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TO: Richard Mountfort/Christine Rice
Product Manager #23
Registration Division (TS-767)

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Exposure Assessment Branch
Hazard Evaluation Division (TS-769C)



THRU: Paul F. Schuda, Chief
Exposure Assessment Branch
Hazard Evaluation Division (TS-769C)



Attached, please find the EAB review of...

Reg./File #: 1109-1

Chemical Name: Copper(II) sulfate pentahydrate

Type Product: Fungicide/algaecide/antimicrobial/insecticide/herbicide

Product Name: Copper sulfate

Company Name: Tennessee Chemical Company/ Cu(II) sulfate Registration

Standard Task Force

Purpose: Review of protocol for combined program to respond to requirements in copper sulfate/copper(II) Registration Standards

Date Received: 10/2/87

Action Code: 630

Date Completed: 12/24/87

EAB #(s): 80006

Monitoring study requested:

Total Reviewing Time: 2 days

Monitoring study voluntarily:

Deferrals to:

 Ecological Effects Branch

 Residue Chemistry Branch

 Toxicology Branch

249

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1. CHEMICAL:

Common Name: Copper sulfate or cupric sulfate.

Chemical Name: Copper(II) sulfate pentahydrate

Chemical Formula: $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

Formulation: Several formulations (crystalline; soluble concentrate) alone or with other inorganic chemicals. Formulation is expressed in terms of metallic copper equivalent (in percent).

2. TEST MATERIAL: Not applicable

3. STUDY/ACTION TYPE: Review of protocols for combined testing program submitted by the copper sulfate task force to respond to requirements in copper sulfate/copper(II) Registration Standards.

4. STUDY IDENTIFICATION: The registrant submitted protocols (together with a letter dated 9/25/1987) in response to an Agency letter dated 9/15/1987 listing the Environmental Fate data requirements (163-1, Adsorption/desorption; 164-1, soil dissipation field study; 164-2, aquatic [sediment] dissipation field study) for the Copper Sulfate Registration Standard. Included in the package were the following submissions:

Copper Sulfate Standard Protocol Meeting. 1987. Job Number CSTF0010. Prepared by HydroQual, Inc., Mahwah, NJ, June 1987. No EPA Accession Number.


Literature Review to Characterize the Adsorption Potential of Copper in the Environment. 1987. Project Number CSTF0010. Prepared by HydroQual, Inc., Mahwah, NJ, September 30, 1987. No EPA Accession Number.

Approach for Soil Dissipation Field Study (Draft). 1987. Project Number CSTF10010. Prepared by HydroQual, Inc., Mahwah, NJ, September 30, 1987. No EPA Accession Number.

Approach for Aquatic Sediment Dissipation Field Study. 1987. Prepared by HydroQual, Inc., Mahwah, NJ, September 30, 1987. No EPA Accession Number.

5. REVIEWED BY:

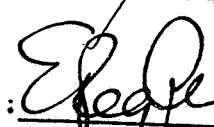
Silvia C. Termes
Chemist, Review Section #3
EAB/HED/OPP

Signature: 

Date: JAN 28 1988

6. APPROVED BY:

Emil Regelman
Supervisory Chemist
Review Section #3
EAB/HED/OPP

Signature: 

Date: JAN 28 1988

7. CONCLUSIONS:

The reviewed protocols are acceptable in general. Specific comments and suggestions are included in the RECOMMENDATIONS section. Note that these protocols had been reviewed by EAB at the time of the meeting with the registrant(10/29/1987) and few recommendations were already made at that time, which are now expanded here.

8. RECOMMENDATIONS:

Dissipation field work

A justification for the deviation from multiple site sampling must be included, as stated in item 2 of the Summary.

For laboratory desorption studies(drafted under the field dissipation study), it is recommended that a mineralogical characterization of the field soils used be included in the report. It is also recommended that, besides reporting particle size distribution, the specific surface area of the soil be included(as obtained by BET methods, for example). For the aqueous phase, it is recommended that pH, E_h , and conductivity be included and that, if feasible, other anionic and cationic species besides those related to the copper(II)-water system be monitored (Ion Chromatography may prove to be a useful technique). The same is applicable to desorption experiments with aquatic sediments.

For the aquatic(sediment) dissipation studies, it is recommended that the analyses of the interstitial water be supplemented by E_h measurements. This is important since the samples will be analyzed for "H₂S" and it is well-known that pH and E_h play a very important role in determining the actual sulfur species to be expected(that is, HS⁻, S²⁻, S_n²⁻, SO₄²⁻, etc.).

Adsorption/desorption studies

Because this study will be based on a literature review, the reviewer wishes to point out the extensive work carried on copper(II) adsorption/desorption ("activation/deactivation") on minerals performed by researchers in the minerals processing field, which include results from both basic and applied research.

As with the dissipation studies, it is important that the registrant is aware of the importance of pH and E_h in adsorption/desorption processes, since pH and E_h play a very important role in adsorption/desorption of metallic species.

9. BACKG ROUND:

a. Introduction

The reviewed protocols were submitted in response to an EPA letter dated 9/15/1987 listing the Environmental Fate requirements for the Copper Sulfate Registration Standard. In October 29, 1987, a meeting between EPA personnel and members of the Copper Sulfate Task Force (including representatives from HydroQual, Inc.) was held at EPA to discuss the submitted protocols. At the time of the meeting, these protocols had already been reviewed by EAB. The points discussed in the meeting are summarized in the Appendix (Summary of Meeting prepared by Product Manager, dated 10/30/1987).

b. Directions for use

Not applicable for this review.

10. DISCUSSION OF INDIVIDUAL STUDIES:

Summary of Submitted Protocols

A. Copper Sulfate Standard Protocol Meeting

This submission summarizes the proposed study.

The key issue addressed was the effective toxicity of copper sulfate when applied to terrestrial and aquatic systems, which includes the availability of toxic forms of copper in the environment, the partitioning characteristics of copper, and the speciation characteristics of copper as a function of field conditions.

Copper toxicity. A review of copper toxicity studies pointed out the importance of two critical issues:

1. That the copper species of concern are those related to copper activity and not necessarily to the total concentration of copper.
2. That complexation or sorption properties of copper in realistic environmental conditions must also be characterized.

Aquatic availability. The availability of copper to aquatic organisms is controlled by the tendency of copper to sorb to particulate material and by the speciation of dissolved copper, for which pH and the presence of "complexing" species play an important role. Therefore, copper speciation models can be applied for computing

the effective copper toxicity over a range of total copper, pH, dissolved organic matter, and alkalinity. The use of these models is proposed.

Proposed scope of study. The chemical fate model MEXAMS will be used. This program is comprised of two sub-models: MINTEQA2 (a geochemical [speciation] sub-model) and EXAMS (a conventionally used exposure assessment model). A literature review will provide the relevant binding constants required as input to the speciation sub-model. The pertinent literature on chemical properties and fate of copper will be reviewed as part of the evaluation process. Other proposed studies included were:

- 163-1 Adsorption/Desorption
- 164-1 Soil Dissipation Field Study
- 164-2 Aquatic (Sediment) Dissipation Studies

B. Literature Review to Characterize the Partitioning Characteristics of Copper in the Environment

Copper can be partitioned to:

- soils in agricultural fields
- suspended solids in water bodies receiving runoff from agricultural areas treated with copper compounds or treated directly with copper sulfate
- aquatic sediments in water bodies receiving these direct and indirect inputs of copper

A substantial data base is available to characterize the adsorption of copper ions to soil. Adsorption of copper to soil takes place by three primary mechanisms: complexation by soil organic matter, specific adsorption, and ion exchange. The latter is only likely to be important when the concentration of copper is high. An extensive literature review of copper adsorption is presented in the protocol submission. Results indicate an inverse relationship between the partition coefficient and particle size class and that a reduction in the organic content of fines reduces the partition coefficient. Thus, particle size and organic matter content have implications to the fate of copper applied to agricultural fields since runoff solids tend to be the finer, organically rich fractions of the field soils.

Adsorption of copper is strongly dependent on pH because, in general, CuOH^+ is more readily adsorbed than Cu^{2+} . Experimental evidence is abundant in the literature.

Experimental results characterizing the partitioning of copper in natural water systems are less readily available than in field soils. Thus, partitioning of copper in water systems will be evaluated on the basis of an analysis of the field data included in the STORET data base. Previously analyzed data has indicated that the concentration of solids suspended in a water column must be included in an environmental fate analysis. Although the effect of pH has not been characterized to date, further analysis of the effect of pH will be undertaken.

A substantial data base is available to characterize the partitioning of copper in aquatic sediments. As with field soils and water particulates, the results are quite variable because of the complex physico-chemical interactions controlling sorption of copper to particulate matter.

Thus, significant data base is presently available to characterize the partitioning of water in field soils, water bodies, and aquatic sediments to allow performing an environmental fate assessment for copper.

Reviewer's comment

Extensive work on copper adsorption/desorption ("activation/deactivation") on mineral surfaces is available from the minerals processing literature, which can provide further data to the proposed work.

C. Approach for Soil Field Dissipation Field Study for Copper (Draft)

Modifications of the conventional protocol will be necessary because:

1. Copper levels in the top 3-inches resulting from the maximum application rate are comparable to levels of naturally occurring copper in soils (10-100 ppm).
2. Copper will not metabolize or degrade under field conditions; it will only accumulate with continued use.
3. Only a fraction of the copper bound to soil particles lost in runoff from a treated field will desorb once it enters a water body.

A preliminary runoff simulation indicated that the copper concentration associated with the runoff reaches a steady-state in about 10-12 y period in a tilled agricultural setting and longer in an orchard setting, where the soil yield is expected to be lower. Thus, it is critical to evaluate the degree to which the runoff of aged, bound copper soil will desorb from the runoff solids.

Field soils with an extended copper application record (10-20 yrs) will be sampled to characterize the long-term accumulation of copper in the upper soil horizon. The samples will be used in laboratory experiments to study the fraction of soil desorbed from these soils over a short time scale, and hence the amount of copper available for impact on aquatic organisms.

Field sampling and laboratory procedures

Samples will be collected from a variety of agricultural settings treated with copper for an extended period of time. The settings will range from untilled citrus orchards with sandy soils in the southeast United States to relatively organically rich tilled soils in tomato fields in the northern part of the country. