Farmers. http://www.ams.usda.gov/AMSv1.0/getfile?dDocName=STELPRDC5067032&acct=nopgeninfo

Merck Index. **1960**. *Merck Index of Chemicals and Drugs*. 7th ed. Merck Inc., Rahway, NJ. 1642 pp.

Mhatre, G.N. and Pankhurst, C.E. **1997**. Bioindicators to detect contamination of soils with special reference to heavy metals. In *Biological Indicators of Soil Health*, Pankhurst C.E., B.M Doube, V.V.Gupta, eds. CAB International, Wallingford UK.

MSDS-Copper Octanoate. Copper soap fungicide. Woodstream Corporation. PA. http://www.biconet.com/disease/infosheets/CopperSoapFungicide.pdf

MSDS-Copper Oxychloride. Copper oxychloride. Jummel Croton Inc., NJ http://www.axxousa.com/msds/msdsp/cuoxcl_p.html

MSDS-Copper Sulfate 1. CAS Registry Number: 7758-99-8. National Toxicology Program http://ntp.niehs.nih.gov/index.cfm?objectid=E882F73B-BDB5-82F8-F38750006C2E67E8

MSDS-Copper Sulfate 2. Copper (II) sulfate pentahydrate. Fisher Scientific. http://avogadro.chem.iastate.edu/MSDS/CuSO4-5H2O.htm

MSDS-Copper Sulfate 3. Safety data for copper (II) sulfate. *Oxford University. The Physical and Theoretical Chemistry Laboratory*. http://msds.chem.ox.ac.uk/CO/copper_II_sulfate.html

Norgrove L. **2007**. Effects of different copper fungicide application rates upon earthworm activity and impacts on cocoa yield over four years. *Eruopean J. Soil Biol*., 43, S303-S310.

Obbard, J.P. and Jones, K.C. **2001**. Measurement of symbiotic nitrogen-fixation in leguminous host-plants grown in heavy metal-contaminated soils amended with sewage sludge. *Environmental Pollution*, 111, 311-320.

Ontario. **2001**. Ontario Fact Sheet - Copper in the environment. *Government of Ontario, Canada. Ministry fo the Environment Programs and Initiatives.* http://www.ene.gov.on.ca/cons/4141e.htm

Organic Production 1. Organic small fruit disease management guidelines – Fungicides for use in organic production systems. *Ohio State University.* http://www.oardc.ohio-state.edu/fruitpathology/organic/fungicidesystems.htm

Organic Production 2. Integrated management of grape diseases. *Ohio State University.* http://www.oardc.ohio-state.edu/fruitpathology/organic/grape/organic.html

Peel MD. **1998**. Crop rotations for increased productivity. *North Dakota State University.* http://www.ag.ndsu.edu/pubs/plantsci/crops/eb48-1.htm

Piatak NM, Seal II RR, Hammarstrom JM, Kiah RG, Deacon JR, Adams M, Anthony MW, Briggs PH and Jackson JC. **2007**. Geochemical characterization of mine waste, mine drainage, and stream sediments at the Pike Hill copper mine superfund site, Orange County, Vermont. *U.S. Department of the Interior, U.S. Geological Survey. Scientific Investigation Report*. 2006-5303.

Preddice TL. **2009**. New York State Fish Minorities, 2009 – A summary report for fishery managers, staff & administrators. *Ney York State Department of Environmental Conservation*. *Albany, New York.* http://www.dec.ny.gov/docs/fish_marine_pdf/fishkills2009.pdf

RED-Cu. **2009**. Reregistration eligibility decision (RED) for coppers. U.S. EPA, May 2009 http://nepis.epa.gov - enter search terms : RED Copper 2009

Reddy, M.R., Lameck, D. and Rezania, M.E. **1989**. Uptake and distribution of copper and zinc by soybean and corn from soil treated with sewage sludge. *Plant and Soil,* 113, 271-274.

Rehm G and Schimitt M. **2009**. Copper for crop production. University of Minnesota. July 2009 http://www.extension.umn.edu/distribution/cropsystems/DC6790.html

Reinecke AJ, Reinecke SA and Lambrechts H. **1997**. Uptake and toxicity of copper and zinc for the African earthworm, *Eudrilus eugeniae* (Oligochaeta). *Biol. Fert. Soils*, 24, 27-31.

Schulte, E. E., Kelling, K.A., **1999**. Soil and Applied Copper. *University of Wisconcin-Extension*, A2527. http://www.soils.wisc.edu/extension/pubs/A2527.pdf

Schwaillier P. **2006**. Control of apple scab and fire blight. *Michigan State University*. http://www.organicfruit.msu.edu/objectives.htm

Sittig, **1980**. Pesticide Manufacturing and Toxic Materials Control Encyclopedia. *Noyes Data Corp*., Park Ridge NJ.

Soil Association-Information Sheet. Pestcides and organic farming – a last resort. *Soil Association – Organic Standard.* http://www.usaid.gov/our_work/environment/compliance/ane/workshops/Jordan2007/day3/Q/PesticidesOrganicLastResort.pdf

Stehouwer R and Roth G. **2004**. Copper sulfate hoof baths and copper toxicity in soil. *PennState-College of Agricultural Sciences.* http://www.das.psu.edu/news/dd200403-03

Sullivan, P. **2004**. Sustainable management of soil-borne plant diseases. *National Sustainable Agriculture Information Service*. http://www.attra.org/attra-pub/soilborne.html

Swift CE, Hammon R and Larsen HG. **2007**. Backyard orchard: Apples and pears. *Colorado State University-Extension*. http://www.ext.colostate.edu/pubs/garden/02800.html

US EPA-Copper Octanoate. Pestcide Fact Sheet - Copper Octanoate. *US EPA-Office of Prevention,* Pesticide and Toxic Substances (7501C).

US EPA-IPM. Integrated pest management (IPM) principles. *U.S. Environmental Protection Agency*. http://www.epa.gov/pesticides/factsheets/ipm.htm

Valenzuela H. **2010**. Earthworms in the farm. *University of Hawaii at Manoa*. http://www.ctahr.hawaii.edu/sustainag/news/articles/V5-Valenzuela-worm.pdf

Van-Zwieten L, Merrington G and Van-Zwieten M. **2004**. Review of impacts on soil biota caused by copper residues from fungicide application. *Super Soil 2004. 3rd Australian New Zealand Soils Conference. University of Sydney, Australia.* http://www.regional.org.au/au/asssi/supersoil2004/s3/oral/1573_vanzwieten.htm

Vegetable-IPM. Database of IPM resources (DIR) – Vegetable IPM. *Oregon State University. Integrated Plant Protection Center*. http://ipmnet.org/cicp/vegetable/vegindex.htm

Yonekura, M. **1979**. Biological control of weeds by tadpole shrimps in paddy field - weed efficacy of tadpole shrimps in transplanted rice fields. *Weed-Research-Japan*, 24, 64-68.

Woody CA. **2007**. Copper – Effects on freshwater food chains and salmon: A review. Fisheries Research and Consulting. http://www.fish4thefuture.com/pdfs/Woody_Copper_Effects_to_Fish%20-%20FINAL2007.pdf

Wurts WA. Update: Use of bluestone (copper sulfate) for algae control. Kentucky State University. Cooperative Extension Program. http://www.ca.uky.edu/wkrec/bluestone.pdf