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Agency

Prevention, Pesticides  
and Toxic Substances  
(7508P)

EPA 738-R-06-020  
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# Reregistration Eligibility Decision (RED) for Coppers

**REREGISTRATION ELIGIBILITY DECISION  
FOR COPPERS**

Case Nos. 0636, 0649, 4025, 4026

Approved by:

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Date

## TABLE OF CONTENTS

Glossary of Terms and Abbreviations .....	3
EXECUTIVE SUMMARY .....	5
I. Introduction .....	10
II. Chemical Overview .....	12
A. Regulatory History .....	12
B. Chemical Identification .....	12
C. Use Profile .....	15
D. Estimated Usage of Copper Pesticides .....	18
III. Summary of Coppers Risk Assessments .....	22
A. Human Health Risk Assessment .....	22
1. Background on Copper .....	23
2. Exposure Sources of Copper .....	23
3. Human Metabolism of Copper .....	23
4. Toxicity Summary for Copper .....	24
5. FQPA Safety Factor Considerations .....	28
6. Aggregate Risk from Coppers (Dietary and Residential) .....	29
7. Occupational Exposure .....	29
8. Incidence Data on Copper Exposure .....	29
B. Ecological Risk Assessment .....	30
1. Environmental Fate .....	31
2. Ecological Exposure and Risk .....	32
3. Ecological Incidents .....	56
A. Determination of Reregistration Eligibility .....	58
B. Public Comments and Responses .....	58
C. Regulatory Position .....	59
1. FQPA Findings .....	59
2. Endocrine Disruptor Effects .....	60
3. Cumulative Risks .....	60
D. Tolerance Reassessment Summary .....	61
1. Tolerances Proposed to be Revoked .....	61
2. Tolerances Listed Under 40 CFR §180.1021 .....	62
E. Regulatory Rationale .....	63
1. Human Health Risk Management .....	63
2. Ecological Risk Management for Non-target Organisms .....	65
3. Urban Uses .....	75
4. Advisory Language .....	77
5. 303(d) - Designated Impaired Water Bodies .....	78
V. What Registrants Need to Do .....	82
A. Manufacturing-Use Products .....	82
1. Generic Data Requirements .....	82
2. Labeling for Manufacturing-Use Products .....	82
B. End-Use Products .....	82
1. Additional Product-Specific Data Requirements .....	82
2. Labeling for End-Use Products .....	83
C. Labeling Changes Summary Table .....	83

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## Glossary of Terms and Abbreviations

ai	Active Ingredient
aPAD	Acute Population Adjusted Dose
APHIS	Animal and Plant Health Inspection Service
ARTF	Agricultural Re-entry Task Force
BCF	Bioconcentration Factor
CDC	Centers for Disease Control
CDPR	California Department of Pesticide Regulation
CFR	Code of Federal Regulations
ChEI	Cholinesterase Inhibition
CMBS	Carbamate Market Basket Survey
cPAD	Chronic Population Adjusted Dose
CSFII	USDA Continuing Surveys for Food Intake by Individuals
CWS	Community Water System
DCI	Data Call-In
DEEM	Dietary Exposure Evaluation Model
DL	Double layer clothing {i.e., coveralls over SL}
EC	Emulsifiable Concentrate Formulation
EDSP	Endocrine Disruptor Screening Program
EDSTAC	Endocrine Disruptor Screening and Testing Advisory Committee
EEC	Estimated Environmental Concentration. The estimated pesticide concentration in an environment, such as a terrestrial ecosystem.
EP	End-Use Product
EPA	U.S. Environmental Protection Agency
EXAMS	Tier II Surface Water Computer Model
FDA	Food and Drug Administration
FFDCA	Federal Food, Drug, and Cosmetic Act
FIFRA	Federal Insecticide, Fungicide, and Rodenticide Act
FOB	Functional Observation Battery
FQPA	Food Quality Protection Act
FR	Federal Register
GL	With gloves
IDFS	Incident Data System
IPM	Integrated Pest Management
RED	Reregistration Eligibility Decision
LADD	Lifetime Average Daily Dose
LC <sub>50</sub>	Median Lethal Concentration. Statistically derived concentration of a substance expected to cause death in 50% of test animals, usually expressed as the weight of substance per weight or volume of water, air or feed, e.g., mg/l, mg/kg or ppm.
LD <sub>50</sub>	Median Lethal Dose. Statistically derived single dose causing death in 50% of the test animals when administered by the route indicated (oral, dermal, inhalation), expressed as a weight of substance per unit weight of animal, e.g., mg/kg.
LOAEC	Lowest Observed Adverse Effect Concentration
LOAEL	Lowest Observed Adverse Effect Level
LOC	Level of Concern
LOEC	Lowest Observed Effect Concentration
mg/kg/day	Milligram Per Kilogram Per Day
MOE	Margin of Exposure
MP	Manufacturing-Use Product
MRID	Master Record Identification (number). EPA's system of recording and tracking studies submitted.
MRL	Maximum Residue Level
N/A	Not Applicable
NASS	National Agricultural Statistical Service
NAWQA	USGS National Water Quality Assessment
NG	No Gloves

NMFS	National Marine Fisheries Service
NOAEC	No Observed Adverse Effect Concentration
NOAEL	No Observed Adverse Effect Level
NPIC	National Pesticide Information Center
NR	No respirator
OPP	EPA Office of Pesticide Programs
ORETF	Outdoor Residential Exposure Task Force
PAD	Population Adjusted Dose
PCA	Percent Crop Area
PDCI	Product Specific Data Call-In
PDP	USDA Pesticide Data Program
PF10	Protections factor 10 respirator
PF5	Protection factor 5 respirator
PHED	Pesticide Handler's Exposure Data
PHI	Preharvest Interval
ppb	Parts Per Billion
PPE	Personal Protective Equipment
PRZM	Pesticide Root Zone Model
RBC	Red Blood Cell
RED	Reregistration Eligibility Decision
REI	Restricted Entry Interval
RfD	Reference Dose
RPA	Reasonable and Prudent Alternatives
RQ	Risk Quotient
RTU	(Ready-to-use)
RUP	Restricted Use Pesticide
SCI-GROW	Tier I Ground Water Computer Model
SF	Safety Factor
SL	Single layer clothing
SLN	Special Local Need (Registrations Under Section 24(c) of FIFRA)
TEP	Typical End-Use Product
TGAI	Technical Grade Active Ingredient
TTRS	Transferable Turf Residues
UF	Uncertainty Factor
USDA	United States Department of Agriculture
USFWS	United States Fish and Wildlife Service
USGS	United States Geological Survey
WPS	Worker Protection Standard

## EXECUTIVE SUMMARY

EPA has completed its review of public comments on the revised copper risk assessments and is issuing its risk management decision for conventional (agricultural) uses of copper pesticides. There are currently three tolerances being reassessed for coppers. The revised risk assessments are based on review of the required target data base supporting the use patterns of currently registered products and additional information received. After considering the risks identified in the revised risk assessments, comments, and mitigation suggestions from interested parties, EPA developed its risk management decision for uses of copper that pose risks of concern. As a result, the Agency has determined that the agricultural uses of copper-containing products are eligible for reregistration provided that data needs are addressed, risk mitigation measures outlined in this document are adopted, and labels are amended accordingly. The decision is discussed fully in this document.

Copper pesticides (copper or cupric ion) are extensively used in various agricultural settings. Tens of millions of pounds are applied annually, predominantly in crop and algaecide applications. Major crops and/or crops with high application rates include citrus, tree nuts, tomato, pepper, grape, berries and peach. Included in the scope of the ecological risk assessments are its use as a broad-spectrum fungicide on many food and ornamental crops, and direct water applications as an algaecide, aquatic herbicide, bactericide and molluscicide. Coppers also have residential uses as a garden and lawn fungicide and as a root-killer in sewer systems. Coppers are also registered for antimicrobial applications, including uses as an anti-foulant and preservative in wood and other materials. Although there are several forms of copper-containing active ingredients under review, the active component of toxicological interest is the cupric ion. Within the scope of this Reregistration Eligibility Decision (RED), the human health assessment addressed cupric ion sources from both agricultural and antimicrobial applications of copper-containing products, whereas the ecological assessment addresses agricultural uses only. The Agency will complete its ecological assessment on antimicrobial applications of copper products at a later date in a separate document.

### Risk Summary

Copper is a naturally occurring metal that is efficiently regulated in the human system and current available literature and studies do not indicate any systemic toxicity associated with copper exposure. Thus, a qualitative human health assessment was conducted. Copper dietary exposures do not pose any risks of concern. There are no residential or occupational risks of concern resulting from exposure to copper products. Because several current agricultural product labels do not specify typical application rates, minimum retreatment intervals or frequency of treatments, the Agency made several assumptions on how coppers were applied to assess potential exposure to non-target organisms. Based on these conservative assumptions, the screening-level ecological assessment indicated that copper can pose acute risks to various organisms, with the greatest risk to aquatic organisms resulting from direct water applications and runoff from fields adjacent to water bodies.

**Dietary Risk.** Acute and chronic dietary (food and drinking water) risks from copper pesticides are not of concern to the Agency. Copper is ubiquitous and naturally occurs in many food

sources such as nuts, organ meats and grains. Humans have the capability to metabolize and regulate copper levels in the body. Given the role copper plays as an essential element to the human body, its ubiquitous nature in food and drinking water, and the lack of systemic toxicity resulting from copper, acute and chronic dietary endpoints were not selected. Thus, a quantitative toxicity assessment was not conducted for dietary, dermal, oral or inhalation exposures.

**Occupational and Residential Risk.** Some copper species may cause acute dermal and eye irritation in exposed individuals. Workers can be exposed to copper pesticides through mixing, loading and/or applying the pesticide (handlers) or re-entering treated sites. Exposure may also occur to residential handlers from home-use products. The irritating effects of individual coppers are addressed through appropriate Personal Protective Equipment (PPE) or precautionary labeling language for occupational or residential users, respectively. Since no systemic toxicological endpoints of concern were identified for dermal exposures to coppers, no dermal, oral or inhalation endpoints of toxicological concern were established. Occupational and residential exposures to copper pesticides are not of concern to the Agency.

**Aggregate Risk.** Aggregate risk refers to the combined risk from dietary (food and drinking water) and residential or other non-occupational exposures. Aggregate risk can result from one-time (acute), short-term or chronic exposures. Because of the lack of systemic toxicity, copper exposures from combined sources do not pose any health risks of concern.

**Ecological Risk.** The ecological risk assessment addresses only agricultural and direct aquatic uses of copper-containing pesticides. The Biotic-Ligand Model was used to assess potential exposures and risk to freshwater aquatic animals, whereas standard available models were used to assess exposures to all other freshwater and marine/estuarine non-target organisms.

Terrestrial Organisms. The screening-level ecological risk assessment suggests potential risk to terrestrial animals exposed to copper resulting from use as an agricultural pesticide. Risk quotients (RQs) reflecting dietary exposure and toxicity to birds and mammals exceed both acute and chronic levels-of-concern (LOCs). The ecological risk assessment presents both maximum labeled rates and average typical application rates for terrestrial crops. Mitigation measures which will reduce the maximum application rates for crop uses of coppers down to levels similar to the typical rates evaluated result in significantly reduced acute and chronic RQs, but these RQs still exceed acute and chronic LOCs for most feed items and weight classes of animals considered.

There is some uncertainty in the finding of risk to birds and mammals because although copper is toxic at high concentrations, it is also an important essential trace element for organisms. Animals have the ability to cope with some amount of excess copper exposure by storing it in the liver and bone marrow. As indicated by the laboratory toxicity studies, exposure to high levels of copper in the diet can overwhelm the ability of birds and mammals to maintain homeostasis. However, animals which are repeatedly exposed to levels of copper which do not cause permanent harm may undergo enzymatic adaptation which allows them to cope with greater levels of exposure.



RQs based on limited toxicity data for terrestrial plants do not exceed the acute LOC from exposure through spray drift. Available data from a honey bee acute toxicity study indicated that copper is practically nontoxic to honey bees. However, because exposure estimates for other insects cannot readily be determined, the potential risk of copper pesticides to other insects is unknown.

Aquatic Organisms. Aquatic organisms also require some amount of copper as a nutrient, but the main cause of copper toxicity to aquatic organisms is through rapid binding to the gill membranes, which causes damage and interferes with osmoregulatory processes. Copper in the water column occurs as dissolved ions and as a part of inorganic and organic complexes. The toxic form of copper in water is the cupric ion. The amount of cupric ion in the environment, and its toxicity to aquatic animals through gill damage, is dependent on a number of water quality parameters including pH, alkalinity, and dissolved organic carbon.

The screening-level ecological risk assessment considered a wide range of water chemistries, as represented by 811 water samples collected by the United States Geological Survey nationwide. Risk to freshwater animals is presented as a percentage of the 811 resulting RQs which exceed either acute or chronic levels of concern. Since the model used to perform this analysis cannot currently be used for aquatic plants or estuarine/marine animals, these were assessed using a single RQ per taxon.

Fewer than 1% of the 811 RQs for freshwater fish exceed the acute level of concern for application rates up to 7.5 pounds of metallic copper per acre (lbs Cu<sup>2+</sup>/A); the percentage exceeding the chronic LOC ranges from 0% at 1 lb Cu<sup>2+</sup>/A to 5.3% at 7.5 lbs Cu<sup>2+</sup>/A. Almost all revised maximum application rates for agricultural pesticidal uses of copper fall below 7.5 lbs Cu<sup>2+</sup>/A. There is a greater percentage of RQs which exceed LOCs for freshwater invertebrates. At 1.0 lb Cu<sup>2+</sup>/A, 3.2% and 4.2% of the 811 RQs exceed the acute and chronic LOCs, respectively. At 7.5 lbs Cu<sup>2+</sup>/A, these percentages increase to 25% and 32%, respectively. RQs for freshwater non-vascular plants exceed the acute LOC for application rates of 1.5 lbs Cu<sup>2+</sup>/A or greater, and acute and chronic LOCs for estuarine/marine animals at rates of about 3.0 lbs Cu<sup>2+</sup>/A and above. The screening assessment does not indicate a risk to freshwater vascular plants or estuarine/marine plants.

The percentage of freshwater animal RQs exceeding acute and chronic LOCs and the magnitude of RQs for other aquatic organisms at revised application rates are significantly reduced from those derived for maximum application rates on current copper pesticide labels. Advisory language describing conditions which might result in greater spray drift of copper to water bodies will help reduce that potential exposure. In addition, advisory language will be added which describes the water quality conditions which would likely result in greater concentrations and toxicity of copper in nearby water bodies.

The risk assessment concludes that direct water applications of copper would result in greater than 95% of RQs exceeding acute and chronic LOCs for freshwater fish, invertebrates and plants. The risk assessment assumes treatment of an entire water body to achieve the maximum application rate, a water concentration of 1 ppm. Even with input from the user community indicating that standard practice for most aquatic uses requires a lower application

rate, and treatment of only a portion (up to 25-33%) of a water body at a time, direct aquatic applications may result in risk to aquatic organisms. Treatment of only a portion of a water body may allow fish and some invertebrates to leave the area being treated. Those that do not, or cannot leave the treated area, may be at risk of adverse effects.

**Benefits of Copper Use.** Copper is significant as a cost-effective pesticide on crops and for direct aquatic applications with no toxicity concerns to humans. The use of coppers on agricultural crops as a fungicide and bactericide is significant to growers, as copper is generally cost-effective, broad-spectrum, and in some cases the only available pesticide to manage the target pest(s). Coppers are also among the few pesticides that are permitted for use on crops with organic certifications. Copper products are used extensively for the management of nuisance algae, aquatic weeds, mollusks, leeches. Algae and aquatic weeds may block and restrict water quality and flow in irrigation and drinking water systems, which would require much costlier management measures if these pests are not properly controlled. Algae may also produce various toxic chemicals that may cause various problems for humans and animals, ranging from dermal reactions to more severe toxicity problems, and in some cases, death for exposed animals. Catfish aquaculture relies on copper sulfate to manage algae that may produce toxins that cause off-flavors, rendering the entire fish crop unmarketable. Management of aquatic pests is important for drinking water quality, as well as recreational waters to manage snail populations that may host schistosomes that cause Swimmer's Itch, and leeches.

**Endangered Species.** At certain application rates, risk quotients in the screening-level risk assessment for coppers exceed acute and chronic LOCs for various listed species of animals and plants, should exposure actually occur. Acute and chronic LOCs are exceeded for birds, mammals, and marine/estuarine fish and invertebrates. Freshwater non-vascular plants exceed the acute LOCs. Screening-level modeling indicates that a number of sites exceed the endangered species LOC for freshwater fish and invertebrates. Further, potential indirect effects to any listed species dependent upon a species that experiences effects from use of copper can not be precluded based on the screening level ecological risk assessment. These findings are based solely on EPA's screening-level assessment and do not constitute "may affect" findings under the Endangered Species Act for any listed species. If the Agency determines that the use of copper "may affect" listed species or their designated critical habitat, EPA will employ provisions in the Services regulations (50 CFR Part 402). Until species and site-specific analyses are complete, the risk mitigation measures being implemented in this RED will reduce the likelihood that endangered and threatened species may be exposed to copper at levels of concern.

**Regulatory Decision.** The Agency has determined that all agricultural uses (terrestrial and aquatic crops, bactericide on crops, urban fungicide, and sewer root-killer treatment) of copper pesticides are eligible for reregistration provided that the risk mitigation measures and label refinements outlined in this document are adopted, and label amendments are made to reflect these measures.

**Mitigation Summary.** Because of the high number of registered crop sites, the Agency assessed a subset of crops based on high application rates, high frequency of applications, and/or high usage of copper products on that particular crop. EPA worked with the registrants and USDA to

conduct extensive outreach efforts to the user community for additional refined information on the actual use and needs of copper pesticides. Based on use information from the user community, refined data indicated that most typical use rates are significantly lower than current labeled maximum use rates. As a result, the registrants have agreed to refine their labels by reducing application rates, defining application intervals, and determining seasonal maximum application rates. Additional use pattern details for each crop are described in Appendix A.

Label language restricting spray applications of copper pesticides under certain weather conditions, and advisory language describing steps users can take to minimize spray drift, will be added to the agricultural use labels for copper pesticides. Registrants of copper-based pesticides will be required to provide spray drift study data to fulfill guideline requirements. In addition, advisory language will be added to copper pesticide product labels to inform users of surface water quality conditions which can lead to greater bioavailability and toxicity of copper to non-target aquatic organisms.

**Next Steps.** The Agency is issuing this RED document for public comment for agricultural uses of copper pesticides as announced in a *Notice of Availability* in the **Federal Register**. In the future, EPA intends to issue product-specific DCIs (PDCI) for data necessary to complete product reregistration for agricultural end-use products containing copper.

## **I. Introduction**

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. The amended Act calls for the development and submission of data to support the reregistration of an active ingredient, as well as a review of all submitted data by the U.S. Environmental Protection Agency (EPA or the Agency). Reregistration involves a thorough review of the scientific database underlying a pesticide's registration. The purpose of the Agency's review is to reassess the potential risks arising from the currently registered uses of the pesticide, to determine the need for additional data on health and environmental effects, and to determine whether or not the pesticide meets the "no unreasonable adverse effects" criteria of FIFRA.

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. In reassessing these tolerances, the Agency must consider, among other things, aggregate risks from non-occupational sources of pesticide exposure, whether there is increased susceptibility to infants and children, and the cumulative effects of pesticides with a common mechanism of toxicity. When a safety finding has been made that aggregate risks are not of concern and the Agency concludes that there is a reasonable certainty of no harm from aggregate exposure, the tolerances are considered reassessed. EPA decided that, for those chemicals that have tolerances and are undergoing reregistration, tolerance reassessment will be accomplished through the reregistration process.

As mentioned above, FQPA requires EPA to consider available information concerning the cumulative effects of a particular pesticide's residues and "other substances that have a common mechanism of toxicity" when considering whether to establish, modify, or revoke a tolerance. The reason for consideration of other substances is due to the possibility that low-level exposures to multiple chemical substances that cause a common toxic effect by a common toxic mechanism could lead to the same adverse health effect as would a higher level of exposure to any of the substances individually. 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.

This document presents EPA's revised human health and ecological risk assessments, its progress toward tolerance reassessment, and the RED for agricultural uses of copper. The ecological risk assessment addressing antimicrobial applications of copper will be assessed at a later date. The Agency worked extensively with the registrants, USDA and the grower community to reach the decisions as outlined in the RED. The document consists of six sections. Section I contains the regulatory framework for reregistration tolerance reassessment. Section II provides a profile of the use and usage of the chemical. Section III gives an overview of the revised human health and ecological risk assessments based on submitted data, public comments,

input and data received as a result of extensive communications with the grower community through USDA, and other information received in response to the preliminary risk assessments. Section IV presents the Agency's reregistration eligibility and risk management decisions. Section V summarizes label changes necessary to implement the risk mitigation measures outlined in Section IV. Section VI contains the Appendices, which list related information, supporting documents, and studies evaluated for the reregistration decision. The revised risk assessments for copper are available in the Federal Public Docket, under docket number EPA-HQ-OPP-2005-0558, at [www.regulations.gov](http://www.regulations.gov).

## II. Chemical Overview

### A. Regulatory History

The first recorded use of copper as a fungicide was in the mid-1700s, treating cereal seeds with copper sulfate pentahydrate to control stinking smut or bunt. In the 1880s, the French scientist Pierre Marie Alexis Millardet discovered the broad-spectrum fungicidal properties of copper from the use of copper sulfate in the form of Bordeaux mixture (copper sulfate, hydrated lime and water). The first registration for a copper-containing pesticide was issued in 1956. Currently, 16 copper active ingredients (ai) have active food use registrations subject to tolerance reassessment and reregistration review.

EPA issued Registration Standards for copper sulfate in March 1986, *Guidance for the Reregistration of Pesticide Products Containing Copper Sulfate as the Active Ingredient*, and for the Group II copper compounds, *Guidance for the Reregistration of Pesticide Products Containing Group II Copper Compounds as the Active Ingredient* in April 1987. As a result, Generic Data Call-In (GDCI) notices were issued in 1987 to the registrants for various copper compounds to submit data in support of reregistration.

These comprehensive DCIs required various ecological fate and effects studies. Additional DCIs were issued in 1993, which required various product chemistry studies, avian toxicity studies and residue studies. These DCIs were issued so that data required by 40 CFR Part 158 would be available to EPA before reregistration occurred.

### B. Chemical Identification

Agricultural copper pesticides are formulated using various forms of copper, which ultimately dissociates into the cupric ion, the active component of concern. Copper is a broad-spectrum fungicide, bactericide, aquatic herbicide, algacide and molluscicide for use on a variety of agricultural crops, ornamentals and turf.

**Common Name:** Copper

**Trade Names:** Major trade names include Kocide, CuproFix, Basicop, K-Tea, Cutrine Ultra, and Triangle Brand.

#### **Technical Registrants:**

In support of the agricultural uses of copper, the Copper Sulfate Task Force (CSTF) was formed in 1986 to represent the interests of several registrants. The current members of the CSTF are listed below.

#### Copper Sulfate Task Force Members (agricultural applications)

Albaugh, Inc.  
Cerexagri, Inc.

NuFarm Americas, Inc.  
Old Bridge Chemicals

Chem One Ltd.  
Chemical Specialties, Inc.  
Drexel Chemical Company  
Fabrica de Sulfato el Aguila S.A. de C.V.  
Griffin L.L.C.  
Isagro Copper S.p.A.  
Micro-Flo Company  
Nordox Industrier AS,  
c/o Monterey Chemical Co.

PBI/Gordon  
Phelps Dodge Sales Co., Inc.  
Phibro-Tech, Inc.  
Quimetal Industrial S.A.  
Spiess-Urania Chemicals GMBH  
Teck Cominco American, Inc.

Copper Reregistration Task Force (antimicrobial applications)

FULL MEMBERS:

American Chemet Corporation  
Arch Wood Protection, Inc.  
Bardylke Chemicals Ltd.  
Chemical Specialties, Inc.  
J.H. Baxter & Company  
Nordox AS

Osmose, Inc.  
Peninsula Copper Industries  
Peninsula Copper Industries  
Rohm and Haas Company  
SCM Metal Products, Inc.

ASSOCIATE MEMBERS:

International Paint LLC (Akzo Nobel Chemicals Inc.)  
ISP Minerals

Non-Task Force Members

Applied Biochemists

Table 1 lists the copper pesticides and its respective cases that are addressed in the RED.

**Table 1. Copper Compounds Subject to Reregistration.**

Case	Chemical Name	EPA PC Code	C.A.S. Number	Registrants	
Copper Sulfates #0636	Basic Copper Sulfate	008101	1344-73-6	CSTF	
	Copper Sulfate Pentahydrate	024001	7758-99-8		
	Copper sulfate monohydrate	024402	1332-14-5	Cancelled	
	Copper sulfate Anhydrous	024408	7758-98-7		
Group II Copper Compounds #0649	Copper Chloride	008001	1332-40-7	CSTF	
	Copper Ammonium Carbonate	022703	33113-08-5		
	Basic Copper Carbonate	022901	1184-64-1	CSTF	
	Copper Hydroxide	023401	20427-59-2		
	Copper Oxychloride	023501	1332-65-6		
	Copper Oxychloride Sulfate	023503	8012-69-9		
	Copper Ammonia Complex	022702	16828-95-8		
	Chelates of Copper Copper Gluconate	023305	814-91-5	CSTF	
	Copper chloride dihydrate	023701	10125-13-0	Cancelled	
	Copper Nitrate	076102	3251-23-8		
	Copper Oxalate	023305	814-91-5		
	Chelates of copper citrate	044005	10402-15-0		
	Copper and Oxides #4025	Cuprous Oxide	025601	1317-39-1	CRTF
Antimicrobial Uses Only					
Copper (metal)		022501	7440-50-8	CRTF	
Cupric Oxide	042401	1317-38-0			
Copper Salts #4026	Copper Salts of Fatty and Rosin Acids	023104	9007-39-0	CSTF	
	Copper Ethylenediamine	024407	13426-91-0	Applied Biochemists	
	Copper Triethanolamine Complex	024403	82027-59-6		
	Copper 2-ethylhexanoate (hexanoic acid)	041201	22221-10-9	Cancelled	
	Copper etidronic acid complex	024404	50376-91-5		
	Copper dehydroabietyl ammonium 2-ethylhexanoate	041202	53404-24-3		
	Copper ethylenediaminetetraacetate (EDTA)	039105	12276-01-6	Unsupported	
	Copper linoleate	023303	7721-15-5	Cancelled	
	Copper oleate	023304	10402-16-1		
	Copper salts of the Acids of Tall Oil	023103	61789-22-8		
	Cupric ferric subsulfate complex	042402	12168-20-6		
	Antimicrobial Uses Only				CRTF
	Copper Naphthenate	023102	1338-02-9		
Copper 8-quinolinolate	024002	10380-28-6			
Other Copper Compounds	Copper Octanoate	023306	20543-04-8	CSTF	
	Copper Ethanolamine Complex	024409	14215-52-2	Applied Biochemists	



**Case Numbers:** Reregistration cases included in the scope of this RED includes #0636, #0649, #4025, #4026, and other food-use copper compounds.

**Chemical Properties:** Table 2 describes the chemical properties for each of the copper compounds that have registered food uses.

**Table 2. Copper Chemical Properties**

Common name	Formula*	Molecular weight*	Percent Copper*
Copper sulfate pentahydrate	CuSO <sub>4</sub> · 5H <sub>2</sub> O	249.65	25.4
Basic copper sulfate	3Cu(OH) <sub>2</sub> · CuSO <sub>4</sub>	468.29	54.2
Copper hydroxide	Cu(OH) <sub>2</sub>	81.56	77.9
Cuprous oxide	Cu <sub>2</sub> O	143.08	88.8
Copper carbonate	Cu(OH) <sub>2</sub> CuCO <sub>3</sub>	221.12	57.5
Copper ammonium complex	Cu(NH <sub>3</sub> ) <sub>4</sub> <sup>2+</sup>	131.58	48.3
Copper ammonium carbonate complex	CuNH <sub>3</sub> (HCO <sub>3</sub> ) <sub>2</sub>	190.54	33.3
Basic copper chloride	3 Cu(OH) <sub>2</sub> · CuCl <sub>2</sub>	427.133	59.5
Copper oxychloride	Cu <sub>2</sub> Cl(OH) <sub>3</sub>	213.57	59.5
Copper oxychloride sulfate	3Cu(OH) <sub>2</sub> · CuCl <sub>2</sub> + 3Cu(OH) <sub>2</sub> · CuSO <sub>4</sub>	879.43	57.8
Copper salts of fatty and rosin acids	Mixture of compounds	NA	NA
Copper ethylenediamine	C <sub>2</sub> H <sub>8</sub> N <sub>2</sub> Cu	123.54	51.43
Copper triethanolamine complex	C <sub>6</sub> H <sub>15</sub> O <sub>3</sub> NCu <sup>+2</sup>	212.54	29.89
Copper ethanolamine complex	C <sub>2</sub> H <sub>7</sub> ONCu <sup>+2</sup>	124.54	51.01
Copper octanoate	C <sub>8</sub> H <sub>16</sub> O <sub>2</sub> Cu	207.54	30.61

\*approximate formula, may vary slightly depending on manufacturing processes, molecular weight and percent copper calculated based on formula

### C. Use Profile

Copper is a broad-spectrum fungicide, bactericide, aquatic herbicide, algacide and molluscicide for use on a variety of agricultural crops, ornamentals and turf. There are over two hundred registered agricultural use sites, which include food, direct aquatic applications and home-owner uses. The major crops that were assessed in this RED include citrus, strawberry, tomato, pepper, rice, filbert, walnut, peach, apple, and grape. The following is information on the currently registered agricultural and direct aquatic uses of coppers, including an overview of use sites and application methods. A detailed description of uses of copper eligible for reregistration is available in Appendix A.

<b>Type of Pesticide:</b>	Coppers are registered for use as a fungicide, bactericide, algaecide, herbicide, insecticide (leech), anti-fouling, wood preservative.
<b>Target Pests:</b>	Copper compounds control a broad spectrum of pests, including fungi, bacteria, aquatic weeds, algae, mollusks, and leeches.
<b>Mode of Action:</b>	With fungal and algae organisms, the cupric ion binds to various groups including sulfidic groups, imidazoles, carboxyls and phosphate (thiol) groups that result in non-specific denaturing of proteins, leading to cell leakage. In mollusks, copper disrupts peroxidase enzymes and affects the functioning of the surface epithelia.
<b>Use Sites:</b>	<p><b>Agricultural Crops.</b> Copper is registered for use on virtually all food/feed crops, including orchard, row, field, and aquatic crops. Crops include, but are not limited to: root and tubers, leafy vegetables (including brassica), bulb vegetables, fruiting vegetables, citrus, stone fruit, pome fruit, legumes, cucurbits, berries, cereals and tree nuts. Copper is also registered for several ornamental crops, such as flowering/non-flowering plants and trees.</p> <p><b>Aquatic Applications of Copper Pesticides.</b> Copper is registered for use on numerous aquatic use sites. Below is a description of algaecide, herbicide, molluscicide, and macro-invertebrate use.</p> <p><u>Algaecide Applications.</u> Copper applications for algae control include: aquaculture facilities, drainage systems (canal, ditch and lateral), ponds (farm, industrial and recreational), fountains, lakes, reservoirs (crop and non-crop irrigation, potable), sewage lagoons, stocking (tank, water trough and ponds) and irrigation canals.</p> <p><u>Herbicide Applications.</u> Copper applications for aquatic weed control include: aquaculture facilities, drainage systems (canal, ditch and lateral), ponds (farm, industrial and recreational), lakes, reservoirs (crop and non-crop irrigation, potable), sewage lagoons, stocking (tank, water trough and ponds) and irrigation canals.</p> <p><u>Molluscicide and Macro-Invertebrate Applications.</u> Copper is registered for use to control freshwater snails that may be a vector for harmful trematodes. Copper is also used to control leeches, and tadpole shrimp in rice fields.</p>

Antimicrobial Applications. Copper is registered for use as a wood preservative, mildewcide, water treatment, bactericide, and as an anti-fouling in many products including paint, glue, building materials and construction materials.

- Tolerances:** There are currently three tolerances established for coppers: 40 CFR§180.136, 40 CFR§180.538, and 40 CFR§180.1021.
- Use Classification:** Copper is a general use pesticide for agricultural, residential and industrial applications.
- Formulation Types:** Formulations of copper-containing pesticides include dust, liquid concentrate, dry flowable, wettable powder (including water-soluble packets), granule, water-dispersible granule, powder, ready-to-use liquid, aerosol, and solid.
- Application Methods:** Agricultural copper application methods include aerial, airblast, groundboom, rights-of-way equipment, mechanical duster, low- and high-pressure handwand sprayer, handgun sprayer, push-type spreader, dips, drip system, hose-end sprayer, and automatic-metering system.
- Application methods for direct aquatic applications of copper include broadcast dry, broadcast spray, dragging, injection (flowing water), slug or dump, or spot spray.
- Application Rates:** The ecological risk assessment addresses a range of application rates up to the maximum labeled use rates. Copper application rates vary depending on the use pattern and the severity of disease or pest infestation. Additionally, input from user growers indicate that actual use rates are lower than current maximum labeled rates. From various efforts with outreach to the public through the CSTF and USDA, refined use rates information was used to refine and characterize the risk assessment. Below is a description of the use rates assessed in the ecological assessment.
- Maximum Labeled Rates. The highest maximum labeled rate assessed was for filberts at 31.8 lbs pounds of metallic copper per acre (lbs Cu<sup>2+</sup>/A), and for potatoes at 3.2 lbs Cu<sup>2+</sup>/A. For both uses, the Agency assumed four applications at weekly application intervals.
- Typical Use Rates. The highest typical application rate for food crops is 6 lbs Cu<sup>2+</sup>/A for filbert crops. However, the typical use rate for all other crops ranges from 0.25 lbs Cu<sup>2+</sup>/A up to approximately 4.0 lbs Cu<sup>2+</sup>/A. For control of tadpole shrimp in rice fields, up to 2.5 parts per million (ppm) may be used. For

direct water applications of copper for management of aquatic weeds and algae control, the maximum concentration of metallic copper is 1.0 ppm. For leech or snail control, up to 1.25 ppm of metallic copper may be used. Because rates vary depending on disease pressure or severity of pest infestation, determining a maximum number of applications was not feasible. Thus, The Agency assumed the same four applications at weekly application intervals, as for the maximum labeled rates previously described. The maximum residential application use rate is 0.5 lb Cu<sup>2+</sup>/A for root control in sewer systems.

**Application Timings:** Depending on the crop and stage of development, applications are recommended during virtually all stages of crop/fruit development including dormant applications; petal fall; bud break; early bloom; post bloom; early spring; early summer; late summer; early fall; late fall; after harvest. Treatment timings for direct aquatic uses vary, depending on the proliferation of the target pest.

**D. Estimated Usage of Copper Pesticides**

Available usage data on the use of copper compounds on growing crops greatly varies. The Agency’s Screening Level Usage Analysis (SLUA) for the two major copper compounds is described below. According to other available data sources, there is some uncertainty as to the actual figures of copper used for agricultural crops, such as reporting errors of the copper compound used on that site. The CSTF 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.

**SLUA for Copper Hydroxide**

	Crop	Lbs. A.I.	Percent Crop Treated	
			Avg.	Max.
1	Almonds	600,000	25	30
2	Apples	100,000	10	15
3	Apricots	40,000	30	45
4	Avocados	100,000	5	10
5	Beans, Green	70,000	25	50
6	Blackberries	4,000	30	35
7	Blueberries	4,000	20	55
8	Broccoli	1,000	<1	5
9	Cabbage	6,000	5	10
10	Cantaloupes	3,000	<1	5
11	Carrots	20,000	10	20
12	Cauliflower	1,000	5	5
13	Celery	30,000	35	45

14	Cherries	100,000	15	25
15	Collards	1,000	5	5
16	Cucumber	40,000	10	15
17	Cucumbers	20,000	10	20
18	Dry Beans/Peas	80,000	5	5
19	Eggplant	3,000	35	60
20	Garlic	9,000	10	15
21	Grapefruit	700,000	55	70
22	Grapes	400,000	65	95
23	Greens, Mustard	<500	5	5
24	Greens, Turnip	1,000	5	5
25	Hazelnuts (Filberts)	20,000	10	15
26	Lemons	50,000	20	30
27	Lettuce	3,000	<1	5
28	Limes	30,000	85	85
29	Nectarines	90,000	40	55
30	Olives	30,000	15	20
31	Onions	100,000	30	40
32	Oranges	1,800,000	40	50
33	Peaches	200,000	25	30
34	Peanuts	20,000	<1	5
35	Pears	30,000	10	25
36	Peas, Green	4,000	<1	<2.5
37	Pecans	20,000	<1	<2.5
38	Peppers	200,000	35	50
39	Pistachios	70,000	10	15
40	Potatoes	90,000	5	15
41	Prunes & Plums	100,000	15	15
42	Pumpkins	20,000	10	25
43	Raspberries	4,000	25	40
44	Rice	10,000	<1	<2.5
45	Spinach	6,000	10	25
46	Squash	10,000	10	15
47	Strawberries	5,000	5	10
48	Sugar Beets	4,000	<1	<2.5
49	Sweet Corn	1,000	<1	<2.5
50	Tangelos	20,000	60	65
51	Tangerines	60,000	45	65
52	Tomatoes	800,000	30	65
53	Walnuts	1,400,000	45	55
54	Watermelons	50,000	15	25
55	Wheat	5,000	<1	<2.5

### SLUA for Copper Sulfate Pentahydrate

	Crop	Lbs. A.I.	Percent Crop Treated	
			Avg.	Max.
1	Almonds	100,000	5	5
2	Apples	60,000	5	5
3	Apricots	9,000	10	15
4	Avocados	40,000	<1	5
5	Beans, Green	10,000	5	10
6	Blackberries	1,000	10	10
7	Blueberries	2,000	5	20
8	Cabbage	1,000	<1	<2.5
9	Cantaloupes	1,000	<1	<2.5
10	Carrots	10,000	<1	5
11	Cauliflower	<500	<1	<2.5
12	Celery	5,000	5	5
13	Cherries	50,000	5	10
14	Cotton	6,000	<1	<2.5
15	Cucumber	2,000	<1	<2.5
16	Cucumbers	1,000	<1	5
17	Dry Beans/Peas	10,000	<1	<2.5
18	Grapefruit	100,000	15	25
19	Grapes	100,000	15	30
20	Hazelnuts (Filberts)	10,000	10	10
21	Lemons	40,000	15	20
22	Lettuce	<500	<1	<2.5
23	Limes	<500	<1	<2.5
24	Onions	10,000	<1	5
25	Oranges	900,000	15	35
26	Peaches	100,000	10	20
27	Peanuts	20,000	<1	<2.5
28	Pears	10,000	5	10
29	Pecans	3,000	<1	<2.5
30	Peppers	30,000	5	10
31	Pistachios	1,000	<1	<2.5
32	Potatoes	30,000	<1	5
33	Prunes & Plums	30,000	5	5
34	Pumpkins	5,000	<1	5
35	Raspberries	7,000	30	40
36	Rice	300,000	<1	5
37	Spinach	2,000	5	10
38	Squash	3,000	<1	5
39	Strawberries	<500	<1	5
40	Sugar Beets	20,000	<1	5
41	Sweet Corn	1,000	<1	<2.5
42	Tangelos	1,000	5	10

43	Tangerines	5,000	10	10
44	Tomatoes	40,000	<1	5
45	Walnuts	200,000	5	10
46	Watermelons	3,000	<1	<2.5
47	Wheat	3,000	<1	<2.5

### **III. Summary of Coppers Risk Assessments**

The following is a summary of EPA's human health and ecological risk assessments for coppers, as presented fully in the documents, "*Coppers: Revised Human Health Chapter of the Reregistration Eligibility Decision Document (RED). Reregistration Case numbers 0636, 0649, 4025 and 4026,*" dated June 29, 2006, and "*Error Corrections for the Ecological Risk Assessment for Re-Registration of copper sulfate (case #0636), group II copper compounds (case #0649), and copper salts (case #0649) for use on crops and as direct water applications,*" dated April 20, 2006. The human health and ecological risk assessment documents and supporting information listed in Appendix C were used to reach the safety finding and regulatory decision for coppers. The revised risk assessments and related documents are available online at [www.regulations.gov](http://www.regulations.gov) under Public Docket EPA-OPP-HQ-2005-0558.

As part of the public participation process, the Agency solicited additional information from the public, including grower groups, to further refine the risk assessments and to provide input for risk mitigation suggestions. Because current agricultural-use labels for copper-containing products contain inconsistent use rates and use application information, the Agency made several assumptions in the ecological risk assessment. After conducting the preliminary risk assessments, EPA determined that additional information on use rates and other application information were necessary in order to refine the risk assessments.

In October 2005, the Agency requested that the registrants collect additional use information from user groups, which was submitted shortly before the Phase 3 public comment period. Although there was insufficient time to fully review the received data at that time, a preliminary cursory review showed that this data was insufficient to fully refine the risk assessments. Thus, the Agency solicited additional specific use information on major crops and direct aquatic uses during the Phase 3 public comment period. As a result of response from the public as well as outreach to the user community, several groups provided refined use information that was considered and incorporated in the revised risk assessments, as well as in the RED. This information was used to refine labels to further mitigate estimated risks.

As a result of comments received during the Phase 3 public comment period, the following major revisions were made to the ecological risk assessment:

- Assessment of root-killer sewer treatment use with the E-FAST model
- Addition of screening spray drift assessment for agricultural uses
- Inclusion of available information on mammalian homeostatic capabilities, including a 22% absorption factor to account for dietary metabolism effects
- Addition of screening risk assessment for marine/estuarine organisms
- Incorporation of typical use rates

#### **A. Human Health Risk Assessment**

This section of the document summarizes the human health risk estimates for exposures to pesticide products containing copper as the active ingredient. In this qualitative assessment, the EPA has considered aggregate or combined exposures from food, drinking water and non-



occupational sources. The aggregate risk from all copper sources must be considered to reassess the tolerance for residues of copper in food and water, in accordance with FQPA. EPA's reliance on any study in the risk assessment is in accordance with the Agency's Final Rule promulgated on January 26, 2006, related to Protections for Subjects in Human Research, which is codified in 40 CFR Part 26.

## **1. Background on Copper**

Copper is a naturally-occurring, ubiquitous element in the environment. Copper is found in water, air, and occurs naturally in various foods including organ meats, seafood, beans, nuts, and whole grains. In most foods, copper is bound to macromolecules rather than as a free ion. For many animals, copper is essential for the homeostasis of life. The role of copper in maintaining normal health both in humans and animals has been recognized for many years. Copper is an essential cofactor for approximately a dozen copper-binding proteins for the proper regulation of copper homeostasis in humans. A deficiency of copper or a defect in copper-carrying proteins may result in symptoms such as anemia, defective blood vessel development, growth retardation, a compromised immune function or connective tissue symptoms.

## **2. Exposure Sources of Copper**

Humans are exposed to copper primarily from food and drinking water sources, as well as in the air. Copper is found naturally in various foods, including organ meats, seafood, beans, nuts, and whole grains. It has been estimated that approximately 40% of dietary copper is consumed from yeast breads, white potatoes, tomatoes, cereals, beef, dried beans and lentils. The recommended dietary allowance (RDA) of copper, as established by the National Academy of Science, ranges from 0.34 milligrams per day (mg/d) in young children to 1.3 mg/d for pregnant and lactating females. The estimated total daily oral intake of copper (food plus drinking water) is between 1 and 2 mg/d, although oral intake may sometimes exceed 5 mg/d.

Copper may also be found in drinking water, commonly due to the use of copper plumbing fixtures and water pipes. Copper may also enter drinking water systems via contamination from mining operations, incineration, industrial discharges, water treatments and sewage treatment facilities. Other non-biological sources of copper include smelters, iron foundries, power stations and combustion sources such as municipal incinerators. For water quality management, a Maximum Contaminant Level Goal (MCLG) of 1.3 milligrams per liter (mg/L, or 1.3 ppm) has been set by the EPA for copper in drinking water.

In addition to dietary sources, copper pesticide use may also result in oral, dermal and inhalation exposures. There is potential for exposure to occupational mixers, loaders, and applicators of copper pesticide products, as well as to residential homeowners who may apply copper-containing pesticide products in and around their homes.

## **3. Human Metabolism of Copper**

Although the metabolism pathways are not clearly known, 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.

Some less common genetic conditions in humans may cause abnormal copper metabolism, causing either excessive retention or incapable of absorbing copper. Some disorders that result in copper toxicity include Wilson's Disease, Occipital Horn Syndrome, Tyrolean Infantile Cirrhosis, Indian Childhood Cirrhosis, Idiopathic Copper Toxicosis, and aceruloplasminemia. For example, Wilson's disease is due to the inability for biliary excretion of copper which leads to the gradual accumulation of copper predominately in the liver and brain. In contrast, Menkes disease is an X-linked neurodegenerative disorder in infants characterized by poor growth and unusual "kinky" hair texture. In Menkes disease, clinical effects include low ceruloplasmin concentrations and decreased concentrations of copper in the liver and brain. The major cause of this copper deficiency is minimal copper absorption by the intestinal mucosa and transport of copper across the blood-brain-barrier, independent of copper intake.

#### **4. Toxicity Summary for Copper**

Toxicity assessments are designed to predict whether a pesticide could cause adverse health effects in humans (including short-term or acute effects such as skin or eye damage, and lifetime or chronic effects such as cancer, development and reproduction deficiencies, etc.) and the level or dose at which such effects might occur. The Agency 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.

The component of toxicological interest in copper pesticides is elemental copper (cupric ion). Humans have homeostatic capabilities to regulate copper in the system. Effects such as severe dermal, eye, and inhalation irritation seen in acute toxicity studies are a function of the body's response mechanisms to reduce excessive copper exposure, rather than as a result of systemic toxicity. Acute toxicity studies are available for several of the copper compounds. These acute studies show that copper generally has low acute toxicity, with the exception of cuprous oxide for acute inhalation. Based on available literature and studies submitted by the registrant, there is no evidence of copper or its salts being carcinogenic or posing any other systemic toxicity in animals having normal copper homeostasis. Thus, endpoints were not established to quantify any potential risks from exposure to copper.

*Acute Toxicity.* Acute toxicity studies are available for most copper species, with the exception of copper ammonium carbonate, copper-ammonia complex, chelates of copper gluconate, copper oxychloride sulfate, basic copper sulfate, and copper ethanolamine complex. Table 3 below describes available acute toxicity studies on the respective copper compounds.

**Table 3. Available Acute Toxicity Studies on Copper-Containing Compounds**

Copper Type	PC Code	Acute Oral LD <sub>50</sub> (mg/kg)	Acute Dermal LD <sub>50</sub> (mg/kg)	Acute Inhalation (mg/L)	Primary Eye Irritation	Dermal Irritation	Dermal Sensitization
Copper chloride (57.7% Cu)	008001	M= 1796 F= 2006 Tox Cat. III 43769501	> 2000 (M & F) Tox Cat III 43769502	None Available	Corneal opacity cleared by 21 days Tox Cat. II 43769503	Non-irritating Tox Cat. IV 43769504	None Available
Chelates of copper gluconate	024405	None Available					
Copper ammonium carbonate	022703	None Available					
Copper carbonate (96%)	022901	> 2000 Tox Cat III 41889302	None Available	None Available	Corrosive, opacity at 21 days Tox Cat I 41889301	Non-irritating Tox Cat IV 41889302	None Available
Copper hydroxide (77%)	023401	M = 2253 F= 2160 Tox Cat. III 41421602	>2000 Tox Cat III 00159371 00259424	77% M= 1.53 mg/L F = 1.04 mg/L 00160580 88% F = 0.5 mg/L Tox Cat. III	Irritative Corneal opacity, iris irritation, chemosis, invasion of cornea by blood vessels Tox. Cat. I	At 72 hrs, very slight erythema  Tox Cat. IV	Non-sensitizing  Guinea Pig
Copper-ammonia complex	022702	None Available					
Copper oxychloride (94.1%)	023501	M= 1537 F=1370 Tox Cat. III 00155931	M&F=710 (281-1791) Tox Cat II	>1.7 mg/L Tox Cat. III 00155932	Corneal opacity redness and vascularization Tox Cat. I 00155934	Non-irritating Tox Cat IV 00155935	Nonsensitizing  00155936
Copper oxychloride sulfate	023503	None Available					
Basic copper sulfate	008101	None Available					
Copper sulfate anhydrous	024408	None Available					
Copper sulfate pentahydrate (99%)	024401	M= 790 F= 450 Tox Cat II 43396201	>2000 Tox Cat IV 43452201	None Available	Severe eye irritation day 1 to day 21 Tox Cat. I 43396201	Non-irritating Tox Cat IV 43396201	

Copper Type	PC Code	Acute Oral LD <sub>50</sub> (mg/kg)	Acute Dermal LD <sub>50</sub> (mg/kg)	Acute Inhalation (mg/L)	Primary Eye Irritation	Dermal Irritation	Dermal Sensitization
Copper metallic	022501	50% copper M= 1414 F= 1625 Tox Cat. III 00162424	8.5% elemental >2000 Tox Cat. III 00150641	23% metallic >0.1 but <0.59 Tox Cat III 00156396	50% metallic opacity, irritation, redness, chemosis, cleared by day 21 Tox Cat. II 00126194	50% metallic erythema, edema, irritation, cleared day 14 Tox Cat. IV 00126194	26% metallic nonsensitizing guinea pig 00144555 8.5% elemental nonsensitizing rabbit 00152166
Cupric oxide (97.6%)	042401	> 5050 (M&F) Tox Cat IV 41502401	>2020 (M&F) Tox Cat III 41502402	>2.08 (M&F) Tox Cat III 41502403	Irritation cleared in 7 days Tox Cat III 41502404	Irritation cleared day 21 PI Index= 1.49 Tox Cat III 41502405	Non-sensitizing (guinea pig) 41502406
Cuprous oxide (57%)	025601	> 5000 Tox Cat IV 00078971	> 2000 slight erythema, edema Tox Cat III 00245650	40.9% ai 0.1 to 0.59 Tox Cat I 42240303	Opacity, iris irritation, redness, and chemosis clearing by day 14 Tox Cat II 00078974	Severe erythema, edema PIS=6.1/8 Tox Cat I 00078970	Non-sensitizing (guinea pig) 00078970
Copper from triethanolamine complex [K-TEA]	024403	99% M= 1170 F= 1312 Tox Cat. III 41759301	99% > 2000 mg/kg No deaths Tox Cat. III 41759302	None Available	99% moderate irritation of cornea, iris, conjunctive cleared by day 7. Tox Cat. III 41759303	99% mild irritation cleared by day 3 Tox Cat. IV 41759304	None Available
Copper 8-quinolinolate	024002	99.5% >5000 M&F Tox Cat. IV	99.5% >2000 M&F Tox Cat. III 43558501	96% 0.09 M& 0.03 F Tox Cat. II 43611901	98% corneal opacity, redness to day 21 Tox Cat. I	99.7% Non-irritating Tox Cat. IV	99.7% Non-sensitizing guinea pig
Elemental copper (ethylenediamine)	024407	KOMEEN 96%, K-Tea 99% M=527 F= 462 Tox Cat. II 41759201	KOMEEN & K-Tea >2000 Tox Cat. III 41759202	KOMEEN & K-Tea M= 1.36 F= 0.56 Tox Cat. III 42130001	KOMEEN & K-Tea moderate irritation Tox Cat. III 41759203	KOMEEN & K-Tea redness, edema, cleared by day 3 41759204	KOMEEN & K-Tea non sensitizing guinea pig 42130002

Copper Type	PC Code	Acute Oral LD <sub>50</sub> (mg/kg)	Acute Dermal LD <sub>50</sub> (mg/kg)	Acute Inhalation (mg/L)	Primary Eye Irritation	Dermal Irritation	Dermal Sensitization
Copper naphthenate	023102	8% Cu M= >5050 F= >5050 Tox Cat. IV 43643701	8% Cu M= >2020 F= >2020 Tox Cat. III 43643702	9.5% Cu M&F=>2.96  Tox Cat. III	1. 8% Cu irritation, chemosis, cleared by 48 hrs, Tox Cat. III 43643703 2. 45% Cu opacity, redness, chemosis & discharge at 72 hrs Tox Cat. I 00266172	8% Cu erythema/es char slight edema PIS=1.1 Tox Cat. III 43642704 2. 80% Cu 72 hrs severe erythema, edema Tox Cat. II 00260891	9.5% Cu sensitizer
Copper octanoate, 10% fatty acids	023306	>2000 M&F Tox Cat. III 43947504	> 2000 M&F Tox Cat. III 43947505	> 0.38 M&F Tox Cat. III 43970201	irritation, cleared by 48 hrs. Tox Cat. IV 43937506	slight erythema, edema, cleared by 72 hrs. Tox Cat. IV 43947507	Non-sensitizing guinea pig 44116101
Copper salts of fatty and rosin acids (Cu & zinc neoisoate 35%)	023104	> 7000 Tox Cat. IV	> 2000 Tox Cat. III	None Available	no irritation Tox Cat. IV	Edema, erythema, PIS=1.0 Tox Cat III	None Available
Cuprous thiocyanate (99%)	025602	> 5000 Tox Cat IV 40834601	> 2000 Tox Cat III 40834601	> 0.5 mg/L Tox Cat. II 40834605	non-irritant 40834605	non-irritant 40834604	non-sensitizing 40834603
Copper ethanolamine complex	024409	None Available					

Copper generally has moderate to low toxicity (Toxicity Category II, III and IV) 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. Most dermal irritation studies indicate Toxicity Category III or IV; however, cuprous oxide produced Toxicity Category I irritation. Copper was generally non-sensitizing in animals, except for copper naphthenate which was a skin sensitizer. When ingested, copper can be a gastric irritant and produce corrosion of the gastric and intestinal epithelium. Open literature and data submitted by the registrants indicate that acute responses to large copper concentrations are a result of acute irritation. Inhalation of copper as dusts or mists is likely to be irritating to the respiratory system. Acute responses to ingesting large amounts of copper may produce a metallic taste, abdominal pain, nausea and vomiting, or diarrhea, especially if the stomach is empty and copper is taken with acidic foods, beverages, or with other supplements.

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.*** 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. Available short-term feeding studies with rats and mice indicate decreased food and water intake with increasing oral concentrations of copper, with irritation of the stomach at higher copper concentrations. High levels of excess copper administered in the drinking water of mice suggested an altered immune response; however, the inhibition of immune responses is not unusual since other trace elements have been linked with immuno-suppression. In addition, cations like zinc, mercury, and lead have also been reported to alter immune responses. The mechanism by which copper may be exerting a response in the immune system has not been fully determined.

Longer feeding studies indicate decreased feed intake with reductions in body weight gains, and increased copper concentration of the liver. Some available literature indicates that chronic inhalations of copper may become cancerous, specifically seen in some professional vineyard workers that were chronically exposed to Bordeaux mixture (copper sulfate and hydrated lime mixture). However, this information is not definitive since no information is available on the level of copper exposure to the workers, or any other substances with which they might have come into contact. 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.

## **5. FQPA Safety Factor Considerations**

FFDCA, as amended by FQPA, directs the Agency to use an additional 10X safety factor (SF), to account for potential pre- and postnatal toxicity and completeness of the data with respect to exposure and toxicity to infants and children. FQPA authorizes the Agency to modify the 10X FQPA SF only if reliable data demonstrate that the resulting level of exposure would be safe for infants and children. In humans, there does not appear to be any reports in the literature of teratogenesis induced by exposure to excess copper. The only teratogenic effects observed in available animal studies occurred after exposure with copper salts at high doses which were likely maternally toxic. Moreover, there is no evidence to suggest susceptibility in infants and children. Since copper is an essential trace element, with copper deficiency more common in humans than toxicity from the excess, and since the dietary (food and drinking water) contribution of copper to the total diet is low, endpoints to quantitatively assess dietary risk were not selected. EPA has low concerns and no residual uncertainties with regard to pre- or postnatal

toxicity from copper exposures. Since a qualitative assessment was conducted for potential human health exposure to copper, the 10X FQPA SF was not retained.

## **6. Aggregate Risk from Coppers (Dietary and Residential)**

The FQPA amendments to the Federal Food, Drug, and Cosmetic Act (FFDCA, Section 408(b)(2)(A)(ii)) require “that there is a reasonable certainty that no harm will result from aggregate exposure to the pesticide chemical residue, including all anticipated dietary exposures and other exposures for which there is reliable information.” In accordance with the FQPA, the Agency must consider and aggregate pesticide exposures and risks from three major sources or pathways: food, drinking water, and if applicable, residential or other non-occupational exposures.

Copper is a ubiquitous, naturally occurring metal that is essential to human health, found naturally at low levels in a variety of food products as well as in drinking water from copper plumbing pipes. Additionally, copper generally has low to moderate acute toxicity via the oral, dermal, and inhalation routes of exposure. Available literature and studies do not indicate any systemic toxicity associated with copper exposure. Effects seen in the existing data base are as a result of response mechanisms that protect the body from excessive exposure to copper. Considering all available information on copper and the relatively low toxicity via all exposure routes from all sources, the cupric ion (regardless of the original form/species of copper) when used in pesticide products is unlikely to pose a significant hazard to the general public or any population subgroup. Based on available studies and literature, there are no human health aggregate risks of concern resulting from aggregate dietary and residential exposures.

## **7. Occupational Exposure**

Copper compounds are used on a variety of agricultural, commercial, and residential use sites as fungicides, bactericides, algaecides, herbicides, wood preservatives, and anti-fouling agents. There is potential for exposure to occupational mixers, loaders and applicators of copper-containing pesticides. There is also the potential for post-application exposure. However, adverse effects resulting from dermal, oral or inhalation exposures are due to the irritating properties of copper, rather than a result of systemic toxicity. No dermal, oral or inhalation endpoints were established to determine any potential systemic toxicity resulting from occupational uses of copper products. Thus, there are no occupational risks of concern to the Agency. Although there are no occupational risks of concern, the severe irritating properties of some coppers warrant appropriate precautionary labeling to address any handler or post-application exposures based on acute toxicity categories for individual copper compounds.

## **8. Incidence Data on Copper Exposure**

The EPA’s Incident Data System (IDS) has seven recorded pesticide incidents for copper; five involve copper hydroxide and two involve copper sulfate pentahydrate. According to a review of the scientific literature, copper compounds formulated as dusts and as powders are irritating to the skin, respiratory tract, and the eyes. Most copper compounds have low systemic toxicity, due mainly to their limited solubility and absorption. Occupational exposure to copper

containing compounds frequently results in irritation effects. The majority of the noted effects involved skin and eye irritation, nausea, vomiting, and headaches. These findings from the scientific literature reflect the reported incidents from IDS.

The principle types of copper fungicides included in the Poison Control Center data (1993-2003) are copper sulfate and copper hydroxide. Of the 82 copper exposures identified in the Poison Control Center data, only 20 were seen in a health care facility, and three cases had a moderate medical outcome. The leading symptoms included ocular irritation, vomiting, nausea, and dermal irritation. Data from the California Department of Pesticide Regulation (1982-2003) show that 156 cases (out of 494 reported) were due to copper compounds. The majority of these cases show eye effects, skin effects, or other acute effects (i.e., respiratory effects). Of the top 200 chemicals for which the NPIC received calls from (1984-1991), copper hydroxide was ranked 167<sup>th</sup> and copper sulfate was ranked 179<sup>th</sup>, with 15 and 13 reports of illness to humans, respectively. National Institute for Occupational Safety and Health Sentinel Event Notification Systems for Occupational Risks (NIOSH SENSOR) data reveal that out of 5899 reported cases between 1998- 2003, only 34 cases were documented as involving copper (copper sulfate pentahydrate, copper hydroxide, and copper-ammonia complex). Twenty-five of the 34 documented cases were from California, and most likely overlap the cases discussed above from the California Department of Pesticide Regulation.

Given the long history of copper use over the past several centuries and the extensive use of copper compounds in agricultural and direct aquatic applications, the number of reported incidents related to copper is relatively low. Reported effects (i.e., eye and dermal irritation, emesis, nausea, etc.) were consistent with acute irritation effects that may occur when exposed to products containing copper. These reported incidents do not indicate systemic toxicity effects resulting from copper exposure, but do support a conclusion that acute irritation effects are the primary concern for exposures to copper compounds. The potential acute irritation effects of some copper pesticides warrant appropriate precautionary labeling to address any handler or post-application exposures. With these protective measures in place to reduce potential exposures, there are no risks of concern to the Agency.

## **B. Ecological Risk Assessment**

A summary of the Agency's environmental risk assessment for coppers is presented below. As a bridging strategy to address the range of copper compounds included in this assessment, the Agency has evaluated all copper active ingredients with registered agricultural uses on the basis of the cupric ion ( $\text{Cu}^{2+}$ ) regardless of the original form of the copper compound. Antimicrobial applications of copper will be assessed separately at a later date. The complete revised environmental risk assessment for agricultural uses of coppers may be accessed online at [www.regulations.gov](http://www.regulations.gov) under Public Docket EPA-OPP-HQ-2005-0558. This risk assessment was refined and updated to incorporate comments and additional data submitted by the registrants and other stakeholders.



## 1. Environmental Fate

Copper naturally occurs in the environment, and continuously cycles through natural geothermodynamic processes that binds or releases copper ions. 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.

The copper ion is highly reactive, especially in aquatic environments. Copper can exist in various organic and inorganic forms, including the cupric ion ( $\text{Cu}^{2+}$ ), cuprous ion ( $\text{Cu}^+$ ), inorganic complexes, organic complexes and minerals. In this assessment, the term “speciation” refers to the relative proportion of total copper in these various forms. Figure 1 provides an overview of the chemistry of copper in aqueous systems.

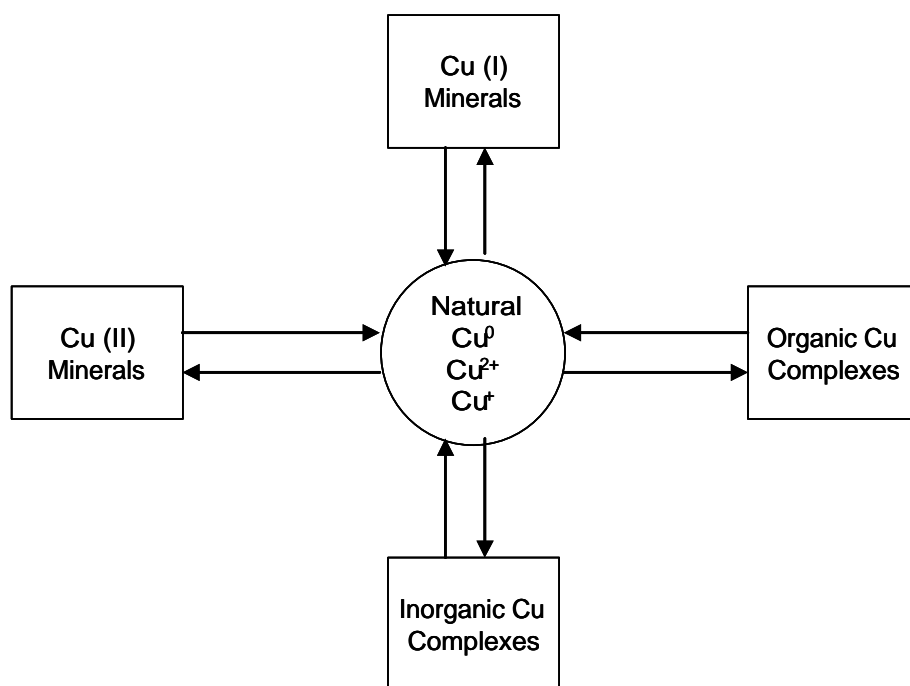


Figure 1 – Environmental Fate Bridging Strategy for Cu Minerals and Complexes

Copper can exist in various oxidation states as inorganic complexes, organic complexes and minerals; Figure 1 distinguishes these mineral states with Roman numerals (e.g., Cu(I) and Cu(II)). The oxidation of Cu(0) to Cu(I) or Cu(II) depends on the redox conditions. Redox potential is the tendency of the environment to deplete molecular oxygen from the system to form oxygen-containing compounds. Redox potential can be measured as an electrical potential in millivolts (mV). It also controls the chemical forms of other compounds in the environment. The form in which Cu(I) or Cu(II) species is found depends on the pH of the medium and the nature and concentration of other chemical species that can form copper-containing species.

This ecological assessment addresses terrestrial crop and direct aquatic uses of Cu(II) salts, oxides, hydroxides, and organic complexes. When used as a pesticide, the cupric ion is released via dissolution of copper salts, oxides/hydroxides and/or by the breakdown of organic complexes and/or degradation of the organic moiety. The extent of dissociation of copper species is controlled by the solubility of the compound, which is dependent on the pH of the environment. It also depends on redox potential, dissolved organic carbon (DOC) and competing ligands. However, for the purposes of this assessment, copper compounds reaching surface water (as simulated by PRZM/EXAMS) is assumed to completely and instantaneously dissociate. As described below, speciation of this loading of dissolved copper is then simulated using the Biotic-Ligand Model (BLM).

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.

## **2. Ecological Exposure and Risk**

The Agency has used the existing environmental database and open literature for coppers to characterize the environmental exposure associated with copper agricultural uses for this screening-level assessment. The risk assessment is based on a subset of representative labels of copper sulfate pentahydrate and copper hydroxide for agricultural uses, which represents a wide range of application rates. Although there are several other registered active ingredients containing copper, the risk assessment assumes instantaneous disassociation of the cupric ion from its counter ion or ligand, which is a conservative estimate for the potential bioavailable amount of copper to exposed organisms. The Agency assessed both maximum labeled rates and typical average use rates. All copper concentrations are expressed in the risk assessments as the copper or cupric ion, the toxic ion of concern.

The Agency's ecological risk assessment compares toxicity endpoints from ecological toxicity data to estimated environmental concentrations (EECs) based on environmental fate characteristics, soil and water chemistry, and pesticide use data. To evaluate the potential risks to nontarget organisms from the use of copper pesticides, the Agency calculates a Risk Quotient (RQ), which is the ratio of the EEC to the most sensitive toxicity endpoint values, such as the median lethal dose (LD<sub>50</sub>) or the median lethal concentration (LC<sub>50</sub>).

RQ values are compared to the Agency's levels of concern (LOCs), which indicate whether a pesticide, when used as labeled, has the potential to cause adverse effects on nontarget organisms. When the RQ exceeds the LOC for a particular category, the Agency presumes a potential risk of concern to that category. Table 4 describes the Agency's LOCs and its respective risk presumptions. These RQ values may be further refined by characterization of the risk assessment. Use, toxicity, fate and exposure are considered when characterizing the risk, as well as the levels of certainty and uncertainty in the assessment.

**Table 4. Agency’s LOCs and Risk Presumptions**

<b>Risk Presumption</b>	<b>LOC Terrestrial Animals</b>	<b>LOC Aquatic Animals</b>	<b>LOC Plants</b>
<b>Acute Risk - there is potential for acute risk; regulatory action may be warranted.</b>	0.5	0.5	1
<b>Acute Endangered Species – there is potential for endangered species risk; regulatory action may be warranted.</b>	0.1	0.05	1
<b>Chronic Risk - there is potential for chronic risk; regulatory action may be warranted.</b>	1	1	N/A

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.

The toxicity of copper to aquatic animals depends on the amount of bioavailable cupric ion in the water. To address potential risk to freshwater organisms, the Agency used the Biotic-Ligand Model (BLM) (Windows Version 2.0.0, 4/03) in addition to standard current methods to assess exposure and toxicity to potentially exposed freshwater organisms. The BLM method is discussed in greater detail below.

The BLM has not yet been parameterized for estuarine/marine organisms, as it has for freshwater animals. This would require evaluating data for specific estuarine/marine species under a sufficient range of water quality conditions to determine the effect of these conditions on copper toxicity. Therefore, since the BLM could not be used, RQs for estuarine/marine animals were calculated using estimates of *total* dissolved copper, and are therefore calculated using conservative exposure values. For freshwater plants, saltwater organisms and terrestrial animals and plants, standard Agency models and methods were used to assess potential copper exposures.

For a more detailed explanation of the ecological risks posed by the agricultural use of coppers, refer to *Error Corrections for the Ecological Risk Assessment for Re-Registration of copper sulfate (case #0636), group II copper compounds (case #0649), and copper salts (case #0649) for use on crops and as direct water applications*, dated April 20, 2006.

**a. Aquatic Organisms**

**1. Freshwater Fish and Invertebrates**

Agricultural Uses

The EECs of *total* dissolved copper (versus Cu<sup>2+</sup> only) in surface water resulting from agricultural uses of copper pesticides were simulated using the Agency’s standard pesticide

transport models PRZM and EXAMS (PRZM/EXAMS). However, the selection of input parameters for these models was complicated by the elemental nature of copper. PRZM/EXAMS require input for both persistence and mobility of the pesticide, and while the various formulations of copper are assumed in the risk assessment to dissociate immediately in water to release the cupric ion, the cupric ion itself does not degrade. All metabolism and degradation parameters were set with half-lives long enough that copper would essentially not degrade over the 30-year simulation. The one exception was the use of a 10-day aquatic dissipation half-life in place of an aerobic aquatic metabolism half-life in EXAMS. This allowed consideration of chronic exposure in the water column, imitating the preferential partitioning of copper away from the dissolved phase and into a bound state in sediment. Soil partitioning coefficients for sand and clay soils were used to allow consideration of scenarios in which greater and lesser amounts of copper were bound to the soil.

Thirty-two separate PRZM/EXAMS modeling scenarios were selected to represent the various crop groupings, which provided a range of geographic conditions and use rates. Use rates for copper sulfate, copper sulfate pentahydrate, and copper hydroxide were derived from representative labels. Because of the vast array of labels, a representative subset of labels was chosen to assess the range of copper application rates. The screening-level risk assessment was based on use sites with the highest application rates found for agricultural uses on crops that account for the majority of agricultural use of copper hydroxide and copper sulfate. The number of applications and application intervals were generally not specified on labels. Therefore, the modeling was conducted assuming four applications at weekly intervals.

Because the PRZM/EXAMS model cannot account for chemical speciation of copper, which affects its toxicity, the BLM was used to estimate the cupric ion concentration in surface water. The BLM, essentially a combined speciation and toxicity model, allows calculation of toxicity values based on site-specific water chemistry. Use of the BLM in this pesticide risk assessment is consistent with the method used by the EPA's Office of Water (OW), which used the BLM to revise the Aquatic Life Criteria (ALC) for copper in 2003. EPA OW is currently preparing guidance on the use of the BLM to derive site-specific ALC for copper based on site-specific water chemistry. Figure 2 describes the use of the BLM in the ecological risk assessment.

**Exposure:  
Developing Activity-based  
Site Specific EECs**

**Effects:  
Developing Activity-based  
Site Specific LC<sub>50</sub>s**

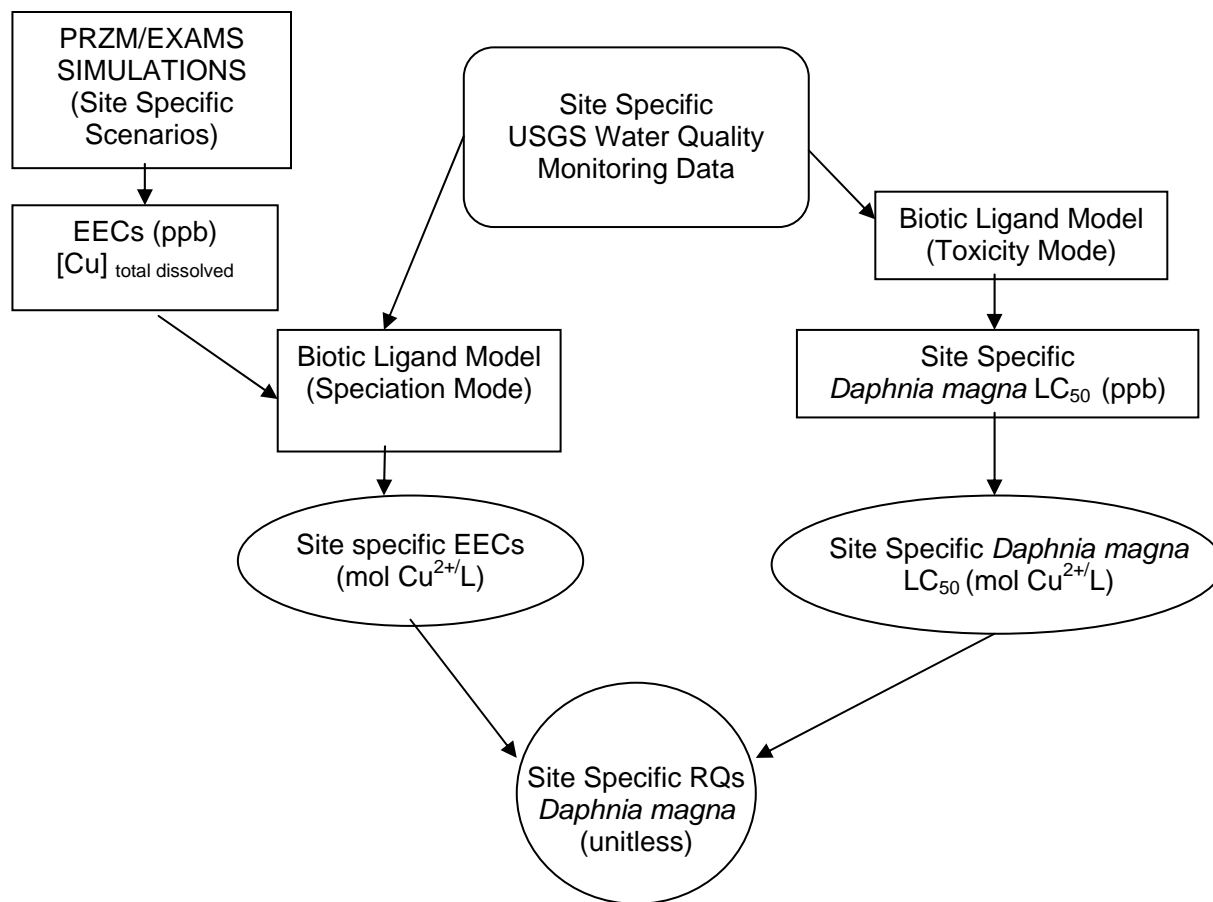


Figure 2. Site-specific aquatic assessment using the BLM

For the copper pesticides risk assessment, PRZM/EXAMS estimated total copper concentrations (peak and 21-day average concentration) for low  $K_d$  (sandy soil) and high  $K_d$  (clay soil) for each crop scenario to derive the copper input concentration in the BLM model. In order to portion out speciated copper among its various forms in water, the BLM also requires water quality input parameters which are mostly not input parameters for PRZM/EXAMS.

Water quality input parameters for the BLM model were populated using United States Geological Service (USGS) water quality monitoring data for filtered water, from nationwide monitoring programs such as NAWQA and NASQAN. The USGS water quality monitoring data were censored to remove all samples with water input parameters outside the range of the model. The samples that were removed were excluded predominantly for having water temperature higher than the range handled by the BLM. However, the other water quality parameters from these samples suggest that the copper exposure and toxicity that would result would likely be within the range for the large number of USGS samples that were used in the BLM.

Eight-hundred eleven USGS sites representing median water quality conditions were used in the BLM to assess a representative range of water column conditions in surface water across the United States. Median conditions were selected rather than worst case conditions because they represent the conditions most likely to occur. Table 5 describes the range of water quality data inputs used in the BLM. Variability across sites is expected to be greater than variability at a single site. BLM simulations provided an estimation of the cupric ion activity (moles/liter) in water for each of the 811 sites.

**Table 5. Summary of USGS Water Quality Data Used in the BLM<sup>1</sup>**

Parameter	Units	Data Range for BLM	Missing Data	Low Value	High Value	Median Value	Average Value
Temperature	°C	10 to 25	0	10	24.5	17.4	17.2
pH	none	4.9 to 9.2	0	5.05	9.2	8.0	7.85
Cu	µg/L	ND	363	1.0	51.4	1.2	2.61
DOC	mg/L	0.05 to 29.65	0	0.2	29.2	3.00	4.06
Humic Acid <sup>2</sup>	%	10 to 60	0	10	29.15	14.90	16.69
Ca <sup>2+</sup>	mg/L	0.204 to 120.24	0	0.95	114	37.6	40.62
Mg <sup>2+</sup>	mg/L	0.024 to 51.9	0	0.18	51.8	10.6	13.02
Na <sup>+</sup>	mg/L	0.16 to 236.9	0	0.88	190	10.3	21.09
K <sup>+</sup>	mg/L	0.039 to 278.4	0	0.09	18	2.2	2.93
SO <sub>4</sub> <sup>2-</sup>	mg/L	0.096 to 278.4	0	0.10	270	26.1	44.46
Cl <sup>-</sup>	mg/L	0.32 to 279.72	0	0.32	266	11	22.66
Alkalinity	mg/L	1.99 to 360	0	2.0	311	116	120.61
S <sup>2-</sup>	mg/L	ND	811	ND	ND	ND	ND

1- Data represent median site water quality conditions within the range of data for development of BLM

2- Humic acid percentage was estimated from the DOC concentration

ND – No data available, oxic conditions assumed

Typically, the Agency would calculate RQs using the most sensitive LC<sub>50</sub> for a taxonomic group and the 1-in-10-year acute and chronic EECs from PRZM/EXAMS. However, potential copper toxicity in natural waters is largely a function of water chemistry, so the toxicity to a particular organism will vary from site to site. Copper is most toxic in waters of low ionic strength and/or low in dissolved organic carbon (DOC). The pH of the water also affects toxicity.

Because the toxicity of copper varies greatly depending on water chemistry, the same water chemistry data collected by USGS was input to the BLM to calculate LC<sub>50</sub>s for *Daphnia magna* (cladoceran, representing aquatic invertebrates), and *Pimephales promelas* (fathead minnow, representing fish). *Daphnia* were the most sensitive genera of aquatic invertebrates for which data were available, and the most sensitive aquatic species overall. Salmonids (genus *Onchorynchus*; genus mean acute value (GMAV) of 29.11 µg/L) are the most sensitive fish species, but at the time of this assessment, the BLM had not yet been implemented to calculate the LC<sub>50</sub> for this genus, thus the fathead minnow LC<sub>50</sub>s produced by the BLM was adjusted by

the ratio of the *Onchorynchus* GMAV to the *Pimephales* GMAV (29.11 µg/L:72.07 µg/L; adjustment factor 0.404).

The chronic toxicity of copper to aquatic animals was also calculated in a manner consistent with that used by OW to derive ALC for copper. The minimum data requirements for developing chronic ALC were not met, so OW elected to use the acute-to-chronic ratio (ACR) approach to derive chronic criteria. OW determined an ACR of 3.23 for freshwater organisms, which was a central value derived from a range of ACRs for freshwater species for which both acute and chronic toxicity data were available. For the ecological risk assessment, the ACR was applied to the acute toxicity value for each of the 811 sites to establish a chronic toxicity value for RQ calculation.

At the time the ecological risk assessment for copper pesticides was conducted, many product labels had inconsistent information on the maximum amount of copper that can be used on many crops. The ecological risk assessment assumes four applications applied one week apart at the maximum label rate in cases when the maximum rates and minimum intervals are not described on the label. In order to allow an evaluation of potential risk at different application rates that might be established on revised copper labels, the Agency performed a regression on the peak cupric ion concentrations based on various application rates in the 32 PRZM/EXAMS simulations run for copper. The data points used to calculate the regression and the resulting regression equation are shown in Figure 3, below.

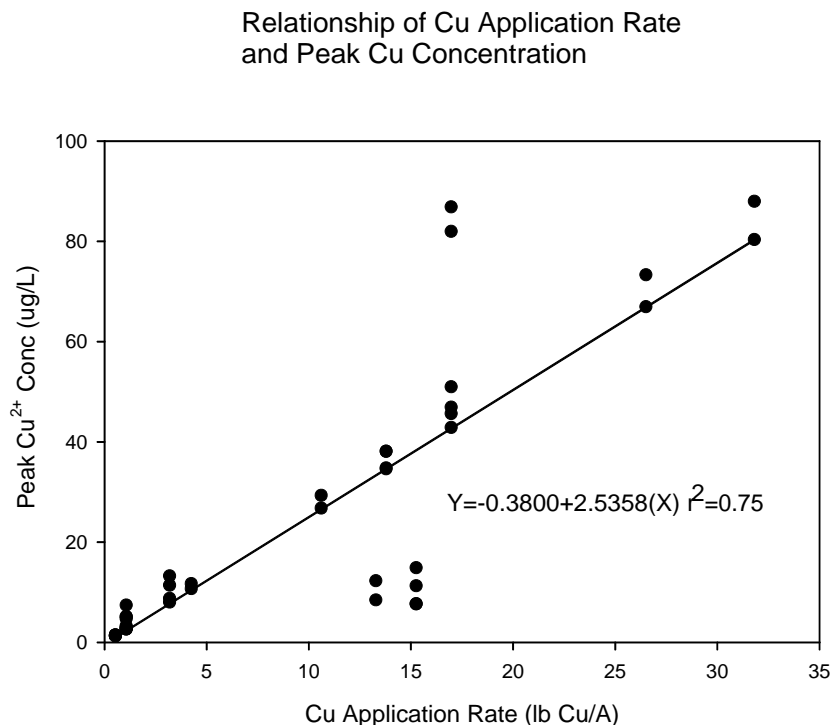


Figure 3 - Correlation of Peak Cu<sup>2+</sup> Concentrations in the Standard Small Water Body with Application Rates

The peak cupric ion concentrations generated from PRZM/EXAMS were the inputs used in the BLM. Using the BLM to estimate site-specific cupric ion concentrations and toxicity

endpoints, individual RQs were calculated for each of the 811 USGS sample sites. The resulting RQs were compared to the Agency’s LOCs for aquatic animals. The potential for acute risk to aquatic animals is described in terms of percentages of the 811 sites that exceed the Agency’s LOC for a range of potential application rates.

The screening-level risk assessment indicates that there are risks greater than the LOC to freshwater invertebrates from terrestrial uses of copper at some portion of the 811 sites modeled, regardless of the application rate. At the maximum label application rate considered in the risk assessment, 31.8 pounds of metallic copper per acre (lbs Cu<sup>2+</sup>/A) for filberts, RQs for nearly all sites exceeded the acute and chronic LOCs. Over 99% of the sites exceeded the acute LOC for invertebrates, and 80% exceeded for fish. Over 98% of the sites exceeded the chronic LOC for invertebrates and 44.9% exceeded for fish.

The percentage of sites for which RQs exceed the acute LOC is significantly less for typical rates more likely to be applied. The percentage of sites ranges from 3.2% at 1.0 lb Cu<sup>2+</sup>/A, and increases to about 25% of sites at an application rate of 7.5 lbs Cu<sup>2+</sup>/A. The RQs derived for freshwater fish with the BLM exceed the acute LOC for less than 1% of sites for application rates of 1.0 lb Cu<sup>2+</sup>/A and above.

The same exposure estimates translate into a greater number of sites exceeding the acute endangered species LOC of 0.05. As shown in Table 6 below, even at a rate of 1.0 lb Cu<sup>2+</sup>/A, aquatic RQs exceed that LOC in 19% of the 811 sites for freshwater invertebrates, while only exceeding the LOC for 1% of those sites for freshwater fish. The level of exceedence of the acute endangered species LOC for freshwater invertebrates and fish increases to 84% and 17%, respectively, based on an application rate of 7.5 lbs Cu<sup>2+</sup>/A.

**Table 6. Summary of Acute LOC Exceedences in Freshwater Environments from Agricultural Uses**

Rate lbs Cu <sup>2+</sup> /A (ppb)	Acute		Acute Endangered Species	
	Invertebrate <sup>1</sup>	Fish <sup>1</sup>	Invertebrate <sup>1</sup>	Fish <sup>1</sup>
1.0 (2.2)	3.2%	<1%	19.0%	1.0%
1.5 (3.4)	5.0%	<1%	29.6%	1.4%
3.0 (7.2)	10.3%	<1%	53.4%	6.0%
5.0 (12.3)	17.0%	<1%	71.5%	10.4%
7.5 (18.6)	24.6%	<1%	84.0%	17.1%

<sup>1</sup> Presented in terms of the percentage of sites in the USGS data set exceeding the acute risk LOC or acute endangered species LOC.

As part of the development of the ALC for copper, OW derived an acute-to-chronic ratio (ACR) of 3.23 for freshwater organisms (USEPA 2003a). The BLM only estimates acute toxicity, so the ACR was applied to site specific LC<sub>50</sub>s for both the daphnids and salmonids to generate site specific chronic toxicity values. These were compared to the 21-day EECs speciated by the BLM to derive chronic RQs. Table 7 shows the percentage of sites for which freshwater animal RQs exceed the chronic LOC. RQs for fish are usually calculated using the 60-day EEC, but a suitable regression could not be fit to the 60-day EECs from the 32 PRZM/EXAMS scenarios. Therefore, although RQs for few sites exceed the chronic LOC for fish at rates up to 7.5 lb Cu<sup>2+</sup>/A, the assessment should be considered conservative because the



21-day EECs are higher than 60-day EECs for any particular site.

**Table 7. Summary of Chronic Risk LOC Exceedences in Aquatic Environments**

Rate lbs Cu <sup>2+</sup> /A(Cu ppb)	Freshwater	
	Invertebrate <sup>1</sup>	Fish <sup>1</sup>
1.0 (2.2)	4.2%	0.0%
1.5 (2.9)	6.3%	0.1%
3.0 (5.3)	13.4%	1.0%
5.0 (8.4)	22.2%	2.5%
7.5 (12.3)	32.4%	5.3%

<sup>1</sup>Presented in terms of percentage of sites in the USGS data set exceeding the chronic risk LOCs

The distribution of the 811 RQ values reflects the distribution of the water quality parameters from the 811 USGS sampling sites. Therefore, the shape of the distribution is the same for each application rate. An example from the ecological risk assessment shows the range of RQs for application to apples at an application rate of 3.8 lbs Cu<sup>2+</sup>/A. Table 8 below shows that the acute LOCs are exceeded for freshwater invertebrates, with a RQ range of 0.01 to 498. The median value, however, is 0.47. Although nearly half of the RQs exceed the acute LOC of 0.5, the distribution of RQs is skewed toward the lower values in the distribution. The acute RQ distribution for fish and the chronic RQ distribution for invertebrates and fish show this same pattern.

**Table 8. Aquatic RQ Summary: Orchard Average Application Rate (3.8 lbs Cu<sup>2+</sup>/A)**

Endpoint for RQ	Minimum RQ	Median RQ	Maximum RQ
<i>Acute</i>			
Invertebrate	0.01	0.47	498
Fish	0.00	0.02	41
<i>Chronic</i>			
Invertebrate	0.02	0.66	352
Fish	0.01	0.05	6.1

Acute LOC for invertebrates and fish = 0.5, Acute endangered species LOC for invertebrates and fish = 0.05, acute, chronic LOC for invertebrates, fish = 1.0

### Exposure via Spray Drift

There is some uncertainty in the level of exceedances because spray drift was not included as part of the potential total copper exposure in the BLM analysis. The assessment did not include spray drift because the labels did not specify the method by which copper would be applied. A screening-level spray drift analysis was conducted separately in the revised risk assessment to evaluate the impact of copper spray drift from terrestrial crop uses on aquatic environments. The analysis assumes drift loadings of 5% of the application rate for aerial spray and 1% of application rate for ground spray into the standard farm pond used in EXAMS. Peak concentrations of copper from spray drift were speciated using the BLM model to estimate the concentration of cupric ion in the pond. Median USGS monitoring site water quality data for the 811 sites were used as input parameters for the BLM model.

Site exceedences of the aquatic LOC and endangered species aquatic LOC were found for both ground and aerial spray drift loadings. At the highest application rate proposed for reregistration (6 lbs Cu<sup>2+</sup>/A, for filberts), a single aerial application would result in 28% and 5% of sites exceeding the acute LOC for freshwater invertebrates and fish, respectively. A corresponding ground spray application would result in 7% and 4% exceedances, respectively. The same simulated exposure suggests that the freshwater invertebrate endangered species LOC would be exceeded at 89% and 32% of sites from aerial and ground spray, respectively. Lower application rates associated with other crops would result in lower estimated exposure, and a smaller percentage of sites at which the LOCs would be exceeded.

### Uncertainties in Freshwater Animal Risk Assessment

There is some uncertainty in the level of exceedances of the acute and acute endangered species LOCs from agricultural uses of copper, because the regression used to predict the exposure input to the BLM was derived from 32 scenarios representing climatic and soil conditions from around the country. In addition, the peak value from each of the 32 scenarios was from a single year of modeling with PRZM/EXAMS. Standard exposure assessments with PRZM/EXAMS simulate 30 years of applications with 30 years of daily rainfall and climate data from a nearby weather station. Since elemental copper does not degrade, the effect of 30 years of applications would be to accumulate copper in the static pond simulated by EXAMS. The EEC simulated from the first of the 30 years of data would likely be less than the standard 1-in-10-year exposure value calculated from a full 30-year simulation, although some of the 32 sites would simulate heavier rainfall in that single year, and others would simulate light rainfall years.

The choice of the soil-partitioning coefficient ( $K_d$ ) used as input to PRZM/EXAMS served to make the estimated number of sites with RQs exceeding acute and chronic LOCs more conservative. The environmental fate assessment reports a range of  $K_d$  values from 0.4 L/g (sand soil) to 3.6 L/g (clay soil). PRZM-EXAMS models were used to estimate copper concentrations for the low  $K_d$  and high  $K_d$  values for each crop scenario to derive the copper input concentration for the BLM model. The regression used to estimate EECs for different application rates used the output from the low  $K_d$  modeling runs, which causes the model to simulate more copper transport from the field, and more copper in the dissolved phase in the pond (and less in the bed sediment). This results in higher copper input to the BLM, and a conservative estimate of the number of sites that would exceed an LOC for a particular application rate.

In addition, the number of applications and application interval was not the same for all 32 simulations, although the majority of them assumed four applications spaced a week apart. The need to assume a number of applications and an application interval is a result of inconsistent product labels for copper pesticides which do not specify the maximum number of applications and minimum treatment interval. Imprecise product labels (unspecified application intervals and application frequencies) represent the greatest source of uncertainty in the ecological risk assessment for copper pesticides. Because the labels do not specify these limits, the potential maximum loading of the chemical into the environment may grossly underestimate or overestimate potential risk.

Finally, as mentioned earlier, the mean water quality characteristics from 811 USGS

sampling sites result in a wide range of copper exposure and toxicity values, but may not represent the full range of potential conditions. This data set of 811 sites represents 47 states (no sites in Maine, South Carolina, or Virginia), but does not represent every region equally. For instance, since the available data set was censored to remove any sites with temperature values outside the range that can be assessed by the BLM, the southeastern United States is not as well represented as other parts of the country.

### Aquatic Uses

The aquatic risk assessment for direct application of copper pesticides to water uses the EXAMS model in conjunction with the BLM to produce RQs over a range of water quality conditions. EXAMS accounts for sediment-to-water partitioning, and the BLM incorporates the effects of copper speciation. Use data indicate a target concentration for algae and aquatic weeds control of 0.1-1 ppm. For snails, leeches, and other similar organisms, application rates may be higher, ranging from 1-2.5 ppm. The risk assessment indicates that for an application rate of 1 ppm, peak concentrations of  $\text{Cu}^{2+}$  are predicted by EXAMS to be approximately 0.9 ppm if the pesticide were to be applied to the entire water body. The estimated average 21-day concentration at this rate is 522 ppb, and the estimated average 60-day concentration is 234 ppb.

For invertebrates, fish, and aquatic plants, >99% of sites exceed the endangered species LOC and the acute risk LOC at this application rate. The chronic risk LOCs for aquatic invertebrates, and fish are exceeded at >96% of the sites. The water body simulated by EXAMS is a 1-hectare, 2-meter deep pond with no outlet. However, were an entire reservoir treated at the same rate (which would require proportionally more copper), the level of predicted risk would be the same.

The risk assessment also considers the potential for risk when only a portion of a water body is treated. The EXAMS model was run in conjunction with the BLM to determine the percentage of water bodies with characteristics of the 811 USGS samples would that exceed LOCs for partial applications. A regression of these simulations suggests risk to freshwater fish and invertebrates.

There is some uncertainty in this finding of risk for partial treatment of water bodies, due to limitations of the exposure model itself. The EXAMS model simulates instantaneous mixing of applied pesticide throughout the approximately 20,000,000-liter pond. Therefore, these simulations of partial treatments are equivalent to full-pond treatments at a fraction of the maximum application rate. Because of the great variance in water body chemistries across the US, this will overestimate the potential risk to some aquatic organisms, and underestimate it for others. The purpose of treating a portion of a water body can be to avoid killing enough plant matter at one time to sharply increase oxygen-demand, and/or to give mobile aquatic animals the opportunity to leave the treated area. When only a portion of the water body is treated, organisms in the vicinity of the treatment can be exposed to the full concentration of copper applied, while others farther from the treated area may not be exposed at all. This is especially true for water bodies such as drinking water reservoirs, which are larger than the standard pond simulated by EXAMS, both because of their size, and the amount of time it takes for total mixing of water in those water bodies.

However, for almost any direct water application of copper products, there are likely to be effects on invertebrates and a reduction of primary production. Fish and larger, more mobile invertebrates may be able to move out of the treated zone until the copper dissipates from the water column, but smaller and more sedentary invertebrates will be affected. Recovery of the affected organisms will vary on a site-to-site basis, and the specific effects on any given ecosystem are impossible to predict given the scale of this assessment. Populations of phytoplankton and zooplankton (the organisms most likely to be lethally affected by use of copper) are dynamic. In aquatic systems where copper is applied frequently the community may shift to more copper tolerant organisms, and/or some of the organisms present may develop metabolic pathways for dealing with higher copper loading.

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.

### Urban Uses

One of the risk assessment goals of the Office of Pesticide Programs (OPP) is to estimate pesticide exposure through all significant routes of exposure from both agricultural and non-crop uses. However, the ecological risk assessment for copper pesticides focuses on the agricultural uses, because pesticide transport models are available to estimate potential aquatic exposure from these uses. Based on laboratory toxicity tests with aquatic animals, aquatic exposure could cause adverse effects in the environment.

Copper is used for a number of non-crop pesticidal uses, including use as a wood treatment, lawn fungicide, pool and fountain algacide, sanitary sewer root killer and ingredient in anti-fouling paints. The wood treatment, anti-foulants, and other antimicrobial uses will be addressed in a separate ecological risk assessment to be produced at a later date by the Agency's Antimicrobials Division. This document addresses the root-killer and lawn uses to a limited degree.

The root-killer use involves flushing two pounds of copper sulfate pentahydrate crystals (0.5 lb elemental copper) down a toilet as often as every six months to control tree root growth in domestic sewer systems. Alternatively, label directions recommend one-half pound of product each month as a "maintenance" treatment. The copper sulfate pentahydrate crystals cling to roots and kill them over time.

The ecological risk assessment evaluates the sanitary sewer root-killer use with the "down-the-drain" model E-FAST 2.0. In these simulations, wastewater containing copper crystals flows from the building and passes through a sanitary sewer and publicly owned treatment works (POTW) before being discharged to surface water. The E-FAST model uses the

total national production of a pesticide and distributes it among all households in the nation. However, since the amount of copper sulfate pentahydrate produced for this use could not be distinguished from that manufactured for other uses, the ecological risk assessment made the conservative assumption that each household in the United States applies 0.5 lb of elemental copper for root-control two times a year. This equates to approximately 2.2 million pounds of metallic copper annually. The CSTF subsequently provided a preliminary estimate of potential use of approximately 857,000 pounds of metallic copper annually. The assessment uses a copper sulfate removal efficiency at the POTW of 1.8%, which was estimated using the model EPISuite.

The ecological risk assessment took the resulting concentrations of copper and used them as input to the BLM. The resulting site-specific copper concentration estimates were compared to the toxicity endpoints the BLM generated for each site. The assessment concluded that if all households in the nation were to apply copper sulfate pentahydrate for root-control at maximum recommended rates, then the acute LOC would be exceeded for 85% and 20% of model sites for freshwater invertebrates and fish, respectively. The corresponding percentage of sites for which the chronic level of concern could be exceeded would be 74% and 13%, respectively. However, freshwater fish and invertebrates will not be directly exposed to the full amount of copper applied for root control, since POTWs are required to first treat waste water received from sanitary sewers.

The finding of risk described above should be considered an upper bound, since not every household in the United States uses copper sulfate pentahydrate for root control. Since this product label states that it is not for use in septic systems, even the total number of households which could potentially use the product is lower than assumed in the risk assessment. However, the use of copper sulfate pentahydrate in this manner does represent a direct introduction of copper into the wastewater stream, which was a point of concern for commenters representing POTWs. Tri-TAC, a technical advisory group for POTWs in California, commented that an estimated 5 to 12% of copper received by POTWs in their state was a result of root-killer use. The California Department of Pesticide Regulation has prohibited the use of copper sulfate pentahydrate in nine counties in California out of concern that POTWs in the San Francisco Bay area could not comply with water quality criteria for copper if this use continued.

The E-FAST model allowed a conservative, qualitative estimate of potential exposure from the root-killer use, but no analogous exposure model has been developed to allow a similar screening-level assessment for pesticides applied in an outdoor urban setting. As a result, the Agency has had to take a qualitative approach to characterize the potential aquatic risk from urban and suburban use of copper.

For outdoor urban uses, the Agency assumes that runoff water from rain and/or lawn watering may transport pesticides to storm sewers and then directly to surface water. Copper transported by runoff or erosion in an urban setting would take a path not only over lawns, but also impervious surfaces such as walkways, driveways and streets. The Agency is unaware of any model which can simulate the different application methods for urban use and the physical representation of the urban landscape, storm sewer and receiving water configuration.

There are models available which can be calibrated to simulate sites and pesticides for

which extensive flow and pollutant data have been collected in advance. The HSPF/NPSM model, for instance, which is included in the EPA's BASINS shell, has been used to calibrate stream flow and copper pesticide use data to simulate loading of these pesticides consistent with concentrations measured in surface water monitoring. Risk assessors with the California Department of Environmental Protection confirmed in conversations with the Agency that they also have used watershed models to calibrate previously collected flow and pesticide monitoring data, but that they did not know of any models capable of predicting concentrations of pesticides that might occur because of outdoor urban uses.

Development of a screening model which could simulate the fate and transport of pesticides applied in an urban setting would require a large body of data which is currently unavailable. For instance, an urban landscape cannot be simulated as easily as an agricultural field. The PRZM model simulates runoff from an agricultural field using readily available data describing surface soil characteristics and laboratory data detailing the persistence and mobility of pesticides in these soils. The agricultural field simulated is homogeneously planted to a single crop, and soil and water are transported from the field to a receiving water body with dimensions consistent with USDA farm-pond construction guidelines.

By contrast, an urban landscape or suburban housing development consists of impervious surfaces such as streets and sidewalks, and pervious surfaces such as lawns and parkland. One could expect much greater mobility for pesticides applied to impervious surfaces, but laboratory soil metabolism studies may not provide an accurate measure of the persistence of pesticides on these surfaces. The path runoff water and eroded sediment might take is less obvious for an urban setting than an agricultural field. First, an urban landscape cannot be considered homogeneous, as the proportion of impervious and pervious surfaces varies for different locations. In addition, the flow path of runoff water and sediment is not necessarily a direct path over land, but can pass below ground through storm sewer networks, be directed, or slowed by pumping stations or temporary holding ponds.

Finally, the timing and magnitude of urban uses is less well defined for urban uses than agricultural uses. While agricultural uses would occur within a predictable window during the growing season, the need for urban uses could occur at different times each year, and might occur at different times within the same watershed. In addition, since records of how and to what extent copper pesticides are applied by homeowners are not well defined, it is harder to estimate the total load to model.

## **2. Freshwater Plants**

Because the BLM has not been parameterized for freshwater plants, it could not be used to assess potential copper exposure and toxicity from the cupric ion to freshwater plants. RQs for freshwater plants were calculated using estimates of total dissolved copper using PRZM/EXAMS, which overestimates the amount of copper that is potentially toxic to exposed organisms. The RQs for aquatic plants are presented in Table 9 as individual RQs for each application rate, because the actual toxicity posed by the cupric ion to these organisms cannot yet be simulated by the BLM.

The most sensitive aquatic plant species tested, the green alga, *Selenastrum capricornutum*, ( $LC_{50} = 3.1$  ppb,  $NOEC = 0.2$  ppb) was selected to represent non-vascular aquatic plants. Duckweed, *Lemna minor*, ( $LC_{50} = 2.3$  ppm,  $NOEC = 0.1$  ppm) was selected to represent vascular aquatic plants. Since site-specific exposure and toxicity values for plants were not generated using the BLM, risk is not described as a percentage of RQs above the LOC; rather a single RQ is presented for each application rate, with EECs calculated using the regression described above. Acute RQs based on the green alga, a target species for direct applications of copper to water, exceed the acute and acute endangered species LOC of 1.0 for application rates at or above 1 lb  $Cu^{2+}/A$ . RQs for vascular plants do not exceed the acute or acute endangered species LOCs. Table 9 is a summary of the acute LOC exceedances for aquatic plants.

**Table 9. Summary of Acute LOC Exceedences in Aquatic Environments from Agricultural Uses**

Rate lbs $Cu^{2+}/A$ (ppb)	Acute		Acute Endangered Species	
	Algae RQ	Vascular RQ	Algae RQ	Vascular RQ
1.0 (2.2)	0.7	<0.01	1.1	0.02
1.5 (3.4)	1.1	<0.01	1.7	0.03
3.0 (7.2)	2.3	<0.01	3.6	0.07
5.0 (12.3)	4.0	<0.01	6.2	0.12
7.5 (18.6)	6.0	<0.01	9.3	0.19

### 3. Estuarine/Marine Fish and Invertebrates

Because the BLM has not been parameterized for estuarine/marine organisms, it could not be used to assess potential copper exposure and toxicity from the cupric ion to estuarine/marine animals. RQs for estuarine/marine animals and plants were calculated using estimates of total dissolved copper using PRZM/EXAMS, which overestimates the amount of copper that is potentially toxic to exposed organisms. In addition, the water body simulated by PRZM/EXAMS, a static farm pond with no outflow, is smaller than estuarine and marine water bodies, and does not take into account the dilutive effect of untreated seawater.

Acute toxicity values for saltwater fish and invertebrates were selected based on the most sensitive assessed species. The most sensitive invertebrate is the mussel (*Mytilus*) with an  $LC_{50}$  of 6.49 ppb and the most sensitive fish is the summer flounder (*Paralichthys dentatus*), with an  $LC_{50}$  of 12.66 ppb. Chronic toxicity data were not available for estuarine/marine animals, so the ACR of 3.23 used for freshwater animals was used to derive chronic RQs for marine/estuarine animals.

As for the freshwater organism assessment, RQs for estuarine/marine organisms were calculated using the same regression on the peak copper concentrations that resulted from various application rates in the 32 PRZM/EXAMS simulations run for copper. At approximately 3 lbs  $Cu^{2+}/A$ , acute RQs exceedences occur for both fish and invertebrates. Table 10 lists the acute RQs for marine/estuarine organisms for a range of copper application rates.

**Table 10. Risk Quotients for Estuarine/Marine Animals**

Application Rate lbs Cu <sup>2+</sup> /A	Acute RQ		Chronic RQ	
	Fish	Invertebrate	Fish	Invertebrate
1.0	0.17	0.35	1.1	0.6
1.5	0.27	0.55	1.5	0.8
3.0	0.56	1.2	2.8	1.3
5.0	0.99	2.0	4.4	2.1
7.5	1.5	3.0	6.4	3.1

#### 4. Estuarine/Marine Plants

Because the BLM has not been parameterized for estuarine/marine plants, it could not be used to assess potential copper exposure and toxicity from the cupric ion to estuarine/marine plants. RQs for estuarine/marine plants were calculated using estimates of total dissolved copper using PRZM/EXAMS, which overestimates the amount of copper that is potentially toxic to exposed organisms. The single estuarine/marine plant species tested, the marine diatom, *Skeletonema costatum*, (LC<sub>50</sub> = 0.25 ppm, NOEC = 0.124 ppm) was selected to represent estuarine/marine plants.

Since site-specific exposure and toxicity values for plants were not generated using the BLM, risk is not described as a percentage of RQs above the LOC; rather a single RQ is presented for each application rate, with EECs calculated using the regression described above. RQs for estuarine/marine plants do not exceed the acute or acute endangered species LOC of 1.0. Table 11 summarizes potential acute risk for estuarine/marine plants.

**Table 11. Acute Risk Quotients for Estuarine/Marine Plants**

Application Rate lbs Cu <sup>2+</sup> /A (Cu ppb)	Acute RQ	Acute Endangered Species RQ
1.0 (2.2)	<0.01	0.02
1.5 (3.4)	0.01	0.03
3.0 (7.2)	0.03	0.06
5.0 (12.3)	0.05	0.1
7.5 (18.6)	0.07	0.13

#### b. Terrestrial Organisms

##### 1. Birds and Mammals

###### *Copper Exposure to Birds and Mammals*

For birds and small mammals, dietary exposure to copper was estimated using the Terrestrial Exposure (TREX, Version 1.1) model. Based on the Kenaga nomogram (Hoerger and Kenaga 1972, Fletcher et al. 1994), TREX calculates estimated copper residues on food items animals may consume. In this screening assessment, the Agency assumes that organisms forage 100% of the time in a treated area and that 100% of their diet is comprised of a particular food item.



A default foliar dissipation half-life for copper of 35 days was assumed, as no foliar dissipation studies have been submitted for the copper compounds addressed in this RED. Because copper is an element, it will not degrade by photolysis or hydrolysis into any other metabolites or other byproducts. Thus, the primary means of removal is wash-off due to precipitation or irrigation (e.g., drip) that governs how long copper remains on plant surfaces. Because the amount of wash-off depends on the amount of precipitation, a plant dissipation study would not capture the variability of wash-off rates across the country; thus, data from this study would not provide any additional information to reduce any uncertainty or risk. Therefore, the Agency is not requiring this study at this time.

The Agency modeled potential exposure to terrestrial animals from residues on forage items based on the highest label application rates and the highest average application rates of copper for orchard and row crops. Current copper labels indicate that the highest orchard label application rate is 31.8 lbs Cu<sup>2+</sup>/A for filberts and the highest row crop label application rate is 3.2 lbs Cu<sup>2+</sup>/A for potatoes. Because intervals between applications and the maximum number of applications were not specified on the product labels, the Agency assumed four applications on a weekly basis per growing season. However, based on use data provided by the CSTF and user groups, typical use is lower. These rates, 3.8 lbs Cu<sup>2+</sup>/A for orchards (apples) and 0.8 lb Cu<sup>2+</sup>/A for row crops (potatoes), were also considered in the risk assessment.

### ***Toxicity to Birds and Mammals***

Copper is an essential micronutrient to many organisms, including birds and mammals. Copper atoms are an important component of several enzymes, and reserve copper is stored in the liver and bone marrow. Unlike aquatic animals, in which toxicity occurs when the cupric ion binds to the gills, acute poisoning of terrestrial organisms requires dietary ingestion of toxic levels of copper.

Terrestrial animals have varying degrees of homeostatic capability to metabolize copper when ingested. Two studies (Johnson and Lee 1988, Yu et al., 1993) estimated copper absorption in rats from dietary sources. Dependent on dose and method of estimation, absorption efficiencies for rats with no known metabolic deficiencies ranged from 22-63%. Absorption efficiency was consistently lower at high doses. Dietary copper concentrations ranged from 0.4-100 ppm. In a study evaluating bioaccumulation models for mice (Torres and Johnson 2001), the authors calculated a “GI absorption-elimination factor” of 28% based on data in the ASTDR<sup>1</sup> *Toxicological Profile for Copper*. Thus, it appears that at least up to dietary concentrations measured in these studies, small mammals have compensatory mechanisms to increase absorption of copper at low concentrations, and reduce absorption of copper at high concentrations, at least from dietary sources. No data were located to indicate at what copper concentration these compensatory mechanisms might be overwhelmed, nor were similar data available for birds.

The TREX model assumes that 100% of the ingested chemical is bioavailable, and uses that estimate as an effective dose (adjusted by allometric equations). Based on the existing data,

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<sup>1</sup>Agency for Toxic Substances and Disease Registry

this does not appear to be the case for copper. Dietary-based endpoints likely incorporate these uptake effects, but dose-based endpoints will not. In order to account for these mechanisms, an absorption efficiency correction of 22% (a high copper availability situation) was applied to the mammal dose-based risk quotient calculations. Bird dose-based calculations were not corrected, as it is uncertain to what extent the actual percentages may be valid across taxa, and dietary-based data were available for acute effects.

Coppers are categorized as moderately toxic to birds on an acute oral and dietary basis. The Agency assessed toxicity to avian species based on the acute oral LD<sub>50</sub> of 98 mg/kg-bw, the acute dietary LC<sub>50</sub> of 991 ppm of copper in feed and the chronic NOAEL of 58 mg/kg-bw. Available avian guideline data are described in Table 12 below.

**Table 12. Avian Guideline Data**

Species	Compound	LD50/LC50 (mg/kg)	LOAEL (mg/kg)	NOAEL (mg/kg)
<i>Acute oral</i>				
Bobwhite	Copper sulfate pentahydrate	384	ND	ND
	as metallic copper	98 <sup>a</sup>		
<i>Acute dietary</i>				
Bobwhite	Tri-basic copper sulfate	1829	NR	NR
	as metallic copper	991 <sup>a</sup>		
<i>Reproductive</i>				
Bobwhite	Copper oxychloride sulfate	NR	500	100
	as metallic copper		289	58 <sup>a</sup>

<sup>a</sup> toxicity endpoint used in assessment  
 ND - not determined, NR - not reported

Available oral data on mammals indicate that copper is moderately toxic on an acute basis. The Agency assessed toxicity to mammals based on the acute oral LD<sub>50</sub> of 114 mg/kg-bw. Because no reproductive or two-generation copper studies conducted with small mammals were available, the Agency opted to use the chronic NOAEL study conducted on the mink from the Superfund site-screening guideline studies. The NOAEL in this study was 85.5 mg/kg diet (11.7 mg/kg-bw on a dose basis). Available acute oral rat toxicity data and chronic mammalian screening values are described below in Tables 13 and 14, respectively.

**Table 13. Acute Oral Toxicity in Rats**

Compound	As Copper Compound	As Metallic Copper
	LD50 (mg/kg-bw)	LD50 (mg/kg-bw)
Copper sulfate pentahydrate	790 (male)	200 (male)
	450 (female)	114 (female) <sup>a</sup>

<sup>a</sup> toxicity endpoint used in assessment

**Table 14. Chronic Mammalian Screening Values**

Category	Benchmark	Effects
Mammals Test species: mink	NOAEL 11.7 mg/kg-bw <sup>a</sup> 85.5 mg/kg diet <sup>a</sup> LOAEL 15.1 mg/kg-bw 110.5 mg/kg diet	Chronic dietary exposure during reproduction. Effects were reduced survivorship of kits. Copper dose represented a base in food (60.5 ppm) plus a supplement (25, 50, 100, and 200 ppm). At 25 ppm in diet, kit survivorship was greater than in controls. Reduced survivorship of kits was noted in the 50 ppm treatment group.

<sup>a</sup> toxicity endpoint used in assessment

### ***Risk to Birds and Mammals***

The terrestrial animal risk assessment for copper pesticides assessed the potential for risk at the highest application rate on any copper label for use on orchards and on row crops. These application rates are 31.8 lbs Cu<sup>2+</sup>/A for orchards (filberts) and 3.2 lbs Cu<sup>2+</sup>/A for row crops (potatoes). RQs were also calculated for the highest average application rate for orchards and for row crops, as determined by the best data available to the Agency at the time the risk assessment was completed. These rates were 3.8 lbs Cu<sup>2+</sup>/A for orchards (apples) and 0.8 lb Cu<sup>2+</sup>/A for row crops (potatoes). Because the maximum number of applications and minimum application interval were not specified on the product labels for these rates, the assessment assumed four applications spaced seven days apart.

The RQs for the maximum application rates exceeded nearly all acute and chronic LOCs for all weight classes of birds and mammals. However, as part of the stakeholder process in formulating risk management decisions, the Agency has worked with copper pesticide registrants and the user community to revise the labels to require lower application rates and more clearly defined seasonal maximum use rates. Therefore, the RQs based on average application rates shown below better reflect the lower rates to be established on revised copper product labels.

The RQs calculated using typical application rates indicate the potential for acute and chronic risk to birds and mammals from dietary exposure. Dietary toxicity studies, in which animals are exposed through ingestion of treated feed, would be expected to reflect the ability of the animals to cope with exposure to a certain amount of copper beyond their dietary need through homeostasis. However, this coping mechanism was clearly overwhelmed in the animals which died in the laboratory toxicity tests.

The design of the laboratory studies leaves some uncertainty in how these effects would translate to effects in the wild. Birds and mammals in the laboratory studies are only fed treated feed, and the RQs in the risk assessment also assume that animals will derive 100% of their diet from treated feed. Although animals in the wild need to eat more than their counterparts in the laboratory (since lab feed is more nutritious, generally), most birds and mammals will spend only a fraction of the time in or at the edge of a treated field. Animals which eat untreated feed as a portion of their diet may have more of an opportunity to cope with ingested copper when the exposure is not continuous. In addition, animals which are repeatedly exposed to levels of copper which do not cause permanent harm may undergo enzymatic adaptation which allows them to cope with greater levels of exposure. The sensitivity to copper toxicity, and the ability to

adapt to repeated exposures, should be expected to vary within species, and between species of birds and mammals.

### Birds

Dose-based and dietary-based endpoints from available avian studies were used to calculate acute RQs. Chronic endpoints for birds were based on data from reproductive studies conducted on the bobwhite quail. The EECs are adjusted to reflect potential dietary exposure based on the size of the animal and the respective amount of feed consumed.

### *Orchard Applications*

The highest label rate for orchard applications was for filberts (31.8 lbs Cu<sup>2+</sup>/A). At this application rate, all size classes of birds exceed the acute, acute endangered species, and chronic levels of concern for all food items. Table 15 describes the avian RQs for acute dose-based and dietary-based RQs, and chronic RQs based on orchard labeled rates.

**Table 15. Avian RQ Summary - Orchard Maximum Label Rate (31.8 lbs Cu<sup>2+</sup>/A)**

Feed Item	Acute dose-based RQs			Acute dietary-based RQs	Chronic RQs
	20g bird	100g bird	1000 g bird	All birds	All birds
Short grass	220	98.7	31.2	13.5	231
Tall grass	101	45.3	14.3	6.2	106
Broadleaf plants/small insects	124	55.5	17.5	7.6	130
Fruits/pods/seeds/large insects	13.8	6.2	2.0	0.9	14.5

The highest average rate for orchard applications was for apples (3.8 lbs Cu<sup>2+</sup>/A). At this application rate, all size classes of birds exceed the endangered species acute risk LOC and the chronic risk LOC for all food items. Birds consuming the short grass, tall grass, and broadleaf plants food categories all exceed the acute risk and chronic risk LOCs, whereas with the fruit food item, larger birds and birds assessed with dietary-based endpoints are below the acute risk LOC. Table 16 describes the avian RQs for acute dose-based and dietary-based RQs, and chronic RQs based on orchard average application rate of 3.8 lbs Cu<sup>2+</sup>/A.

**Table 16. Avian RQ Summary - Orchard Average Rate (3.8 lbs Cu<sup>2+</sup>/A)**

Feed item	Acute dose-based RQs			Acute dietary-based RQs	Chronic RQs
	20g bird	100g bird	1000 g bird	All birds	All birds
Short grass	49.3	22.1	7.0	3.0	51.7
Tall grass	22.6	10.1	3.2	1.4	23.7
Broadleaf plants/small insects	27.7	12.4	4.0	1.7	29.1
Fruits/pods/seeds/large insects	3.1	1.4	0.4	0.2	3.2

*Row Crop Applications*

The highest label rate for row crop applications was for potatoes (3.2 lbs Cu<sup>2+</sup>/A). At this application rate, all size classes of birds consuming the short grass, tall grass, and broadleaf plant food categories exceed the acute risk levels of concern. The small (20g) and medium (100g) birds consuming a diet of fruits, pods, seeds, or large insects exceed the acute risk LOC, using the dose-based calculation. All size classes of birds consuming all food types exceed the endangered species acute risk LOC and the chronic risk LOC. Table 17 describes the avian RQs for acute dose-based and dietary-based RQs, and chronic RQs based on row crop maximum application rate of 3.2 lbs Cu<sup>2+</sup>/A.

**Table 17. Avian RQ Summary - Row Crop Maximum Label Rate (3.2 lbs Cu<sup>2+</sup>/A)**

Feed Item	Acute dose-based RQs			Acute dietary-based RQs	Chronic RQs
	20g bird	100g bird	1000g bird	All birds	All birds
Short grass	41.5	18.6	5.9	2.6	43.5
Tall grass	19.0	8.5	2.7	1.2	20.0
Broadleaf plants/small insects	23.3	10.5	3.3	1.4	24.5
Fruits/pods/seeds/large insects	2.6	1.2	0.4	0.2	2.7

The highest average rate for row crop applications was for potatoes (0.8 lb Cu<sup>2+</sup>/A). At this application rate, birds consuming the short grass, tall grass, and broadleaf plant categories exceed the endangered species acute risk LOC and the chronic risk LOC. Using dose-based RQs, all bird consuming these food categories also exceed the acute risk LOC. Only birds consuming short grass exceed the acute risk LOC using the dietary-based RQs. Birds consuming the fruits and pods food category exceed the endangered species acute risk LOC using dose-based RQs, but not dietary-based RQs. Only the small bird (20g) in this category exceeds the acute risk LOC using the dose-based RQ. Table 18 describes the avian RQs for acute dose-based and dietary-based RQs, and chronic RQs based on row crop average application rate of 0.8 lb Cu<sup>2+</sup>/A.

**Table 18. Avian RQ Summary - Row Crop Average Rate (0.8 lb Cu<sup>2+</sup>/A)**

Feed Item	Acute dose-based RQs			Acute dietary-based RQs	Chronic RQs
	20g bird	100g bird	1000 g bird	All birds	All birds
Short grass	10.4	4.7	1.47	0.6	10.9
Tall grass	4.8	2.1	0.67	0.3	5.0
Broadleaf plants/small insects	5.8	2.6	0.83	0.4	6.1
Fruits/pods/seeds/large insects	0.7	0.3	0.1	<0.1	0.7

Mammals

Acute RQs from dose-based acute mammalian studies have been adjusted to include a 22% absorption factor to account for dietary effects described above. Because dietary-based chronic data were available, the chronic dose-based values were not adjusted.

*Orchard Applications*

The highest labeled application rate for orchard use was for filberts at 31.8 lbs Cu<sup>2+</sup>/A, assuming four applications at weekly intervals. At this application rate, RQs for all size classes of mammals consuming plants or small insects exceed the acute risk, endangered species acute risk, and chronic risk LOCs. Except for 1,000g granivores, all size classes and food groups evaluated exceed the endangered species acute risk LOC. Table 19 summarizes acute and chronic risks to mammals.

**Table 19. Mammal RQ Summary - Orchard Maximum Label Rates (31.8 lbs Cu<sup>2+</sup>/A)**

Feed Items	Acute dose-based RQs (adjusted for 22% absorption efficiency)			Chronic dose-based RQs			Chronic dietary-based RQs
	15g	35g	1000g	15g	35g	1000g	All mammals
Short grass	11.2	9.6	5.1	381	327	172	157
Tall grass	5.1	4.4	2.3	175	150	78.8	71.9
Broadleaf plants/small insects	6.3	5.4	2.8	214	184	96.8	88.3
Fruits/pods/seeds/large insects	0.7	0.6	0.3	23.8	20.5	10.8	9.8
Seeds (granivores)	0.15	0.14	0.06	5.3	4.7	2.2	Not determined

The highest average application rate for orchard use was apples at 3.8 lbs Cu<sup>2+</sup>/A (4 applications, 7-day interval). RQs for all size classes of organisms consuming the short grass, tall grass, broadleaf plants, and small insects exceed both the acute risk LOC and the endangered species LOC. Endangered species acute risk LOCs are also exceeded for the 15g and 35g mammals consuming fruits and large insects. RQs for all diet classes exceed the chronic risk LOC. RQs presented below are based on upper-bound EECs from the Kenaga nomogram (Hoerger and Kenaga 1972, Fletcher et al. 1994). Table 20 describes the mammalian RQs for acute dose-based and dietary-based RQs, and chronic RQs based on orchard average application rate of 3.8 lbs Cu<sup>2+</sup>/A.

**Table 20. Mammal RQ Summary - Orchard Average Rate (3.8 lbs Cu<sup>2+</sup>/A)**

Feed item	Acute dose-based RQs (adjusted for 22% absorption efficiency)			Chronic dose-based RQs			Chronic dietary-based RQs
	15g	35g	1000g	15g	35g	1000g	All mammals
Short grass	2.5	2.2	1.13	85.2	73.2	38.5	35.1
Tall grass	1.2	0.98	0.52	39.1	33.5	17.6	16.1
Broadleaf plants/small insects	1.4	1.21	0.63	47.9	41.2	21.6	19.7
Fruits/pods/seeds/large insects	0.16	0.13	0.07	5.3	4.6	2.4	2.2
Seeds (granivores)	0.03	0.03	0.01	1.2	1.0	0.5	Not determined

### Row Crop Applications

The highest average application rate for row crop use was potatoes at 0.8 lb Cu<sup>2+</sup>/A (4 applications, 7-day interval). Only the RQs for the small mammals consuming short grass exceed the acute risk LOC, although RQs for all size classes of mammals consuming grass, broadleaf plants, and small insects exceed the endangered species acute risk LOC. Dietary-based RQs for the mammals consuming grass, broadleaf plants, and small insects exceed the chronic LOC. RQs presented below are based on upper-bound EECs from the Kenaga nomogram (Hoerger and Kenaga 1972, Fletcher et al. 1994). Table 21 describes the mammalian RQs for acute dose-based and dietary-based RQs, and chronic RQs based on row crop average application rate of 0.8 lb Cu<sup>2+</sup>/A.

**Table 21. Mammal RQ Summary - Row Crop Average Rates (0.8 lb Cu<sup>2+</sup>/A)**

Feed item	Acute dose-based RQs (adjusted for 22% absorption efficiency)			Chronic dose-based RQs			Chronic dietary-based RQs
	15g	35g	1000g	15g	35g	1000g	All mammals
Short grass	0.53	0.45	0.24	17.9	15.4	8.1	7.4
Tall grass	0.24	0.21	0.11	8.2	7.1	3.8	3.4
Broadleaf plants/small insects	0.30	0.25	0.13	10.1	8.7	4.6	4.2
Fruits/pods/seeds/large insects	0.03	0.03	0.01	1.1	1.0	0.5	0.5
Seeds (granivores)	0.01	0.01	<0.01	0.3	0.2	0.1	Not Determined

## 2. Nontarget Insects

Available data from a honey bee acute toxicity study indicated that copper is practically nontoxic to honey bees, with an acute LD<sub>50</sub> > 100 µg/bee. However, because exposure estimates for other insects cannot readily be determined, the potential risk of copper pesticides to other insects is unknown.

### 3. Terrestrial Plants

The Agency assessed potential indirect exposure and risk to plants adjacent to treated areas. The Agency used the TerrPlant model, which calculates EECs for upland and wetland areas adjacent to the application site based on a combination of the potential runoff from the field and spray drift from the method of application. This type of exposure is then compared to seedling emergence endpoints to derive acute RQs. To assess effects from spray drift, estimated EECs are compared against a vegetative vigor endpoint to derive “drift only” RQs.

The Agency could not conduct a complete terrestrial plant risk assessment, since the toxicity dataset for copper is incomplete. Vegetative vigor data for both monocots and dicots were available from the public literature, but no suitable data from the registrant or open literature were found to evaluate the effects of copper on seedling emergence. Therefore, it was only possible to assess the potential risk from drift of copper pesticides alone. Copper is not expected to pose a risk to plants through its fungistatic mode of action. As described above, data available through the ECOTOX database were used to determine that copper pesticides does not appear to pose a risk to terrestrial plants via adverse effects to vegetative vigor. Furthermore, copper did not exceed the acute or endangered species levels-of-concern for vascular aquatic plants. Hence, no additional data is required at this time, as it appears unlikely that copper would pose a risk to terrestrial plants.

Consideration of terrestrial plant exposure from drift from the highest label application rates for copper are sufficient to evaluate the potential risk from vegetative vigor effects. The highest orchard application rate on copper labels at the time the risk assessment was developed was 31.8 lbs Cu<sup>2+</sup>/A for filberts. Because the Terr-Plant model assumes a default spray drift exposure of 1% of applied pesticide for ground-spray applications, and 5% for aerial applications, the drift exposure from that maximum application rate is 0.03 lb Cu<sup>2+</sup>/A and 0.16 lb Cu<sup>2+</sup>/A, respectively.

Raw data to calculate the EC<sub>25</sub> (used to determine the acute RQ) were not available. The more sensitive NOAEC, which is used to evaluate potential effects on endangered plants, was available for both monocots and dicots. Hence, RQs were calculated for endangered species vegetative vigor endpoints for both monocots and dicots, also using the maximum label rates for orchards of 31.8 lbs Cu<sup>2+</sup>/A. As with other effects endpoints, the data were corrected to express the toxicity value in terms of elemental copper. No RQs exceeded the acute endangered species LOC at this rate, which is substantially higher than the maximum application rate on filberts will be after mitigation measures detailed in Section IV take effect. Therefore, there appears to be no acute risk to non-endangered or listed terrestrial plants from spray drift. Toxicity endpoints and RQs for terrestrial plants are summarized below in Table 22.

**Table 22. Coppers RQs for Terrestrial Plants for Spray Drift**

Plant Type	Type of Endpoint	NOAEC (lbs Cu <sup>2+</sup> /Acre)	Acute Endangered Species RQ	
			Ground Spray	Aerial, airblast, spray chemigation
Monocot	Vegetative vigor	6.8	0.05	0.24
Dicot		36.7	0.01	0.04



### c. Endangered Species

The risk assessment for copper pesticides indicates a potential for direct effects on listed species as noted below, should exposure actually occur at modeled levels:

#### Terrestrial organisms

- Mammals
  - Acute RQs exceed the endangered species LOC for all mammals feeding on short grass, tall grass, broadleaf forage and small insects for all application rates modeled.
  - Chronic RQs exceed the LOC for all mammals feeding on short grass, tall grass, broadleaf forage and small insects, and fruits/pods/seeds/large insects for all rates modeled (except 1000g mammals feeding on fruits/pods/seeds/large insects for application rate of 0.8 lb Cu<sup>2+</sup>/A). The chronic RQ for granivores exceeds for smaller mammals at higher application rates (such as the 3.8 lbs Cu<sup>2+</sup>/A representing an average orchard application rate).
- Birds
  - Acute RQs exceed the endangered species LOC for birds feeding on short grass, tall grass, broadleaf forage and small insects, and fruits/pods/seeds/large insects for all application rates modeled.
  - Chronic RQs exceed the LOC for all birds feeding on short grass, tall grass, broadleaf forage and small insects, and fruits/pods/seeds/large insects for all rates modeled (except for birds feeding on fruits/pods/seeds/large insects for application rate of 0.8 lb Cu<sup>2+</sup>/A). The chronic RQ for birds feeding on fruits/pods/seeds/large insects exceeds the LOC at higher application rates (such as the 3.8 lbs Cu<sup>2+</sup>/A representing an average orchard application rate).

#### Aquatic Organisms

- Freshwater animals
  - The percentage of acute RQs for freshwater fish modeled with PRZM/EXAMS and the BLM that exceed the endangered species LOC ranges from 1.0% at 1.0 lb Cu<sup>2+</sup>/A to 17.1% at 7.5 lbs Cu<sup>2+</sup>/A for agricultural uses of copper.
  - The percentage of acute RQs for freshwater invertebrates modeled with PRZM/EXAMS and the BLM that exceed the endangered species LOC ranges from 19.0% at 1.0 lb Cu<sup>2+</sup>/A to 84.0% at 7.5 lbs Cu<sup>2+</sup>/A for agricultural uses of copper .
  - The percentage of chronic RQs for freshwater fish modeled with PRZM/EXAMS and the BLM that exceed the endangered species LOC ranges from 0.0% at 1.0 lb Cu<sup>2+</sup>/A to 5.3% at 7.5 lbs Cu<sup>2+</sup>/A for agricultural uses of copper.

- The percentage of chronic RQs for freshwater invertebrates modeled with PRZM/EXAMS and the BLM that exceed the endangered species LOC ranges from 4.2% at 1.0 lb Cu<sup>2+</sup>/A to 32.4% at 7.5 lbs Cu<sup>2+</sup>/A for agricultural uses of copper.
- For freshwater invertebrates and fish, >99% of sites modeled with PRZM/EXAMS and the BLM exceed the acute endangered species LOC at an application rate of 1 ppm.
- Estuarine/Marine
  - The acute endangered species LOC is exceeded for estuarine/marine fish and invertebrates for agricultural uses at application rates of 1.0 lb Cu<sup>2+</sup>/A and above.
  - The chronic endangered species LOC is exceeded for estuarine/marine fish for agricultural uses at application rates of 1.0 lb Cu<sup>2+</sup>/A and above.
  - The chronic endangered species LOC is exceeded for estuarine/marine invertebrates for agricultural uses at application rates of around 3.0 lbs Cu<sup>2+</sup>/A and higher.
- Plants
  - The acute endangered species LOC is exceeded for non-vascular freshwater plants for agricultural uses at application rates of 1.0 lb Cu<sup>2+</sup>/A and higher.

Further, potential indirect effects to any listed species dependent upon a species that experiences effects from use of copper can not be precluded based on the screening level ecological risk assessment. These conclusions are based solely on EPA's screening-level assessment and do not constitute "may effect" findings under the Endangered Species Act for any listed species.

### **3. Ecological Incidents**

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. For the active ingredients addressed in this RED, the Agency's Ecological Incident Information System (EIIS) reports 24 incidents related to copper pesticide applications. Of the 24 incidents, seven were associated with terrestrial plants with certainty rated as possible or probable. One reported case of damage to tomatoes in Washington state occurred when copper applications were made according to labeled use instructions. The other six incidents affecting corn and peanuts in Indiana, Minnesota and Oklahoma, reported effects including plant damage, incapacitation and pinched corn ears. None of these six incidents reported the legality of the use. Seventeen of the incidents were associated with kills of aquatic organisms, primarily consisting of fish. Of these incidents, ten were classified as possible, probable or highly probable, with the assumption that coppers were used in accordance with the registered label. Reported incidents were generally fish kills, with deaths ranging from 100 to 1,000, with the exception of one case in New York, where the report states that over one million fish were killed. In all cases, mortalities effects were reported, but the mechanisms of toxicity were not specified (direct toxicity or secondary effects such as low dissolved oxygen). The

remaining aquatic incidents were cases of misuse or described effects which are unlikely to be related to copper pesticide applications.

## **IV. Risk Management, Reregistration, and Tolerance Reassessment Decision**

### **A. Determination of Reregistration Eligibility**

Section 4(g)(2)(A) of FIFRA calls for the Agency to determine, after submission of relevant data concerning an active ingredient, whether or not products containing the active ingredients are eligible for reregistration. The Agency has previously identified and required the submission of the generic data required to support reregistration of products containing copper as an active ingredient. The Agency has completed its review of these generic data and has determined that the data are sufficient to support reregistration of all products containing copper that have registered agricultural uses.

The Agency has completed its assessment of the dietary, occupational, residential, and ecological risk (agricultural uses only) associated with the use of pesticide products containing the active ingredient copper. Based on a review of these data and on public comments on the Agency's assessments for copper, the Agency has sufficient information on the human health and ecological effects of copper to make decisions as part of the tolerance reassessment process under FFDCA and reregistration process under FIFRA, as amended by FQPA. The Agency has determined that copper-containing products registered for agricultural uses are eligible for reregistration provided that the risk mitigation measures outlined in this document are adopted and label amendments are made to reflect these measures. Label changes are described in Section V. The antimicrobial ecological assessment of copper compounds will be conducted at a later date. Appendix A summarizes the uses of copper that are eligible for reregistration. Appendix B identifies the generic data requirements that the Agency reviewed as part of its determination of reregistration eligibility of copper, and lists the submitted studies that the Agency found acceptable. Data gaps are identified as generic data requirements that have not been satisfied with acceptable data.

Based on its evaluation of copper, the Agency has determined that agricultural uses (terrestrial and aquatic crops, direct aquatic uses, urban uses) of copper products, unless labeled and used as specified in this document, would present risks inconsistent with FIFRA. Accordingly, should a registrant fail to implement any of the risk mitigation measures identified in this document, the Agency may take regulatory action to address the risk concerns from the use of copper. If all changes outlined in this document are incorporated into the product labels, then all current risks for copper will be adequately mitigated for the purposes of this determination under FIFRA. Once an Endangered Species assessment is completed, further changes to these registrations may be necessary.

### **B. Public Comments and Responses**

Through the Agency's public participation process, EPA worked extensively with registrants, stakeholders and the public to reach the regulatory decisions for copper. Because the June 2005 preliminary ecological risk assessment indicated significant risk exceedances for virtually all non-target organisms, the Agency requested refined use information from the registrants. The Agency initiated outreach efforts with the CSTF and USDA to contact the grower community to provide additional information reflective of actual use rates and other use

information on copper agricultural products. However, these data were still inadequate to fully revise the ecological risk assessment. Thus, EPA requested additional refined use information during the Phase 3 Public Comment period for the grower community and other user groups to provide use information and other input on the use of copper products labeled for agricultural uses. During the public comment period on the risk assessments, which closed on March 27, 2006, the Agency received extensive comments from registrants, commodity/grower groups, cooperative extension specialists, and university/research facilities. The refined use information provided by user groups was used to refine the ecological risk assessment. User groups also provided information on the significance of coppers in agricultural and aquatic applications. These comments in their entirety and the Agency's response are available in the public docket (EPA-HQ-OPP-2005-0558) at <http://www.regulations.gov>.

## **C. Regulatory Position**

### **1. FQPA Findings**

#### **a. Risk Determination**

As part of the FQPA tolerance reassessment process, EPA assessed the risks associated with exposure to copper pesticides. EPA has determined that individual and aggregate risk from all sources of exposure (food, drinking water and residential uses) to copper, including agricultural, direct aquatic, and antimicrobial uses, will not exceed EPA's LOCs. The EPA has concluded that the tolerances for copper meet FQPA safety standards. In reaching this determination, EPA has considered the available information on the special sensitivity of infants and children, as well as aggregate exposure from copper.

#### **b. Determination of Safety to U.S. Population**

The Agency has determined that the established tolerances for copper, with amendments and changes as specified in this document, meet the safety standards under the FQPA amendments to section 408(b)(2)(D) of the FFDCA, and that there is a reasonable certainty no harm will result to the general population or any subgroup from the use of copper pesticides. In reaching this conclusion, the Agency has considered all available information on the toxicity, use practices and exposure scenarios, and the environmental behavior of copper.

As discussed in Section III, the total acute and chronic dietary risks from copper do not exceed EPA's LOC. Also, aggregate risk from exposure to copper from all sources, including agricultural, direct aquatic, and antimicrobial uses, is not of concern. Aggregate exposures include dietary (food and drinking water) and residential uses of copper.

#### **c. Determination of Safety to Infants and Children**

EPA has determined that the established tolerances for copper meet the safety standards under the FQPA amendments to section 408(b)(2)(C) of the FFDCA, that there is a reasonable certainty of no harm for infants and children. The safety determination for infants and children considers factors on the toxicity, use practices and environmental behavior noted above for the

general population, but also takes into account the possibility of increased dietary exposure due to the specific consumption patterns of infants and children, as well as the possibility of increased susceptibility in this population subgroup.

In determining whether or not infants and children are particularly susceptible to toxic effects from exposure to residues of copper, the Agency considered the completeness of the hazard database for developmental and reproductive effects, the nature of the effects observed, and other information. Since copper is a natural essential trace element, with deficiency more common in humans than toxicity from excess, and the low total dietary contribution of copper, toxicity endpoints were not selected. As described in Section IV above, due to an absence of systemic toxicity, risks were not quantified and application of an FQPA SF was unnecessary.

## **2. Endocrine Disruptor Effects**

EPA is required under the FFDCA, as amended by FQPA, to develop a screening program to determine whether certain substances (including all pesticide active and other ingredients) “may have an effect in humans that is similar to an effect produced by a naturally-occurring estrogen, or other endocrine effects as the Administrator may designate.” Following recommendations of its Endocrine Disruptor Screening and Testing Advisory Committee (EDSTAC), EPA determined that there was a scientific basis for including, as part of the program, the androgen and thyroid hormone systems, in addition to the estrogen hormone system. EPA also adopted EDSTAC’s recommendation that EPA include evaluations of potential effects in wildlife. For pesticides, EPA will use FIFRA and, to the extent that effects in wildlife may help determine whether a substance may have an effect in humans, FFDCA authority to require the wildlife evaluations. As the science develops and resources allow, screening of additional hormone systems may be added to the Endocrine Disruptor Screening Program (EDSP).

The available human health and ecological effects data for copper currently do not indicate any evidence of endocrine disruption. Based on current available data, the Agency does not have any concerns for endocrine disruption from exposure to copper pesticides.

## **3. Cumulative Risks**

The FFDCA, as amended by FQPA, requires that the Agency consider “available information” concerning the cumulative effects of a particular pesticide’s residues and “other substances that have a common mechanism of toxicity.” The reason for consideration of other substances is due to the possibility that low-level exposures to multiple chemical substances that cause a common toxic effect by a common toxic mechanism could lead to the same adverse health effect as would a higher level of exposure to any of the substances individually. 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 RED, therefore, EPA has not assumed that the copper ion has a common mechanism of toxicity with other substances. For information regarding EPA’s efforts to determine which chemicals have a common mechanism of toxicity

and to evaluate the cumulative effects of such chemicals, see the policy statements released by the Agency concerning common mechanism determinations and procedures for cumulating effects from substances found to have a common mechanism on EPA's website at <http://www.epa.gov/pesticides/cumulative/>.

#### **4. Endangered Species**

The Agency has developed the Endangered Species Protection Program to identify pesticides whose use may cause adverse impacts on federally listed endangered and threatened species, and to implement mitigation measures that address these impacts. The ESA requires federal agencies to ensure that their actions are not likely to jeopardize listed species or adversely modify designated critical habitat. To analyze the potential of registered pesticide uses that may affect any particular species, EPA uses basic toxicity and exposure data developed for the REDs and considers ecological parameters, pesticide use information, the geographic relationship between specific pesticide uses and species locations and biological requirements and behavioral aspects of the particular species. When conducted, this analysis will consider regulatory changes recommended in this RED that are being implemented at that time. A determination that there is a likelihood of potential effects to a listed species may result in limitations on the use of the pesticide, other measures to mitigate any potential effects, or consultations with the Fish and Wildlife Service or National Marine Fisheries Service as appropriate. If the Agency determines that the use of copper "may affect" listed species or their designated critical habitat, EPA will employ the provisions in the Services regulations (50 CFR Part 402). Until that species specific analysis is completed, the risk mitigation measures being implemented through this RED will reduce the likelihood that endangered and threatened species may be exposed to copper at levels of concern.

#### **D. Tolerance Reassessment Summary**

Tolerance exemptions for residues of copper in/on plant, animal and processed commodities are established under 40 CFR §180.1021. Additional tolerances for potable water and post-harvest use on pears are established under 40 CFR §180.538 and 40 CFR §180.136, respectively.

The Agency has determined that both the 3 ppm tolerance for residues of basic copper carbonate in or on pears of combined copper from post-harvest use under 40 CFR §180.136, and the 1 ppm tolerance for copper residues in potable water under 40 CFR §180.538 should be revoked because these two tolerances are not necessary for human health protection. The Agency has also determined that the copper tolerance expression under 40 CFR §180.1021 should be revised to include all current copper active ingredients with registered food uses.

#### **1. Tolerances Proposed to be Revoked**

**40 CFR §180.136.** The 3 ppm tolerance for residues of basic copper carbonate in or on pears of combined copper from post-harvest use should be revoked. This 3 ppm tolerance is not necessary for human health protection, as many food commodities not treated with copper pesticides have naturally-occurring levels of copper that are higher than those found in or on

pears as a result of residues from treated paper wrappers. In addition, toxicological studies support that potential copper residue levels from the use of treated pear wrappers do not pose a significant risk to human health. Thus, retaining this tolerance is not necessary.

**40 CFR §180.538.** The 1 ppm tolerance for copper residues in potable water should be revoked, as this is an outdated tolerance and no longer applies to current regulations for managing copper residues in drinking water. This 1 ppm tolerance is not necessary for human health protection.

## **2. Tolerances Listed Under 40 CFR §180.1021**

The listed copper active ingredients are currently exempt from tolerance requirements on all raw agricultural commodities under 40 CFR §180.1021. As part of the reregistration process for copper, the Agency concludes that all food use copper formulations are still exempt from the requirement of a tolerance. Should any additional copper active ingredients be registered for new food uses in the future, the need for a tolerance for these formulations will be evaluated at that time.

Copper linoleate and copper oleate should be removed from the list of copper compounds described in 40 CFR §180.1021(4)(b), because there are no current registrations that contain either copper lineoleate or copper oleate. Both copper compounds are currently unsupported in the United States. Bordeaux mixture and copper-lime mixture should also be removed from 40 CFR §180.1021(4)(b), because copper sulfate is the active ingredient in these mixtures, which has been assessed as part of this RED, and is already included as part of 40 CFR §180.1021(4)(b). Cupric oxide should be removed from 40 CFR §180.1021(4)(b) as well, as there are no current products that contain cupric oxide that are registered for food use applications.

There are some copper compounds that have registered agricultural uses on food crops that are not currently described under 40 CFR §180.1021. The Agency has determined that even with the inclusion of these copper compounds as part of tolerance reassessment, that the tolerance exemption is still appropriate for all currently registered copper compounds when used as labeled on growing crops, and the list described under 40 CFR §180.1021(4)(b) should be expanded to include the following copper compounds listed in Table 23.



**Table 23. 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	024001	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
<i>Copper Compounds to Remove</i>			
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.

## E. Regulatory Rationale

The following is a summary of the rationale for mitigation measures necessary for managing risks associated with the use of coppers and for agricultural copper products to be eligible for reregistration. Where labeling revisions are warranted, specific language is set forth in the summary table of Section V (Table 26 of this document).

### 1. Human Health Risk Management

All potential human health acute and chronic exposures (dietary, aggregate, residential, and occupational) are below EPA's level of concern to the Agency for the U.S. general population and all population subgroups, including infants and children. Copper is a ubiquitous element that is essential for proper homeostasis in human health. Residues of copper on foods resulting from agricultural pesticide use are not expected to significantly contribute to the overall dietary intake of copper, as several foods already have naturally-occurring levels of copper.

Based on available literature and studies, there is no indication of systemic effects resulting from copper exposures. Therefore, the minimum handler PPE (long-sleeved shirt and

long pants, socks and shoes) for occupational workers will be required by the RED. However, copper can be a severe irritant with effects resulting from dermal, oral, eye or inhalation exposure that are solely due to the irritating properties of copper. These irritation effects are a result of the body's mechanisms to reduce excessive exposure to copper. Each copper compound and its product formulations can cause different degrees of acute oral, dermal, eye, and inhalation irritation effects. To minimize irritation via these routes, commercial uses of copper-based pesticides will be adequately protected through label-specified handler PPE (based on the toxicity categories of the end-use product) and industrial workplace safety standards. Depending on the acute toxicity of the active ingredient, the minimum re-entry interval (REI) is 12 hours, but may be up to 48 hours for copper compounds with greater acute toxicity categories. To determine the appropriate specific PPE, registrants will need to submit product-specific data as outlined in the product-specific DCIs (PDCI) subsequent to the issuance of this RED.

Post-application restrictions (REIs and early-entry PPE) will default to the measures as required by the Worker Protection Standard (WPS) in 40 CFR §170. Depending on the acute toxicity of the copper compound, the minimum REI is 12 hours, but may be up to 48 hours for copper compounds with greater acute toxicity categories. The early-entry PPE will also be determined by the acute toxicity of the active ingredient. Table 24 below describes the REI for each copper compound. Appropriate REIs and early-entry PPE for each copper compound is described in Table 26. For formulations with residential uses, dermal and eye irritation effects will be addressed via end-use product labeling language.

**Table 24. REIs for each Copper Compound**

REI	Copper Compound	PC Code	Study Reference
48-hour (Toxicity category I)	Copper chloride	008001	No studies available for dermal sensitization
	Chelates of copper gluconate	024405	No studies available
	Copper ammonium carbonate	022703	No studies available
	Copper carbonate	022901	Primary eye irritation
	Copper hydroxide	023401	Primary eye irritation
	Copper ammonia complex	022702	No studies available
	Copper oxychloride	023501	Primary eye irritation
	Copper oxychloride	023503	No studies available
	Basic copper sulfate	008101	No studies available
	Copper sulfate anhydrous	024408	No studies available
	Copper sulfate pentahydrate	024401	Primary eye irritation
	Cuprous oxide	025601	Acute dermal irritation
	Copper triethanolamine complex	024403	No studies available for acute dermal sensitization
	Copper 8-quinolinolate	024002	Primary eye irritation
	Copper naphthenate	023102	Primary eye irritation
	Copper salts of fatty and rosin acids	023104	No studies available for acute dermal sensitization
Copper ethanolamine complex	024409	No studies available	
24-hour (Toxicity Category II)	Copper, metallic	022501	Primary eye irritation
	Copper ethylenediamine	024407	Acute oral irritation
12-hour (Toxicity Category III or IV)	Cupric oxide	042401	Toxicity category III for acute dermal, primary eye and dermal irritation
	Copper octanoate	023306	Toxicity category III for acute oral, dermal and irritation studies

Given the role copper plays as an essential element to the human body, its ubiquitous nature in food and drinking water, low toxicity profile, and the lack of incidents showing any effects resulting from systemic toxicity, there are no systemic human health risks of concern to the Agency; thus, no mitigation is needed beyond that which is required to address the irritation effects associated with copper compounds.

## **2. Ecological Risk Management for Non-target Organisms**

Ecological risk mitigation measures may include lowering application rates, reducing the number of applications in a given year, restricting the timing of applications, extending the period between applications (application interval), and changing pesticide application methods to reduce the potential for spray drift or runoff.

The screening-level ecological risk assessment for copper suggests acute and chronic risk concerns for both freshwater and marine/estuarine organisms resulting from copper exposure at maximum labeled rates. Additionally, the risk assessment suggests potential risk to terrestrial animals exposed to high levels of copper resulting from pesticidal use. However, imprecise product labels represent the greatest source of uncertainty in the ecological risk assessment for copper pesticides. The ecological risk assessment assumed a number of applications and an application interval for most uses because product labels for copper pesticides do not specify the maximum number of applications and minimum treatment interval. Because the labels do not specify these limits, the Agency made conservative assumptions with maximum application and use information, which may underestimate or overestimate potential risk.

The registrants, grower groups, and other stakeholders have agreed to mitigation measures to address potential risks to terrestrial and aquatic animals. Labels for agricultural uses of copper will be revised to more accurately reflect use rates typically required to control specific pests and diseases. This will result in lower maximum allowed application rates for most crops. These labels will define maximum single application rate for each crop, minimum application intervals for each use, and will specify the maximum amount of copper that can be applied each year. The establishment of maximum individual and annual application rates and minimum application intervals will reduce the potential loading of copper into ecosystems by preventing unnecessarily high rates previously permitted and by limiting the frequency of exposure to non-target organisms.

Additional advisory language will be required to minimize potential adverse ecological effects. To reduce any adverse effects from potential spray drift, labels will be revised to include advisory language on reducing the potential for spray drift. Labeling measures include aerial applications only at or below certain wind speed and larger droplet size to reduce drift potential. In addition, registrants will be required to submit spray drift data. For more details on additional labeling requirements, refer to the Table 26. Because the chemistry of a water body greatly influences potential copper toxicity, additional advisory language describing chemistry conditions that likely would lead to increased copper toxicity potential (i.e., low pH and low DOC) will be required on revised labels. Appendix A describes the refined single maximum application rates, defined application intervals with a minimum number of days between retreatments, and maximum seasonal rate that is permitted to be applied per year.

## a. Benefits of Copper Pesticides

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. For detailed discussions on the benefits of the continued use of copper pesticides on the respective major crops/use sites, please refer to the *Cursory Alternatives and Assets Analysis of the Agricultural Uses of Copper Group II Pesticides*, dated June 20, 2006, and the *Copper (Cu++) Alternatives Analysis for the Primary Aquatic Uses*, dated June 20, 2006. Below is a description of specific areas where the benefits of coppers are significant, and where applicable, a discussion of general comparisons against available alternatives.

### 1. Terrestrial Uses

Coppers are significant for use as a broad-spectrum fungicide and bactericide on agricultural crops. Based on its history of use for many centuries, there is little evidence to indicate any significant pest-resistance problems. Copper pesticides are also used to remedy copper-deficient soils. 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. Comments provided by the University of Georgia indicated that IPM programs using copper alternated with antibiotics is used in peach productions. Copper use can reduce heavy reliance on the use of antibiotics for control of bacterial diseases for some crops.

Copper use is significant in various market niches, including those in the US as well as exported commodities. Although organically-grown crops represent a relatively small portion of the agricultural market, organic growers rely heavily on copper pesticides. Several organic growers reasserted that copper is one of the few pesticides available to growers to effectively and efficiently manage target pests, namely bacterial diseases. Another specific niche is the use of treating and preventing Septoria Spot on navel oranges from California for export to the Republic of Korea. There is a current export agreement that requires a pesticide treatment protocol that includes copper treatments on navel oranges for the treatment of Septoria Spot caused by *Septoria citri*.

For many of the major crops, growers have indicated that there are few or sometimes no suitable alternatives to copper pesticides for certain target pests. For example, the Florida Fruit & Vegetable Association noted that copper products are the only registered and effective pesticide available to manage citrus canker to avoid major crop losses. Although citrus canker has only been found in Florida, other major citrus producers outside of Florida such as the Texas Citrus Mutual group has expressed similar concerns and asserted the importance of retaining this use. Copper is currently the only viable or available option to control some bacterial diseases for which there are no registered antibiotics or where pests have developed resistance to some available alternatives. Some growers have reported the lack of suitable alternatives for bacterial

diseases in blueberries, apples, citrus, cherries, and strawberries. The Texas Vegetable Association stated that there are no alternatives for controlling bacterial leaf spot on peppers and tomatoes. In many cases, copper fungicides are the most cost-effective treatment that allows for frequent retreatments and are effective in suppressing or managing bacterial diseases for which there are no suitable alternatives.

## **2. Aquatic Weeds and Algae**

Copper is extensively used in direct aquatic applications including the management of algae, aquatic weeds, and mollusks that may host harmful parasites. Below is a description of some major areas where the use of copper pesticides is significant for its respective target pests.

Aquaculture. A comment from the University of Mississippi noted that aquaculture ponds containing certain cyanobacteria species can cause off-flavors in farm-raised catfish. Unlike many other market animal or grain crop products, an off-flavor in farm-raised fish does not result in a payment penalty; rather, it results in the rejection of all fish destined for market from that particular farm until the algae is properly managed and the off-flavors are purged from the fish. As a preventative measure, full-pond treatments are sometimes used for cyanobacteria control to minimize potential algal blooms that may cause off-flavors. Copper is the only registered chemical for which treatment of these off-flavor causing algae. In the past, special temporary use permits (FIFRA Section 18s) allowed for the use of diuron to control cyanobacteria in catfish and hybrid striped bass aquaculture ponds due to the rejection of off-flavor fish destined for market, but is costlier than using copper.

Drinking Water. Algae can clog water filters, reducing filter run times and requiring frequent backwashing, which all lead to greater coagulant demand and other treatments that impose greater costs to treatment facilities. Some species of algae can cause various off-flavors in drinking water, such as cyanobacteria, which can produce chemicals called cyanotoxins that lead to earthy or musty flavors. Only rarely are taste and odor problems the result of algal toxins in drinking water. Cyanobacterial blooms are not consistent and predictable, but often proliferate quickly during a summer drought. Thus, this requires early detection and treatment of algae to ensure effective treatment with the minimum amount of pesticide needed. These cyanotoxins and other chemicals are often difficult and more expensive to remove during water treatment. The use of copper for this application can be costly, but often times necessary for drinking water quality. Current labels for copper compounds allow for up to 1 ppm of copper in drinking water, which is in accordance with the Agency's 1.3 ppm MCLG for residues of copper in drinking water.

Irrigation/Conveyance Systems. In the western part of the US, 68% of the crops produced rely on irrigated water. Thus, regular maintenance of distribution canals is important for optimal water flow to receiving fields. Dense mats of vegetation can be a mechanical hindrance to valves and gate which divert and control the flow of water. Cyanobacteria and filamentous algae can lead to clogging of water intake screens in lakes and aqueducts. This reduction in water flow can result in millions of dollars lost due to failed crops as well as up-system flooding of areas surrounding the canal. Aquatic weed control in irrigation systems is essential, since debris from

weeds can decrease water flow. In addition, physical clogging by weeds can cause obstructions to valves and gates needed to control or divert water flow to receiving fields.

Quiescent Water Bodies (Recreational, Ornamental). Control of aquatic weeds in quiescent water bodies, such as ponds and lakes, is needed to maintain the safety of recreants and recreational activity operations that include fishing, water sports or swimming. In addition, many of these water bodies are also used as drinking water supplies. On rare occasion, cyanobacteria are known to produce hepatotoxins that may be harmful to humans and other mammals. Excess algae and other vegetation in quiescent or near-quiescent water bodies can impact overall water quality that may lead to decreased food availability and even fish kills. Dense algal or weed mats can block sunlight from reaching submerged biota, potentially affecting the entire ecological cycle, and even pose physical barriers for mobile animals. As the plant debris die back, increased microbial decay would lead to the decrease of dissolved oxygen available to fish and other organisms living in the same water body.

Alternatives. There are several limitations with the available alternatives to copper compounds. For example, dyes and colorants cannot be used in moving waters with an outflow, and some biocides may pose some human health exposure concerns. Multiple herbicides would be required to replace the copper compounds in these systems. Some available alternatives only control vegetation that has emerged above the water surface, while others may only control certain types of weeds.

### **3. Aquatic Invertebrate Control**

Leech. The macro-invertebrates that are controlled by copper sulfate pentahydrate are leeches and tadpole shrimp. Leeches are often a problem in ponds and quiescent waters under drought conditions. While leeches are usually a problem for fish, humans splashing in quiescent waters may become an alternate host to leeches. Currently, copper sulfate pentahydrate is the only registered compound for leech control in open water.

Tadpole Shrimp. Tadpole shrimp are often a problem in rice production, causing damage to newly emerged/young rice plants. Carbaryl is available as an alternative to copper for tadpole shrimp; however, copper sulfate pentahydrate has no human health risks of concern and is the only available pesticide that would still allow for organic rice growers to retain certification for organically-grown rice.

Freshwater Snails. Copper sulfate can be used to control freshwater snails to minimize potential exposure to problematic trematodes. Freshwater snails may act as a vector to schistosomes and other trematode cercariae that may affect exposed swimmers or farm-raised fish. Specific to humans, these schistosomes may penetrate human skin, causing Swimmer's Itch. In catfish production ponds, snails may be infected with a trematode from the *Bolbophorus* species. These trematodes may also cause lesions in exposed catfish, rendering them unmarketable. There is no treatment available for fish infected with this trematode.

## **b. Terrestrial Organisms**

### **1. Birds and Mammals**

The Agency modeled potential exposure to terrestrial animals from residues on forage items based on the highest label application rates and the highest average application rates of copper for orchard and row crops. Current copper labels indicate that the highest orchard label application rate is 31.8 lbs Cu<sup>2+</sup>/A for filberts and the highest row crop label application rate is 3.2 lbs Cu<sup>2+</sup>/A for potatoes. The highest average application rate for orchards and for row crops, as determined by the best data available to the Agency at the time the risk assessment was completed, were 3.8 lbs Cu<sup>2+</sup>/A for orchards (apples) and 0.8 lb Cu<sup>2+</sup>/A for row crops (potatoes). Because intervals between applications and the maximum number of applications were not specified on the product labels, the Agency assumed four applications on a weekly basis per growing season.

The RQs for the maximum and highest average application rates exceeded nearly all acute and chronic LOCs for all weight classes of birds and mammals. However, RQs for the average application rates are much lower, reflecting the significantly reduced EECs. For instance, the highest dose-based acute RQ for birds based on maximum orchard application rates is 220 and the corresponding dietary-based acute RQ is 13.5. By contrast, the highest dose-based acute RQ for birds based on average orchard application rates is 49 and the corresponding dietary-based acute RQ is 3.0.

The RQs for the highest average application rates more closely reflect the application rates that will be on copper product labels after the mitigation measures described above are put into effect. An exception to this is the 6 lbs Cu<sup>2+</sup>/A maximum application rate for filberts, the highest maximum application rate for any crop. However, this high rate will only apply to a small, defined area in the Pacific Northwest where copper is applied on filberts. According to the USDA, approximately 2,000 acres of filberts in this region are treated with copper. Application rates for other crops, which have been chosen based on input received after extensive outreach to grower groups and the public, will range from less than one pound up to 4 lbs Cu<sup>2+</sup>/A. Grower groups indicated that, depending on the crop, disease pressure, and timing, many applications are made at longer than the weekly interval assumed for most crops in the risk assessment. As described in Appendix A, longer minimum application intervals will be established for copper application to many crops.

Because the RQs for the average application rates exceed acute and chronic LOCs, application according to the revised labels can still potentially result in dietary risk to birds and mammals. However, there are some uncertainties in this finding of risk associated with assumptions used in the screening-level assessment itself, and with the response of birds and mammals exposed to copper. For instance, RQs in this assessment were calculated using 95<sup>th</sup> percentile residues from the Kenaga nomogram; mean residues from the Kenaga nomogram are about 2/3 less per application. Therefore, a typical application of copper would be expected to result in lower EECs than indicated in the assessment. In addition, a default foliar dissipation half-life of 35 days was used in the terrestrial exposure model T-REX, because data were not available to indicate how quickly copper might dissipate from leaf surfaces through wash-off. A

shorter foliar dissipation half-life would result in lower RQs for every crop to which multiple applications of copper are made.

As described in the risk assessment, there is additional uncertainty in the risk finding because terrestrial animals have varying degrees of homeostatic capability to metabolize ingested copper. Copper is an essential micronutrient to many organisms, including birds and mammals. The dietary-based RQs for birds likely incorporate these uptake effects to some extent, and an absorption efficiency correction factor was applied to the mammal dose-based RQ calculations.

These RQs still exceed LOCs, but the design of the laboratory studies leaves some uncertainty in how these effects would translate to effects in the wild. Birds and mammals in the laboratory studies are only fed treated feed, and the RQs in the risk assessment also assume that animals will derive 100% of their diet from treated feed. Although animals in the wild need to eat more than their counterparts in the laboratory (since lab feed is more nutritious, generally), most birds and mammals will spend only a fraction of the time in or at the edge of a treated field. Animals which eat untreated feed as a portion of their diet may have more of an opportunity to cope with ingested copper when the exposure is not continuous. In addition, animals which are repeatedly exposed to levels of copper which do not cause permanent harm may undergo enzymatic adaptation which allows them to cope with greater levels of exposure. The sensitivity to copper toxicity, and the ability to adapt to repeated exposures, should be expected to vary within species, and between species of birds and mammals.

Based on these factors, EPA has determined that the reduction in application rates and defining minimum retreatment intervals will greatly reduce potential adverse exposures to non-target terrestrial animals. In addition, this screening-level assessment includes conservative assumptions, such as the animal feeding in a treated area 100% of the time. To date, there are no reported bird or mammal incidents.

## **2. Terrestrial Plants**

The Agency could not conduct a complete terrestrial plant risk assessment, since the toxicity dataset for copper is incomplete. No suitable data from the registrant or open literature were available for evaluating seedling emergence effects. Vegetative vigor data for both monocots and dicots were available from the public literature.

No RQs exceeded the acute or acute endangered species LOC at the rate of 31.8 lbs  $\text{Cu}^{2+}/\text{A}$  for filberts, which is substantially higher than all rates, that will be on copper pesticide labels after mitigation measures detailed above take effect. Therefore, there appears to be no acute risk to non-endangered or listed terrestrial plants from spray drift. In any case, the reduced maximum application rates will reduce the maximum amount of copper to which terrestrial plants will potentially be exposed, and no further mitigation is needed.

## **3. Insects**

Available data from a honey bee acute toxicity study indicated that copper is practically nontoxic to honey bees, with an acute  $\text{LD}_{50} > 100 \mu\text{g}/\text{bee}$ . However, because exposure estimates



for other insects cannot readily be determined, the potential risk of copper pesticides to other insects is unknown. Based on available data, no additional mitigation to address exposure to non-target insects is needed at this time.

### **c. Aquatic Organisms**

#### **1. Agricultural Uses**

The Agency's screening-level ecological risk assessment for copper suggests acute and chronic risk concerns for both freshwater and marine/estuarine organisms resulting from copper exposure at maximum labeled rates, assuming four applications at weekly intervals. However, exposure is expected to be significantly lower based on application rates, defined retreatment intervals, seasonal maximum rates, and advisory spray drift language that will be on copper product labels after the mitigation measures described above are put into effect.

##### Freshwater Animals

The screening-level risk assessment indicates that there are risks greater than the LOC to freshwater invertebrates from terrestrial uses of copper at some portion of the 811 sites modeled, both at the typical and at the maximum labeled application rate. At the maximum application rate considered in the risk assessment, 31.8 lbs Cu<sup>2+</sup>/A for filberts, RQs for nearly all sites exceeded the acute and chronic LOCs. Over 99% of the sites exceeded the acute LOC for invertebrates, and 80% exceeded for fish. Over 98% of the sites exceeded the chronic LOC for invertebrates and 44.9% exceeded for fish.

The rate reductions that will be brought about through mitigation are expected to significantly reduce the number of sites at which freshwater animals are at risk from exposure to copper applied as an agricultural pesticide. The percentage of sites with acute exceedences for invertebrates, for instance, ranges from 3.2% at 1.0 lb Cu<sup>2+</sup>/A applied, and increases to about 25% of sites at an application rate of 7.5 lbs Cu<sup>2+</sup>/A. The RQs derived for freshwater fish with the BLM exceed the acute LOC for less than 1% of sites for application rates of 1 lb Cu<sup>2+</sup>/A up to 7.5 lbs Cu<sup>2+</sup>/A.

Table 25 shows some examples of the reductions in application rates for some of the high application rates for the respective crops. The reduction in the maximum application rate for citrus and grapes, with defined application interval and maximum seasonal rates, brings maximum potential exposure down to a level at which 10% of the 811 RQs considered in the assessment would exceed the acute LOC for freshwater invertebrates, and < 1% of RQs would exceed the acute RQ for fish. Approximately 13% and 1% of the sites would exceed the chronic LOC for freshwater invertebrates and fish, respectively.

**Table 25. Example Comparison of Rates Used in Risk Assessment and Revised Label Rates**

Crop	Current Labeled Rate or Revised Rate	Application Rate lbs Cu <sup>2+</sup> /A	Application Interval (days)	Seasonal Maximum Application (lbs Cu <sup>2+</sup> /A)
Citrus	Current	15.43	7 (assumed)	61.72 (assumed)
	Revised (algal spot, melanose, scab)	3.15	7	12.6
Filbert	Current	31.8	7 (assumed)	63.6 (assumed)
	Revised (eastern filbert blight)	6	14	24
Peach	Current	6.75	7 (assumed)	13.5 (assumed)
	Revised (dormant application)	3.15	30	6.3

Appendix A lists the revised maximum application rates, minimum retreatment intervals and maximum seasonal rates for agricultural uses of copper. The refined maximum single application rates for these crops are significantly less than the highest labeled rate considered in the risk assessment, where most are 3.15 lbs Cu<sup>2+</sup>/A or less. The majority of retreatment intervals are 7 days or longer, with only a few exceptions such as tomatoes and peppers. Although these crops have a 3-day application interval, single application rates were to 0.79 and 1.6 lbs Cu<sup>2+</sup>/A for peppers and tomatoes, respectively. The crop with the highest seasonal application rate is Easter lilies, but the registrant has indicated that this crop is grown in a very small portion of the country, and will revise labels to include language limiting treatment to only one season every four years.

Although the rate reductions are expected to result in fewer freshwater bodies having aquatic animals potentially at risk, there is some uncertainty in the percentage of sites. As detailed earlier, the risk estimates for each application rate were calculated using a regression of the peak values from 32 PRZM/EXAMS scenarios. Because label instructions were inconsistent for use of copper on many crops, many of the 32 scenarios were run based on the maximum single application rate, assuming four applications a week apart. As indicated in Appendix A, revised labels will include the maximum single application rate, maximum seasonal rates, and defined minimum application intervals.

There is also some uncertainty in the peak values used in the regression. Screening assessments were performed using PRZM/EXAMS use the 1-in-10-year peak value as the acute EEC. Because of concerns that EXAMS could not properly simulate 30 years of successive application of a stable pesticide, the peak value from the first year of application was used as the EEC. The EEC simulated from the first of the 30 years of data would likely be less than the standard 1-in-10-year exposure value calculated from a full 30-year simulation, although some of the 32 sites would simulate heavier rainfall in that single year, and others would simulate light rainfall years.

Therefore, EPA has determined that with the reduction of rates, establishing minimum retreatment intervals and defining seasonal maximum rates, estimated exposures described in the screening-level ecological assessment will be significantly lower. Adding advisory language to

product labels to minimize potential spray drift and water chemistry criteria that may lead to greater copper toxicity in water bodies will also reduce potential adverse effects.

### Freshwater Plants

Because the BLM has not been parameterized to assess freshwater plants, it could not be used to assess potential copper exposure and toxicity to freshwater plants. RQs for freshwater plants were calculated using estimates of total dissolved copper using PRZM/EXAMS, which overestimates the amount of copper that is potentially toxic to exposed organisms. The risk assessment provides a single RQ for a range of application rates, based on a regression of results from 32 PRZM/EXAMS scenarios. These RQs signal a potential risk to non-vascular plants (based on algae data) for application rates of 1.5 lbs Cu<sup>2+</sup>/A and above. However, RQs for aquatic vascular plants and endangered species are below the Agency's level of concern.

In addition to the use of total dissolved copper EECs in the calculation of aquatic plant RQs, the uncertainties described above for the regression of the peak values from 32 PRZM/EXAMS scenarios also apply to the aquatic plant assessment. Some potential for risk to aquatic plants is not unexpected, since algae and aquatic plants are target species for direct water applications of copper pesticides. However, the reductions in maximum application rates, and the establishment of maximum seasonal rates and minimum application intervals will reduce the potential for risk to aquatic plants from agricultural applications of copper.

### Marine/Estuarine Organisms

As with freshwater aquatic plants, the RQs for estuarine/marine organisms used in the assessment should be considered conservative because estimates of copper concentrations are for total copper, not the cupric ion. The BLM has not been parameterized for estuarine/marine organisms, so it could not be used to assess potential copper exposure and toxicity to estuarine/marine animals. As for the freshwater organism assessment, RQs for estuarine/marine organisms were calculated using the same regression on the peak copper concentrations that resulted from various application rates in the 32 PRZM/EXAMS simulations run for copper. At a rate of approximately 3 lbs Cu<sup>2+</sup>/A, acute and chronic RQs exceedences occur for both estuarine/marine fish and invertebrates, respectively. Acute RQs for invertebrates are exceeded at 1.5 lbs Cu<sup>2+</sup>/A, and chronic RQs for fish are exceeded at 1 lb Cu<sup>2+</sup>/A. RQs for estuarine/marine plants did not exceed the acute LOC.

In addition to the use of total dissolved copper EECs in the calculation of aquatic plant RQs, and the uncertainties described for use of the peak EEC regression, there is also uncertainty in the use of the PRZM/EXAMS static pond scenario to represent exposure in an estuary. Many crops can be grown adjacent to estuaries, and transport to estuaries in parts of the copper use area is likely. However, the static pond does not simulate the daily ebb and flow of freshwater and saltwater in an estuary, and the resulting changing salinity and hardness of the water would also affect the speciation of dissolved copper.

In spite of these uncertainties, the reductions in maximum application rates, and the establishment of maximum seasonal rates and minimum application intervals will reduce the potential for risk to estuarine/marine animals from agricultural applications of copper.

## **2. Direct Aquatic Uses**

Because of the inconsistent and incomplete use application information on current labels for direct aquatic uses, the Agency made several assumptions in the aquatic risk assessment. The risk assessment assumes treatment of an entire water body to achieve the maximum application rate, a water concentration of 1 ppm. For invertebrates, fish, and aquatic plants, RQs for this rate exceed the endangered species LOC and the acute risk LOC at >99% of sites simulated by the BLM. The chronic risk LOCs for aquatic invertebrates, and fish are exceeded at >96% of the sites

Input from major user groups indicates that typical rates are significantly lower than the maximum rate allowed, ranging from 0.2 to 0.5 ppm for algae management, the greatest use of copper products in direct aquatic applications. Use rates will greatly fluctuate, depending on pest infestation in a given water body. In addition, users indicated that it is standard practice for most aquatic uses to treat only a portion (up to 25-33%) of a water body at a time. The EXAMS model is used in the risk assessment to evaluate the risk from application to a fraction of the water body, but because of limitations in the model, this in essence is an assessment of a fractional application to the entire water body.

As discussed in the risk assessment, even application of copper to only a portion of a water body is likely to result in risk to aquatic organisms. When only a portion of the water body is treated, organisms in the vicinity of the treatment can be exposed to the full concentration of copper applied, while others further from the treated area may not be exposed at all. Fish and larger, more mobile invertebrates may be able to move out of the treated zone until the copper dissipates from the water column, but smaller and more sedentary invertebrates will be affected.

Recovery of the affected organisms will vary on a site-to-site basis, and the specific effects on any given ecosystem are impossible to predict given the scale of this assessment. Populations of phytoplankton and zooplankton (the organisms most likely to be lethally affected by use of copper) are dynamic, as the recovery of these populations is difficult to predict to determine its impact on the rest of the ecosystem. In aquatic systems where copper is applied frequently the community may shift to more copper tolerant organisms, and/or some of the organisms present may develop metabolic pathways for dealing with higher copper exposure.

Because of the great variance in water body chemistries across the US, this will overestimate the potential risk to some aquatic organisms, and underestimate it for others. However, based on refined use information provided by user groups, estimated exposures will be significantly lower. Typical application rates are significantly lower than the maximum assessed rate in the screening-level ecological assessment; thus, adverse effects to non-target organisms are expected to be lower. Additionally, the benefits of properly managing the target pests are significant in protecting human health and animals, including potential harmful toxins from algal

blooms, and water body maintenance to reduce the development and decay of algal and plant matter than can reduce DOC needed by organisms.

### **3. Urban Uses**

One of the risk assessment goals of the Agency is to estimate pesticide exposure through all significant routes of exposure from both agricultural and non-crop uses. However, the ecological risk assessment for copper pesticides focuses on the agricultural and direct aquatic uses, being the greatest usage of copper pesticides, and pesticide-transport models are available to estimate potential aquatic exposure from these uses. Based on laboratory toxicity tests with aquatic animals, adverse effects could occur to exposed organisms in aquatic environments.

Other potential sources of copper-treated products/sites that may result from a number of non-crop pesticidal uses, including use as a wood treatment, lawn fungicide, pool and fountain algacide, sanitary sewer root killer and ingredient in anti-fouling paints. The wood treatment, anti-foulants, and other antimicrobial uses will be addressed in a separate ecological risk assessment to be produced at a later date by the Agency. The ecological risk assessment addresses the root-killer and lawn uses to a limited degree.

#### Root Control in Sewer Lines

The national-scale risk assessment for use of copper sulfate as a sewer line root-killer discussed in the previous chapter provides an upper bound estimate of potential risk. The E-FAST model requires an estimate of total production of a pesticide to come up with a per capita loading estimate, but the total production of copper sulfate pentahydrate for root control can not be distinguished from other uses on the same label. Therefore, the risk assessment assumes that every household in the United States applies a total of 0.5 lb Cu<sup>2+</sup> per application twice a year. This equates to approximately 2.2 million pounds of metallic copper. The CSTF subsequently provided a preliminary estimate of potential use of approximately 857,000 pounds of metallic copper annually.

The ecological risk assessment indicates that if all households in the nation were to apply copper sulfate pentahydrate for root-control at maximum recommended rates in a single year, then the acute LOC would be exceeded for 85% and 20% of model sites for freshwater invertebrates and fish, respectively. The corresponding percentage of sites for which the chronic LOC could be exceeded would be 74% and 13%, respectively. This assessment assumes that all of the copper applied to sanitary sewers will be transported to water bodies in which aquatic animals and plants might be exposed. In fact, much of this copper must be removed by publicly owned treatment works (POTWs), which must limit the amount of copper that pass through to surface water according to the terms of waste-water discharge permits.

Although there are no available models or data to refine the screening-level assessment on urban uses, as well as uncertainties with the available data, the Agency believes that actual exposures are significantly lower. As stated earlier in Section III with respect to the root-killer treatment, the “down-the-drain” model assumes that all households simultaneously used the sewer treatment at the maximum labeled rate. Available information indicates that

approximately 25% of all households have septic systems, for which treatments of copper in this type of sewer system is not permitted. Alternatives to homeowner root-killer treatments include mechanical removal of invasive roots such as high pressure water jet, mechanical snake, and a steel cutter. Other available chemical alternatives include products that contain lye or sulfuric acid.

At least one jurisdiction has considered the risks and benefits of the root control use of copper sulfate pentahydrate on a more regional scale, and determined that mitigation was warranted. For instance, the California Department of Pesticide Regulation has prohibited the use of copper sulfate pentahydrate in nine counties in California out of concern that POTWs in the San Francisco Bay area could not comply with water quality criteria for copper if this use continued. Tri-TAC, a technical advisory group for POTWs in California, commented that an estimated 5 to 12% of copper received by POTWs in their state was a result of root-killer use.

Similar load estimates to POTWs from use of copper as a root killer were not available for other regions. The assessment of copper sources in the San Francisco Bay watershed performed for the Clean Estuary watershed concentrated on urban runoff, not inputs from sanitary sewers to POTWs. Their description of other studies in Maryland and Sweden of copper loadings concentrated on runoff and storm water in a like manner. TMDLs may potentially discuss discharge of copper from POTWs as a point source, but not detail the sources of copper to the POTW itself.

Since this product label states that it is not for use in septic systems, approximately 25% of households cannot use this product. In addition, while it is certain that not all of the remaining households use copper sulfate for root control in the same year, it is not possible to estimate the number that do in any particular year. Homeowners can choose to apply alternative chemicals for root control; some options include sulfamic or sulfuric acid and sodium or potassium hydroxide (Ohio Department of Agriculture, 2002). Even if the amount of root killer product sold were estimated, there are no records of how much homeowners actually use. The preliminary estimate provided by the CSTF is more than 1/3 of the Agency's highly conservative estimate that was assessed. Even with the estimate that the CSTF provided, the Agency believes that this estimate is a conservative value, as this figure is based on annual marketing data. Professional root control services may use copper sulfate pentahydrate, but are more likely to remove roots mechanically. Professionals may also use chemical alternatives such as metam sodium and dichlobenil, diquat or others.

A risk-benefit decision for the root control use of copper sulfate pentahydrate would therefore require consideration of the additional burden placed on POTWs to remove excess copper from the waste stream in addition to the potential risk to aquatic animals and plants. Use data is not available to allow such an evaluation on a nationwide scale. Therefore, no changes will be made to the copper sulfate pentahydrate label for root control use at this time. The Agency will solicit comments on the extent of copper use as a root killer, and the potential burden placed on POTWs by this use, during the comment period which will follow publication of the copper RED.

## Other Urban Uses

As described in Section III, above, the Agency does not currently have a model capable of predicting concentrations of pesticides that might occur because of outdoor urban uses, such as the use of copper as a lawn fungicide. Furthermore, the amount of copper used by homeowners for this use cannot be precisely determined. The relative importance of lawn uses of copper as a potential source of loading to surface water will vary between different watersheds, as there are many other potential urban sources of copper, as described above. No mitigation is proposed for other urban or suburban uses of copper at this time.

### **4. Advisory Language**

To be eligible for reregistration, labeling changes are necessary to implement mitigation measures outlined above. Specific language to incorporate these changes is specified in the Table 26. Generally, conditions for the distribution and sale of products bearing old labels/labeling will be established when the label changes are approved. However, specific existing stocks time frames will be established case-by-case, depending on the number of products involved, the number of label changes, and other factors.

For agricultural products containing copper to be eligible, revised labels need to include the following advisory language to ensure that copper pesticides are used appropriately and to minimize potential adverse exposure effects to humans and other non-target organisms in the environment. To minimize effects to non-target aquatic organisms, aquatic hazard statements on the labels must be revised to describe water chemistry conditions (e.g., low pH level and low DOC) that would likely lead to greater copper toxicity to non-target organisms. Labels also need to include advisory language on measures which users can adopt to reduce spray drift potential, such as language recommending that:

- Application not occur during temperature inversions;
- Applications be made when wind velocity favors on-target deposition (approximately 3 to 10 mph);
- Application not be made when wind speed exceeds 15 mph;
- Aerial spray should be released at the lowest height consistent with pest control and flight safety;
- Ground boom and aerial applications use only medium or coarse spray nozzles; and
- For aerial applications, the spray boom should be mounted on the aircraft as to minimize drift caused by wingtip or rotor vortices. The minimum practical boom length should be used.

Specific label language including these recommendations is detailed in Table 26. With the implementation of these additional advisory label language points, risk to non-target organisms will be reduced.

## 5. 303(d) - Designated Impaired Water Bodies

The California Regional Water Quality Control Board (CRWQCB) commented that copper has been named as a cause for water quality impairments for some 626 water bodies in the United States under section 303(d) of the Clean Water Act (CWA). When a water body is listed as impaired by an identified pollutant, States may be required to devise a plan to regulate the Total Maximum Daily Load (TMDL) of the pollutant entering the water body through point and non-point sources. The development of a TMDL requires identification of the sources of the pollutant in the watershed, and an estimate of the relative load from each source. TMDLs have been approved for 246 of the 626 water bodies for which copper is listed as a cause of impairment. A majority of these sites list other metals in addition to copper as pollutants, either from mining or other non-agricultural sources.

### Impairments Potentially Due to Agricultural Use of Copper

Eight of the 246 approved TMDLs for copper identify agricultural use of copper as the most likely source causing the impairment. These eight are all in Kansas. Land use in the eight watersheds is 95 to 99% combined cropland/pasture and rangeland, with no less than 68% of any watershed characterized as cropland/pasture. The water quality criteria for copper in Kansas are site-specific, based on an equation that takes the hardness of the water into account.

The eight TMDLs for copper in Kansas identify a number of possible agricultural sources of copper. An important source identified is the use of copper sulfate to treat livestock for hoof diseases. Copper sulfate is also used in these watersheds at 3 to 6 lbs  $\text{Cu}^{2+}/\text{A}$  to alleviate copper deficiency in soybeans, and as a feed supplement for swine. Finally, the TMDLs mention that copper can be applied to agricultural crops such as orchards.

The King County Department of Natural Resources and Parks (KCDNRP) in Washington reported water body impairments that might be related to use of copper as an agricultural pesticide. Washington State water quality criteria for copper are 0.0070 mg/L (acute) and 0.0075 mg/L (chronic) at median hardness. The compliance standard is that the 1-hour concentration cannot be exceeded more than once every 3 years. The chronic criterion was reported to be exceeded once at Mill creek (0.0056 mg/L, presumably at a lower hardness) during base flow and the acute criterion once at a tributary of Newaukum Creek (0.0072 mg/L) during storm flow (KCDNRP, 2004).

The Agency's TMDL web site indicates that a TMDL has not been submitted for the Green-Duwamish watershed, in which these Washington water bodies are located. In addition, the State of Washington has not reported the potential sources of the copper pollutant in these waters. However, the report prepared for the KCDNRP identifies the sampling location for Newaukum Creek as representing agricultural and pasture land uses. Land use in the Mill Creek basin is reported to be forest, residential and agricultural.

### Impairments from Aquatic Use of Copper

Two water bodies in California are listed as impaired due to the use of copper as an algaecide applied directly to water. In 2002, the Tinemaha Reservoir in California, which had



previously been listed under 303(d) of the CWA for generic “metals” contamination, was more specifically listed for copper pollution caused by use of copper sulfate as an algacide for taste and odor control in drinking water. However, 10 months of surface water sampling undertaken for the development of a TMDL for the reservoir showed the reservoir to be in compliance with water quality standards for both total and dissolved copper. Therefore, the staff of the CRWQCB recommended in a published report that the Tinemaha Reservoir be removed from the list of impaired water bodies during the next listing cycle.

The Haiwee Reservoir in California was also listed as impaired due primarily to application of copper as an algacide. In addition to the discharge of copper sulfate to the reservoir itself, copper sources include a percentage of “unspecified” copper, such as copper coming in from the Los Angeles Aqueduct (LAA) with no readily identifiable source from the available data and naturally occurring contributions of copper. Potential sources of this copper are historic mining activities, elevated copper in ground or surface waters due to copper-bearing minerals in soil or rock and undetermined water supply management practices in the watershed

The Washington Department of Ecology (WDOE) identifies Steilacoom Lake as a water body impaired by copper with an approved TMDL [http://www.ecy.wa.gov/programs/wq/tmdl/approved\\_tmdls.html](http://www.ecy.wa.gov/programs/wq/tmdl/approved_tmdls.html). In their report, “Copper in Sediments from Steilacoom Lake, Pierce County, WA,” the WDOE reports that copper levels in sediment range to over 1000 mg/kg dry weight, and that the “primary source of the metal in the sediments is many years of application of the algacide, copper sulfate.” Steilacoom Lake is a 320 acre man-made lake with a maximum depth of 20 feet. This urban lake is surrounded by single family homes, and is classified as eutrophic.

The WDOE performed a series of bioassays with the sediment, and reports that aquatic invertebrates *Hyaella azteca* and *Hexagenia limbata* showed significant adverse acute response in bioassays (WDOE, 1992). Both of these invertebrates spend at least a portion of their life span dwelling in bottom sediment. When exposed to Steilacoom Lake sediment, *Hyaella azteca* suffered 30% mortality over 14 days, and *Hexagenia limbata* suffered 50% mortality. No adverse effects were observed in acute or chronic bioassays using *Daphnia magna*, *Ceriodaphnia dubia*, and *Chironomus tentans*.

#### Impairments Due to Antimicrobial Use of Copper

As described above, ecological exposures from antimicrobial uses of copper are not considered in this RED. These uses will be evaluated in a subsequent risk assessment planned to be completed at a later date.

TMDLs have been developed for two water bodies in California impaired by the use of copper in anti-fouling paints applied to boat hulls. An analysis of the likely sources of copper in the Shelter Island Yacht Basin in San Diego Bay concluded that as much as 98% of the copper detected was from leaching of anti-fouling paints from boat hulls and the scrubbing of boat bottoms treated with this paint. The Agency’s Technical Support Document (TSD) for the San Diego Creek and Newport Bay Toxics TMDL (U.S. EPA, 2002) used information from the Shelter Island Yacht Basin TMDL to estimate sources of copper leading to impairment. The

document estimates that 50,000 of 58,000 pounds of copper per year are attributable to copper from anti-fouling paint, with the rest due to urban road runoff, contaminated sediments, atmospheric deposition, and sea water.

A 2004 report titled “Copper Sources in Urban Runoff and Shoreline Activities,” prepared for the Clean Estuary Partnership, summarized the sources of copper carried to the San Francisco Bay via runoff, or introduced directly by shoreline activities. The report also attempted to quantify the loading of copper from each of the sources. Although the uncertainty in these loading estimates varied between sources, and for some sources may have been as high as a 10-fold error in their judgment, it allowed the authors to rank the sources for the amount of copper introduced to the bay. The San Francisco Bay is not currently listed as impaired by copper, but the report details many sources of copper beyond those included in this RED which can lead to impairment of water bodies.

The report lists the pesticidal use of copper in anti-fouling paints on boat hulls as the greatest source of copper in San Francisco Bay (an estimated 20,000 pounds annually). Additional copper contribution from direct application of pesticides to the Bay and its tributaries as an algaecide was considered a smaller contribution, at an estimated 4,000 pounds annually. Other urban copper pesticide uses included landscaping fungicide uses, use as wood preservatives, and use as an algaecide in pools, spas and fountains (<8,000 - <10,000 pounds per year total). The lower source contribution of these other copper pesticides uses is due in part to efforts by municipalities in the San Francisco Bay watershed to reduce the use of copper-based pesticides, both through public outreach and the prohibition of the sale and use of copper-based root control products.

Other urban sources of copper were predicted to add an additional 27,000 pounds of copper to the total load annually. These included wear of vehicle brake pads (>10,000 pounds per year) and vehicle fluid leaks and dumping. Also included in the estimates were deposition of copper air emissions, soil erosion, architectural use of copper, industrial effluent and copper in domestic storm water.

#### Comparison of Ecological Risk Assessment and Watershed Loading Assessments

The screening-level ecological risk assessment indicates the potential for agricultural uses to pose acute and chronic risk to aquatic animals (and acute risk to aquatic plants) under certain water quality conditions. However, there are aspects of the scenario simulated by the combined PRZM/EXAMS model which limit its utility as a tool for predicting which surface water bodies might become impaired from the agricultural use of copper pesticides. PRZM/EXAMS is not a watershed model; it simulates application to a 10-hectare field which is directly adjacent to a pond that is one hectare and two meters deep. Applied pesticide is transported to the pond by runoff and drift, and the pesticide load is instantaneously mixed throughout the 20,000,000-liter pond.

