



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF PREVENTION,
PESTICIDES AND
TOXIC SUBSTANCES

Chemical: Coppers (Copper sulfate, copper group II, copper salts, copper and oxides)

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MEMORANDUM

DATE: October 24, 2005

SUBJECT: 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#4029) for use on crops and as direct water applications

FROM: Paige Doelling Brown, Ph.D., Fisheries Biologist
James Hetrick, Ph.D., Senior Physical Scientist
Kevin Costello, Acting Branch Chief
Environmental Risk Branch 1
Environmental Fate and Effects Division (7507C)

TO: Rosanna Louie, Chemical Review Manger
Thomas Moriarty, Chemical Review Manager
Reregistration Branch 3 (RB3)
Special Review and Re-Registration Division (7505C)

Attached please find Environmental Fate and Effects Division's (EFED) revised environmental risk assessment for the proposed re-registration of copper sulfate, copper group II compounds, and copper salts. Revisions are based on error correction comments provided by the Copper Sulfate Task Force (CSTF) in a letter to the Agency dated September 19, 2005.

The copper compounds are produced by a variety of manufacturers, and are currently registered for a wide variety of crops (both orchard and row crops), turf, and ornamentals, as well as for direct water applications.

As a bridging strategy to address the range of copper compounds included in this action, EFED has evaluated all of them on the basis of ionic copper (the cupric ion Cu^{2+}), regardless of the counter ion, or other moieties included in the complex. Where physical or molecular properties of the complex affect the fate and or toxicity of a particular compound differently than the general case, it is discussed qualitatively in the text. Copper is a unique pesticide. In addition to having toxic properties, it also is an essential trace element for organisms. It is an element and will not break down further. Thus copper introduced to the environment as a pesticide will continue to be processed through natural geochemical cycling. Because of this, EFED has addressed soil and sediment accumulation in the risk assessment in addition to the usual direct endpoints evaluated.

Copper is highly reactive, especially in the aquatic environment, and may exist in a number of ionic states, ion-pairs, and organic complexes simultaneously (known as “speciation”), as well as sorbed to suspended particles. Thus, the total dissolved concentration is not truly reflective of potential copper toxicity. To account for copper speciation, EFED opted to use the Biotic Ligand Model (BLM) in conjunction with the Pesticide Root Zone Model (PRZM)/EXposure Analysis Modeling System (EXAMS) model. The BLM was developed for and used by EPA’s Office of Water to develop Draft Ambient Aquatic Life Criteria for Copper to perform the aquatic toxicity assessment. It has been reviewed and approved by EPA’s Scientific Advisory Board (SAB).

The water quality data used in BLM simulation were derived from 811 USGS monitoring sites to evaluate site specific toxicity and copper speciation in a variety of surface water conditions. It is assumed these water quality conditions are representative of water quality in ambient surface across the United States. Thus, the aquatic evaluation is presented in terms of percentage of sites where the risk quotients (RQ) exceed a particular level of concern (LOC), rather than just a single RQ value.

Based on the label analysis provided by BEAD, application rates for copper vary widely, both for crops (0.3-32 lbs Cu/acre) and direct water applications (0.25-3.4 ppm dissolved Cu). Thus, while EFED has assessed the risk associated with the highest label permitted application rates from representative labels and state average use rates, we have also included a number of “what-if” estimations to provide additional benchmarks for the risk managers.

Key components of the risk assessment are as follows:

Aquatic assessment

- Site water chemistry, especially the alkalinity, pH, and dissolved organic carbon (DOC), determines copper toxicity through speciation of dissolved Cu. Because site conditions differ, EFED has used the BLM and USGS monitoring data to develop site specific LC₅₀s in terms of dissolved Cu¹ as well as predict the concentration of Cu²⁺ ion (Cu activity). Exposure to copper was based on the concentration of Cu²⁺ ion rather than dissolved Cu. Aquatic RQs were developed based on Cu activities.
- An analysis of ambient water quality conditions at the USGS monitoring stations indicate five out of the 811 monitoring sites (<1%) have ambient Cu²⁺ concentrations exceeding the *Daphnia* LC₅₀ (on an activity basis). Water quality conditions at these sites included low pH (acidic), low DOC, and low alkalinity. Additionally, some of the sites were associated with point sources of Cu contamination such as stormwater outfalls.
- Based on water chemistry, the site specific estimated LC₅₀s for aquatic invertebrates ranged from 0.3 to 1,900 ppb dissolved Cu, with the majority (90%) between 1 and 200 ppb dissolved Cu. The majority (91%) of site specific LC₅₀s for fish were <600 ppb dissolved Cu.
- Direct water applications: A concentration of 990 ppb dissolved Cu (for algal control) was used to evaluate effects from this type of application. At this concentration, RQs at 100% of the sites exceed acute LOCs for invertebrates, fish, and aquatic plants. Chronic RQs at >95% of the sites exceed LOCs for invertebrates and fish.
- Orchard crops and grapes: Orchard crops and grapes typically have the highest application rates, and based on usage estimates from BEAD, are the greatest users of copper sulfate and copper hydroxide. Estimated peak concentrations at label rates ranged from 17 to 350 ppb total dissolved copper depending on crop and application site. At the highest concentration (350 ppb dissolved Cu, PA apple scenario) RQs at >99% of the sites exceed the acute LOC for aquatic invertebrates and plants, and RQs at 80% of the sites exceed the acute LOC for fish. The chronic LOC is exceeded at 98% of the sites for aquatic invertebrates and 45% of the sites for fish.

¹ The risk assessment is based on concentration of Cu²⁺ ion (Cu activity) because this accounts for the speciation of copper, which greatly affects toxicity. Site specific LC₅₀s and runoff concentrations are presented in terms of dissolved Cu because that is what is most commonly measured and regulated.

- Row crops: Row crop label application rates are substantially lower than orchard crops. Usage estimates from BEAD show that tomatoes and peppers are the most heavily treated with copper sulfate and copper hydroxide. Estimated peak concentrations ranged from 2 to 55 ppb dissolved Cu. At the highest concentration (55 ppb dissolved Cu) RQs at 58% of the sites exceed the acute LOC for aquatic invertebrates, RQs at 14% of the sites exceed the acute LOC for fish, and RQs at 98% of the sites exceed the acute RQ for aquatic plants. The chronic LOC is exceeded at 55% of the sites for aquatic invertebrates and 10% of the sites for fish.
- Based on field studies submitted to the Agency, the dissipation half-life for dissolved copper is 10 days. This dissipation half-life reflects the time for 50% disappearance of copper from the water column into the sediment. Application intervals listed in labels include “as needed” and 7-14 day intervals, potentially introducing copper into the environment much more quickly than it will dissipate.
- EFED analyzed a wide range of use scenarios, and found that at concentrations of approximately 5 ppb dissolved Cu, 5% of the sites exceeded the acute LOC for aquatic invertebrates. At concentrations between 45 and 50 ppb Cu, approximately 50% of the sites exceeded the acute LOC for aquatic invertebrates. Based on correlations of peak Cu concentrations with single application rates, 5 ppb should be expected at an application rate of approximately 2 lb Cu/acre, and a concentration of 50 ppb should be expected at an application rate of approximately 20 lb Cu/acre. Peak concentrations, while partly a function of application rate, can vary widely dependent on site characteristics, climate, and timing of application.
- A substantial portion (80-90%) of the copper that runs off the field is sorbed to suspended sediment in runoff waters. While this component is not expected to be readily bioavailable, copper concentrations in the sediment of the receiving waters or depositional areas downstream will be elevated. Estimated first year sediment pore water² concentrations ranged from 0.4 to 45 ppb dissolved Cu. Estimated sediment pore water concentrations after 30 years of accumulation ranged from 13.7 to 2680 ppb dissolved Cu. Sediment pore water concentrations, on both a 1-year and 30-year basis, may be high enough to cause toxic effects to benthic organisms in some locations.

Terrestrial Assessment

² Sediment pore water is an estimate of the bioavailable fraction.

- The acute oral LD₅₀ for birds was 98 ppm Cu and for mammals was 114 ppm Cu. The acute dietary LD₅₀ for birds was 991 ppm Cu. Copper is classed as moderately toxic to both birds and mammals.
- The NOAEC for monocots was 6.8 lb Cu/acre and for dicots was 36.7 lb Cu/acre.
- In all cases, toxicity values for various compounds were expressed on the basis of copper, rather than the copper containing compound. This somewhat reduced the variability in toxicity levels between the various compounds. Copper sulfate appears to be more toxic than some of the other compounds, possibly due to the fact that it is extremely soluble, thereby making the Cu²⁺ ion more readily available to the organism following ingestion. Some studies suggest that the composition of food contaminated with copper may also affect bioavailability.
- At the highest orchard application rate, RQs for all sizes and food classes of birds exceeded the acute risk, chronic risk, and endangered species acute risk LOCs. At the highest row crop application rate, RQs for all sizes and food classes of birds exceeded the chronic risk, and endangered species acute risk LOCs. Most birds also exceeded the acute risk LOCs, with the exception of the large (1000g) bird eating fruits and pods (dose-based) and the class of birds eating fruits and pods (dietary-based).
- At the highest orchard application rate, RQs for all sizes and food classes of mammals exceeded the chronic risk and endangered species acute risk LOCs. RQs for all sizes and food classes of mammals except the largest granivores exceed the acute risk LOC. At the highest row crop application rate, RQs for all sizes and food classes of mammals except the granivores exceeded the acute risk, the chronic risk, and the endangered species acute risk LOCs.
- At sites where copper is continuously applied, it will accumulate in the soil, although the degree of bioavailability is uncertain, and will vary dependent on site conditions. Concentrations of 60-100 ppm Cu are potentially harmful to soil invertebrates, terrestrial plants, and soil microorganisms. Based on modeling, potentially harmful concentrations may be reached within 2-20 years, dependent on site conditions, application rates, and frequency of application. Although the model evaluates the application site, overspray areas where wildlife may reside and/or forage may be affected as well.
- Some plants concentrate copper from soil, potentially making it available to herbivorous and omnivorous organisms. Copper concentrations in plants were calculated, and appear to remain <100 ppm, even at the highest application rate. While this is above the dose-based LD₅₀ for birds and approaches the dose-based LD₅₀ for mammals, it is significantly below the dietary-based LD₅₀ for birds. Concentration of copper by plants is expected to pose little to no risk for birds and mammals.

Uncertainties, Assumptions, and Limitations

- PRZM/EXAMS modeling was used to estimate the runoff and drift of applied Cu. This modeling was conducted using a range of K_d values to represent differential sorption in sand and clay-textured soils. With the exception of aquatic dissipation from the water column, Cu was assumed to be persistent in soil and sediment. A comparison of edge-of-field Cu copper loss and distributions of Cu on suspended sediment and runoff water were similar for PRZM simulations and field monitoring studies.
- Median water quality parameters for 811 USGS monitoring sites were used to represent water quality conditions across the United States. These data are expected to represent the most likely water quality conditions in ambient surface waters.
- Chemical speciation modeling using the BLM was conducted without consideration of competitive equilibria with other common metals (such as Fe^{3+} , Zn^{2+} , Al^{3+} , etc.) or redox conditions. Redox conditions in the water column and surface sediments were assumed to be oxidic (aerobic). This assumption is an expected condition in order to support aquatic organisms. The lack of consideration of other metals in the speciation modeling is expected to underestimate prediction of Cu^{2+} concentrations in the water column due to the metal competition for ion pairs and ligands. Cupric ion concentrations, as predicted by PRZM/EXAMS/BLM, are within the range of Cu^{2+} concentrations for known Cu minerals. These data suggest the simulation modeling is not outside of the thermodynamic bounding conditions for Cu mineral stability.
- A bridging strategy was implemented to assess a variety of Cu compounds and complexes using a unified assessment approach. This strategy assumes complete dissociation into Cu^{2+} and the counter ion. This assumption is expected to provide a conservative estimate of Cu^{2+} concentrations in the exposure assessment.
- Application rates for the various copper compounds were derived from representative labels. Highest label application rates were 32 lb Cu/acre for orchard crops and 3.6 lb Cu/acre for row crops. These application rates may not reflect the maximum rates for all copper compounds. Additionally, the labels did not clearly state the number of applications or a maximum application rate of copper for a year or season. Therefore, the aquatic exposure assessment assumed 4 applications at 7 day intervals.
- First year peak aquatic copper concentrations were used due to the long half-life of copper, rather than the 1-in-10 year peak concentrations typically used in EFED assessments. Because of the way the model is written, the long half-life made copper appear to accumulate in the water body at much greater concentrations than would actually occur. However, the first year peak concentration may not be the highest peak concentration in the 30-year simulation.

- The plant uptake of Cu was estimated using a regression equation. This regression equation has an extremely low coefficient of determination (r^2). Therefore, there is considerable uncertainty associated with predicted Cu uptake.
- The BLM has been parameterized, validated, and tested for animals in freshwater ecosystems. It is appropriate for assessing copper speciation for aquatic plants, but not toxicity. A version is currently under development to address aquatic plants, as well as marine and estuarine systems.
- Copper is both highly reactive and a trace nutrient, thus there is significant uncertainty in estimating effective toxic doses to terrestrial organisms. Composition of the diet, homeostatic mechanisms, and species sensitivity may vary widely.

Data Requirements

EFED used data from registrant-submitted studies, other Agency programs, and open literature. No specific data requirements were identified.

Endangered Species Statement

Endangered species LOCs were exceeded at both the highest label application rate and the highest average application rate for aquatic plants, aquatic invertebrates, fish, birds, and small mammals. Terrestrial plants were the only category of organism quantitatively evaluated that did not exceed endangered species LOCs.

EFED's LOCATES program was used to determine what endangered species might potentially be affected by use of copper-containing pesticides. LOCATES identified a total of 494 animal species as occurring in counties containing crops on which copper-containing pesticides are registered for use. Some terrestrial plants may be at risk because they require animals as their primary vector of dispersal or pollination. LOCATES identified a total of 685 plant species as occurring in counties containing crops on which copper-containing pesticides are registered for use.

Additional analysis regarding co-occurrence of pesticide application and species location, and better information regarding application rates are required to refine the estimate of what endangered species may be affected by use of copper-containing pesticides.