In a typical screening-level ecological risk assessment, 30 years of applications and weather data are used to calculate daily concentrations in the pond. These daily concentrations represent the concentration from the previous day reduced by a day’s worth of biotic and abiotic

degradation, plus the instantaneous mixing of additional load added that day. Since the model simulates a static pond, the concentration is not reduced by outflow from the pond.

The exercise of predicting if a specific water body or stream segment could become impaired is more complex than the edge-of-field model represented by PRZM/EXAMS. The loading of a pesticide within a watershed is likely to come from fields at varying distances from a water body. The entire watershed is unlikely to be treated with the pesticide. In addition, the different sizes of water bodies and the possibility of flow would result in slower mixing than simulated by the model, or flashiness in the concentrations caused by flow of the contaminant downstream.

The screening-level risk assessment is meant to represent a vulnerable scenario which allows the Agency to be confident in a finding of no risk if no LOCs are exceeded. When an LOC is exceeded, the Agency does not assume that specific water bodies will be at risk, but those classes of organisms in some waters with certain characteristics and/or associated land use may be at risk from particular pesticide uses. In the case of copper, the BLM allows further refinement of the assessment in that certain water quality conditions in surface water may lead to increased exposure, due to increased bioavailability and toxicity to aquatic organisms.

Although the assessment does not attempt to predict copper loading from agricultural uses on a watershed scale, mitigation measures put in place in response to risks identified by the screening assessment will serve to reduce potential loading from these uses. As indicated in the ecological risk assessment, the percentage of sites (represented by 811 USGS sampling stations) which have estimated RQs above the LOCs for freshwater animals would be significantly lower at application rates lower than the maximum rates previously allowed on copper product labels. The RQs for estuarine/marine animals and plants, although not calculated with the BLM for a range of sites, are also significantly reduced at lower application rates.

As mentioned previously, the Agency's Office of Water (OW) has established a draft ALC for copper, and is working on a revised ALC which will use the BLM to take site-specific water chemistry into account. OPP has collaborated with OW during the development of the copper RED on the use of BLM, sharing information gathered in the process to help in the development of the revised ALC for copper. Once the revised ALC is completed, states will be able to use the BLM to derive consistent, site-specific standards that meet local needs.

## V. What Registrants Need to Do

The Agency has determined that agricultural uses of coppers are eligible for reregistration provided that the risk mitigation measures outlined in this document are adopted and label amendments are made to reflect these measures. To implement the risk mitigation measures, the registrants will be required to amend their product labeling to incorporate the label statements set forth in the Label Summary Table (Table 26) below. In the near future, the Agency intends to issue Data Call-In (DCI) Notices requiring label amendments, product-specific data and additional generic (technical grade) data. Generally, registrants will have 90 days from receipt of a DCI to complete and submit response forms or request time extension and/or waiver requests with a full written justification. For product-specific data, the registrant will have eight months to submit data and amended labels. For generic data, due dates can vary depending on the specific studies being required. Below is a list of additional generic data and label amendments that the Agency intends to require for coppers to be eligible for reregistration.

### A. Manufacturing-Use Products

#### 1. Generic Data Requirements

The generic data base supporting the reregistration of agricultural uses of copper has been reviewed and determined to be substantially complete. However, the Agency has identified data necessary to confirm the reregistration eligibility decision for coppers. These studies are listed below and will be included in the generic DCI for this RED, which the Agency intends to issue at a future date.

#### Environmental Toxicology

<b>Old Guideline</b>	<b>New Guideline</b>	<b>Description</b>
201-1	840.1100	Spray Droplet Size Spectrum
202-1	835.4200	Spray Drift Field Deposition

#### 2. Labeling for Manufacturing-Use Products

To ensure compliance with FIFRA, manufacturing-use product (MP) labeling should be revised to comply with all current EPA regulations, PR Notices, and applicable policies. The MP labeling should bear the labeling contained in Table 26.

### B. End-Use Products

#### 1. Additional Product-Specific Data Requirements

Section 4(g)(2)(B) of FIFRA calls for the Agency to obtain any needed product-specific data regarding the pesticide after a determination of eligibility has been made. Registrants must review previous data submissions to ensure that they meet current EPA acceptance criteria and if not, commit to conduct new studies. If a registrant believes that previously submitted data meet current testing standards, then the study MRID numbers should be cited according to the instructions in the Requirement Status and Registrants Response Form provided for each

product. The Agency intends to issue a separate product-specific data call-in (PDCI), outlining specific product-specific data requirements. These data requirements will also be included in the PDCI.

## **2. Labeling for End-Use Products**

To be eligible for reregistration, labeling changes are necessary to implement measures outlined in Section IV above. Specific language to incorporate these changes is specified in Table 26. Generally, conditions for the distribution and sale of products bearing old labels/labeling will be established when the label changes are approved. However, specific existing stocks time frames will be established case-by-case, depending on the number of products involved, the number of label changes, and other factors.

### **C. Labeling Changes Summary Table**

For coppers to be eligible for reregistration, all agricultural labels of copper-containing products must be amended to incorporate the risk mitigation measures outlined in Section IV. Table 26 describes specific label amendments.

## Copper Compounds Labeling Changes Summary Table 26

In order to be eligible for reregistration, all product labels must be amended to incorporate the risk mitigation measures outlined in Section IV. The following table describes how language on the labels should be amended.

Description	Copper Compounds Required Labeling Language	Placement on Label
<i>Manufacturing-Use Products</i>		
Required on all MUPs for all Copper Compounds containing directions for any use	“Only for formulation into [fill blank with the appropriate pesticide type(s): fungicides, bactericides, algacides, herbicides, leech control, freshwater snail control, anti-foulants and wood preservatives] for the following use(s) [fill blank only with those uses that are being supported by MP registrants].”	Directions for Use
One of these statements may be added to a label to allow reformulation of the product for a specific use or all additional uses supported by a formulator or user group.	<p>Note: Manufacturing Use Products can not have end use directions. Similarly, End Use Products can not have formulation directions.</p> <p>“This product may be used to formulate products for specific use(s) not listed on the MP label if the formulator, user group, or grower has complied with U.S. EPA submission requirements regarding support of such use(s).”</p> <p>“This product may be used to formulate products for any additional use(s) not listed on the MP label if the formulator, user group, or grower has complied with U.S. EPA submission requirements regarding support of such use(s).”</p>	Directions for Use
Environmental Hazards Statements Required by the RED and Agency Label Policies	“This pesticide is toxic to fish and aquatic invertebrates. Do not discharge effluent containing this product into lakes, streams, ponds, estuaries, oceans or other waters unless in accordance with the requirements of a National Pollutant Discharge Elimination System (NPDES) permit and the permitting authority has been notified in writing prior to discharge. Do not discharge effluent containing this product to sewer systems without previously notifying the local sewage treatment plant authority. For guidance contact your State Water Board or Regional Office of the EPA. Do not contaminate water when disposing of equipment washwaters or rinsate.”	Directions for Use
Required on all MUPs for All Copper Compounds	<p>For all copper compounds label, the Ingredient Statement panel must state and describe the ingredient(s) in the following manner:</p> <ul style="list-style-type: none"> <li>- the original form/species (i.e., copper hydroxide, copper ethanolamine complex, copper sulfate pentahydrate) as the active ingredient,</li> <li>- the percentage of active ingredient contained in the product,</li> <li>- the respective Chemical Abstracts Service (CAS) number must be listed,</li> <li>- and the amount of metallic copper equivalent must be expressed as the percentage by weight directly below the Ingredient Statement.</li> </ul>	Front Panel, Ingredient Statement

<i>End-Use Products Intended for Occupational Use (WPS and non-WPS)</i>		
Required on all EUPs for All Copper Compounds	<p>For all copper compounds label, the Ingredient Statement panel must state and describe the ingredient(s) in the following manner:</p> <ul style="list-style-type: none"> <li>- the original form/species (i.e., copper hydroxide, copper ethanolamine complex, copper sulfate pentahydrate) as the active ingredient,</li> <li>- the percentage of active ingredient contained in the product,</li> <li>- the respective Chemical Abstracts Service (CAS) number must be listed,</li> <li>- and the amount of metallic copper equivalent must be expressed as the percentage by weight directly below the Ingredient Statement.</li> </ul>	Ingredient Statement
Environmental Hazards Statements	<p>For labels that include terrestrial uses (remove “drift” if a granular formulation), include the following statement(s):</p> <p>“For terrestrial uses: Do not apply directly to water, or to areas where surface water is present or to intertidal areas below the mean high water mark. Do not contaminate water when disposing of equipment washwater or rinsate.”</p> <p>“This product may contaminate water through runoff. Poorly draining soils and soils with shallow water tables are more prone to produce runoff that contains this product. Drift and runoff may be hazardous to aquatic organisms in water adjacent to treated areas.”</p> <p>For labels that include direct aquatic uses, include the following statement :</p> <p>“Waters treated with this product may be hazardous to aquatic organisms. Treatment of aquatic weeds and algae can result in oxygen loss from decomposition of dead algae and weeds. This oxygen loss can cause fish and invertebrate suffocation. To minimize this hazard, do not treat more than ½ of the water body to avoid depletion of oxygen due to decaying vegetation. Wait at least 10 to 14 days between treatments. Begin treatment along the shore and proceed outwards in bands to allow fish to move into untreated areas. Consult with the State or local agency with primary responsibility for regulating pesticides before applying to public waters, to determine if a permit is required.”</p>	Environmental Hazards Statement

<p>Environmental Hazards Statements</p> <p>(All Copper Compounds)</p>	<p>For terrestrial and aquatic uses of copper-containing products, include the following statements:</p> <p>“ENVIRONMENTAL HAZARDS”</p> <p>“This pesticide is toxic to fish and aquatic invertebrates and may contaminate water through runoff. This product has a potential for runoff for several months or more after application. Poorly draining soils and soils with shallow water tables are more prone to produce runoff that contains this product. For terrestrial uses, do not apply directly to water, to areas where surface water is present or to intertidal areas below the mean high water mark. Do not contaminate water when disposing of equipment wash-waters or rinsate.”</p> <p>“Certain water conditions including low pH (<math>\leq 6.5</math>), low dissolved organic carbon (DOC) levels (3.0 mg/L or lower), and “soft” waters (i.e., alkalinity less than 50 mg/L), increases the potential acute toxicity to non-target aquatic organisms.”</p> <p>For copper products with terrestrial uses (remove “drift” if a granular formulation), include the following statements:</p> <p>“Drift and runoff may be hazardous to aquatic organisms in waters adjacent to treated areas. “</p>	<p>Precautionary Statements under Environmental Hazards</p>
	<p>For end-use products that include use of copper compounds to treat potable water sources, the following statement must be included:</p> <p>“Potable water sources treated with copper products may be used as drinking water only after proper additional potable water treatments.”</p>	<p>Precautionary Statements: Hazards to Humans and Domestic Animals</p>



<p>Minimum Handler PPE Requirements</p> <p>(All Copper Compounds)</p> <p>NOTE: PPE established on the basis of Acute Toxicity of the end-use product must be compared to the active ingredient PPE in this document. In the case of multiple active ingredients, the more protective PPE must be placed on the product labeling. For guidance on which PPE is considered more protective, see PR Notice 93-7.</p>	<p>“Personal Protective Equipment (PPE)”</p> <p>“Mixers, loaders, applicators, and other handlers must wear the following: - long-sleeve shirt, - long pants, - shoes plus socks.”</p> <p><b>Instruction to Registrant:</b> If chemical resistant gloves, apron or footwear are required by the product specific data, add the following statement:</p> <p>“Some materials that are chemical-resistant to this product are (<i>registrant inserts correct chemical-resistant material</i>). If you want more options, follow the instructions for category [<i>registrant inserts A,B,C,D,E,F,G, or H</i>] on an EPA chemical-resistance category selection chart.”</p>	<p>Precautionary Statements: Hazards to Humans and Domestic Animals</p>
<p>Signal Word</p>	<p>For products subject to the WPS that are classified as toxicity category I or II must also bear the corresponding Spanish signal word and statement:</p> <p>”Si usted no entiende la etiqueta, busque a alguien para que se la explique a usted en detalle. (If you do not understand the label, find someone to explain it to you in detail.)”</p>	<p>Front Panel</p>
<p>User Safety Requirements</p> <p>(All Copper Compounds)</p>	<p>“Follow manufacturer’s instructions for cleaning/maintaining PPE. If no such instructions for washables exist, use detergent and hot water. Keep and wash PPE separately from other laundry.”</p> <p>“Discard clothing and other absorbent material that have been drenched or heavily contaminated with the product’s concentrate. Do not reuse them.”</p>	<p>Precautionary Statements: Hazards to Humans and Domestic Animals immediately following the PPE requirements</p>
<p>User Safety Recommendations</p> <p>(All Copper Compounds)</p>	<p>“USER SAFETY RECOMMENDATIONS”</p> <p>“Users should wash hands before eating, drinking, chewing gum, using tobacco, or using the toilet.”</p> <p>“Users should remove clothing/PPE immediately if pesticide gets inside. Then wash thoroughly and put on clean clothing.”</p> <p>“Users should remove PPE immediately after handling this product. As soon as possible, wash thoroughly and change into clean clothing.”</p>	<p>Precautionary Statements under: Hazards to Humans and Domestic Animals immediately following Engineering Controls</p> <p>(Must be placed in a box.)</p>

	<p>Note to Registrant: If gloves are required on the label (either for handlers or early entry workers), add the following in addition to the above:</p> <p>“Wash the outside of gloves before removing.”</p>	
<p>Restricted-Entry Interval for products with WPS uses</p> <p>Note: REI’s are determined by the acute toxicity of each copper compound which can vary. For products containing more than one copper compound, the most restrictive REI must appear on the label.</p>	<p>“Do not enter or allow worker entry into treated areas during the restricted entry interval of (insert the correct REI as specified below):</p> <p><b>Products containing any of the following copper compounds require a 48 hour REI:</b>  Basic copper chloride (008001)  Chelates of copper gluconate or copper citrate (023305)  Copper ammonium carbonate (022703)  Copper carbonate (022901)  Copper hydroxide (023401)  Copper ammonia complex (022702)  Copper oxychloride (023501)  Copper oxychloride sulfate (023503)  Basic copper sulfate (008101)  Copper sulfate pentahydrate (024401)  Cuprous oxide (025601)  Copper 8-quinolinolate (024002)  Copper naphthenate (023102)  Copper ethanolamine complex (024409)</p> <p><b>Products containing any of the following copper compounds require a 24 hour REI:</b>  Copper, metallic (022501)</p> <p><b>Products containing any of the following copper compounds require a 12 hour REI:</b>  Copper ethylenediamine (024407)  Cupric oxide (042401)  Copper octanoate (023306)  Copper triethanolamine complex (024403)  Copper salts of fatty and rosin acids (023104)</p>	<p>Directions for Use, Agricultural Use Requirements Box</p>
<p>Early Entry Personal Protective Equipment for products with WPS uses</p> <p>Note: Early Entry PPE is determined by the acute toxicity of each copper</p>	<p>PPE required for early entry to treated areas that is permitted under the Worker Protection Standard and that involves contact with anything that has been treated, such as soil or water, is (insert correct Early Entry PPE specified below)</p> <p><b>Products containing any of the copper compounds listed directly below require the following early entry PPE:</b></p>	<p>Directions for Use, Agricultural Use Requirements Box</p>

<p>compound which can vary. For products containing more than one copper compound, the most restrictive REI must appear on the label.</p>	<p>Coveralls over long-sleeved shirt and long pants, chemical-resistant gloves made of any waterproof material, chemical-resistant footwear plus socks; chemical resistant headgear if overhead exposure, protective eyewear, and chemical-resistant apron when mixing, loading, cleaning equipment or spills, or otherwise exposed to the concentrate:</p> <p>Chelates of copper gluconate or copper citrate (024405)  Copper ammonium carbonate (022703)  Copper ammonia complex (022702)  Copper oxychloride (023501)  Copper oxychloride sulfate (023503)  Basic copper sulfate (008101)  Cuprous oxide (025601)  Copper naphenate (023102)  Copper ethanolamine complex (024409)</p> <p><b>Products containing any of the copper compounds listed directly below require the following early entry PPE:</b></p> <p>Coveralls,  shoes plus socks,  chemical-resistant gloves made of any waterproof material, and protective eyewear.</p> <p>Basic copper chloride (008001)  Copper carbonate (022901)  Copper hydroxide (023401)  Copper sulfate pentahydrate (024401)  Copper 8-quinolinolate (024002)  Copper, metallic (022501)</p> <p><b>Products containing any of the copper compounds listed directly below require the following early entry PPE:</b></p> <p>Coveralls,  shoes plus socks  chemical-resistant gloves such as or made out of any waterproof material</p>	
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	<p>Copper ethylenediamine (024407)  Cupric oxide (042401)  Copper octanoate (023306)  Copper triethanolamine complex  Copper salts of fatty and rosin acids</p>	
Double Notification Statement	<p>Products containing any of the copper compounds listed directly below require the following statement:</p> <p>“Notify workers of the application by warning them orally and by posting warning signs at entrances to treated areas.”</p> <p>Chelates of copper gluconate (024405)  Copper ammonium carbonate (022703)  Copper ammonia complex (022702)  Copper oxychloride (023501)  Copper oxychloride sulfate (023503)  Basic copper sulfate (008101)  Cuprous oxide (025601)  Copper naphthenate (023102)  Copper ethanolamine complex (024409)</p>	Directions for Use, Agricultural Use Requirements Box
Entry Restrictions for products with non-WPS uses on the label	<p><b>Entry Restriction for products applied as a spray:</b></p> <p>“Do not enter or allow others to enter until sprays have dried.”</p> <p><b>Entry Restriction for products applied dry:</b></p> <p>“Do not enter or allow others to enter until dusts have settled.”</p>	If no WPS uses on the product label, place the appropriate statement in the Directions for Use Under General Precautions and Restrictions. If the product also contains WPS uses, then create a Non-Agricultural Use Requirements box as directed in PR Notice 93-7 and place the appropriate statement inside that box.
General Application Restrictions for products with WPS or non-WPS uses on the label	<p>“Do not apply this product in a way that will contact workers or other persons, either directly or through drift. Only protected handlers may be in the area during application. For any requirements specific to your State or Tribe, consult the State or Tribal agency responsible for pesticide regulation.”</p>	Place in the Direction for Use, following the misuse statement.

Other Application Restrictions	Maximum Application Rates, Application Interval (days) and Seasonal Maximum Application Rates must be specified on all product labels. See Appendix A for the correct application rates and intervals for each site or crop.	Directions for Use under General Precautions and Restrictions and/or Application Instructions
	<i>Products Primarily Used by Consumers/Homeowners</i>	
Entry Restrictions	<p><b>Entry Restriction for products applied as a spray:</b></p> <p>“Do not allow adults, children, or pets to enter the treated area until sprays have dried.”</p> <p><b>Entry Restriction for products applied dry:</b></p> <p>“Do not allow adults, children, or pets to enter the treated area until dusts have settled.”</p>	Directions for use under General Precautions and Restrictions
General Application Restrictions	“Do not apply this product in a way that will contact adults, children, or pets, either directly or through drift.”	Place in the Direction for Use
Environmental Hazards	“This pesticide is toxic to fish and aquatic invertebrates and may contaminate water through runoff. For terrestrial uses, do not apply directly to water. Do not contaminate water when disposing of equipment washwaters or rinsate.”	Precautionary Statements

**Appendix A**

Crop		Maximum per Application Rate (lbs Cu <sup>2+</sup> /A) <sup>1</sup>	Maximum Annual Rate (lbs Cu <sup>2+</sup> /A) <sup>2</sup>	Minimum Retreatment Interval <sup>3</sup>	Notes
<b>TREE FRUIT</b>					
Pome Fruit (apple, pear, quince)	Fall, late dormant	8.0	16.0	n/a (only 1 application per season permitted)	Quince use not permitted in California
	Bloom, growing season	0.5		5 days	
Atemoya, Sugar Apple (Annona)		3.15	12.6	7 days	Not for use in California
Avocado		3.15	18.9	14 days	
Banana		1.05	18.9	7 days	
Carambola		2.1	10.5	7 days	Not for use in California
Citrus (grapefruit, kumquat, lemon, orange, pummelo, tangelo, tangerine, lime)		3.15	12.6	7 days	
Guava		1.23	4.92	7 days	
Mamey Sapote		2.1	8.4	14 days	Not for use in California
Mango		2.6	18.2	30 days	Not for use in California
Olive		3.15	6.3	30 days	
Papaya		2.63	21.2	14 days	Not for use in California
Passion Fruit		2.36	9.44	7 days	Not for use in California
Persimmon		1.0	6.0	14 days	
Stone Fruit (peach, plum, nectarine, almond, apricot, cherry, prune)	Dormant, late dormant	8.0	18.0	7 days	
	Bloom/ growing season	1.5		5 days	
<b>TREE NUTS</b>					
Betel Nut (Guam)		0.75	8.25	7 days	
Cacao		2.25	15.75	14 days	

<b>Crop</b>	<b>Maximum per Application Rate (lbs Cu<sup>2+</sup>/A)<sup>1</sup></b>	<b>Maximum Annual Rate (lbs Cu<sup>2+</sup>/A)<sup>2</sup></b>	<b>Minimum Retreatment Interval<sup>3</sup></b>	<b>Notes</b>
Coffee	2.1	12.6	14 days	
Filbert	6	24	14 days	Permitted only in Washington State and Oregon
Litchi	1.23	4.92	7 days	Not for use in California
Macadamia	2.36	9.44	7 days	
Pecan, Pistachio	2.1	8.4	14 days	
Walnut	3.15	25.2	7 days	
<b>FIELD CROPS</b>				
Alfalfa	0.53	1.12	30 days	
Corn (Field Corn, Popcorn, Sweet Corn)	1.05	4.2	7 days	Not permitted in California
Peanut	0.79	4.74	7 days	
Potato	2.5	25	5 days	
Soybean	0.79	4.74	7 days	
Sugar Beet	1.31	7.86	10 days	
Tobacco	2.0	8.0	10 days	
Wheat, Barley, Oats	0.53	1.06	10 days	
<b>SMALL FRUITS</b>				
Brambles (aurora, blackberry, boysen, cascade, chehalem, logan, marion, raspberry, santiam, thornless evergreen)	2.0	10.0	7 days	
Blueberry	2.1	8.4	7 days	Not for use in California
Cranberry	2.1	6.3	7 days	
Currant, Gooseberry	2.5	10.0	10 days	
Strawberry	1.5 (severe disease)	8.19	7 days	
	1.0			
<b>VEGETABLE</b>				
Bean (Dry, Green)	0.79	4.74	7 days	
Beet (Table Beet, Beet Greens)	1.31	7.86	10 days	

<b>Crop</b>	<b>Maximum per Application Rate (lbs Cu<sup>2+</sup>/A)<sup>1</sup></b>	<b>Maximum Annual Rate (lbs Cu<sup>2+</sup>/A)<sup>2</sup></b>	<b>Minimum Retreatment Interval<sup>3</sup></b>	<b>Notes</b>
Carrot	1.0	5.0	7 days	
Celery, Celeriac	1.0	5.3	7 days	Not for use on celeriac in California
Crucifers (broccoli, brussel sprout, cabbage, cauliflower, collard greens, mustard greens, turnip greens)	0.53	2.65	7 days	
Cucurbits (cantaloupe, casaba, chayote, cucumber, gourd, honeydew, muskmelon, pumpkin, squash, watermelon)	1.05	5.25	5 days	
Eggplant	0.79	7.9	7 days	
Lettuce (endive, escarole)	1.0	8.0	5 days	
Okra	1.05	5.25	5 days	Not for use in California
Onion, Garlic	1.0	6.0	7 days	
Pea	0.79	3.95	7 days	
Pepper	0.79	11.85	3 days	
Spinach	0.79	3.95	7 days	
Tomato	0.53	17.4	3 days	
Watercress	0.53	2.12	7 days	Not for use in California
<b>VINES</b>				
Grape	3.0	20.0	3 days	
Hops	0.53	2.65	10 days	
Kiwi	2.1	6.3	30 days	
<b>MISCELLANEOUS</b>				
Chives	0.53	2.65	7 days	Not for use in California
Dill	0.79	3.95	7 days	Not for use in California
Ginseng	1.05	5.25	7 days	
Parsley	1.0	2.0	10 days	Not for use in California
Turfgrass	3.0	9.0	10 days	



<b>Crop</b>	<b>Maximum per Application Rate (lbs Cu<sup>2+</sup>/A)<sup>1</sup></b>	<b>Maximum Annual Rate (lbs Cu<sup>2+</sup>/A)<sup>2</sup></b>	<b>Minimum Retreatment Interval<sup>3</sup></b>	<b>Notes</b>
<b>ORNAMENTALS</b>				
Lilies, Easter	2.5	75.0	7 days	Maximum pounds of metallic copper which may be applied in a 12 month period. Do not apply any additional copper pesticide to this land for 36 months.
All Other Ornamentals	2.0	20.0	7 days	Application restrictions apply for several ornamentals in California
<b>DIRECT AQUATIC RATES<sup>4</sup></b>				
Sewer Line Treatment	0.5	2.0	6 months	No more than two applications per calendar year. Not permitted in the State of Connecticut and California counties
Algae, cyanobacteria, aquatic weeds (Elodea spp., hydrilla, Potamogeton spp., irrigation canal weed, annual naiads)	1 part per million (ppm)	n/a	14 days	No more than ½ of the water body may be treated at one time. If the treated water is to be used as a source of potable water, the metallic copper concentration must not exceed 1 ppm.
Schistosome-infected freshwater snail control	1.5 ppm	n/a	n/a	No more than two applications per calendar year. In the State of New York, this pesticide is a restricted use pesticide.
Algae control in aquaculture	0.4 ppm	n/a	n/a	
Tadpole shrimp in rice fields	2.5 ppm	n/a	n/a	

<b>Crop</b>	<b>Maximum per Application Rate (lbs Cu<sup>2+</sup>/A)<sup>1</sup></b>	<b>Maximum Annual Rate (lbs Cu<sup>2+</sup>/A)<sup>2</sup></b>	<b>Minimum Retreatment Interval<sup>3</sup></b>	<b>Notes</b>
Leech control	1.5 ppm	n/a	n/a	

1 – Maximum pounds of metallic copper which may be applied to an acre for each application. Product labels must also include application rates described in liquid units or pounds of total product.

2 – Maximum amount of metallic copper which may be applied to an acre each growing season. Lower single application rates at higher application frequencies may be used.

3 – Minimum number of days between each application.

4 – The use of this product in may pose a hazard to certain federally designated endangered species known to occur in specific areas of the following counties and its respective states: Solano (CA); Lawrence, Wayne, Hancock (TN); Lauderdale, Limestone, Madison (AL); Grayson, Smyth, Scott, Washington, Lee (VA). Before using this product, refer to the appropriate EPA Bulletin specific to your area. This Bulletin identifies areas where the use of this pesticide is prohibited, unless specified otherwise.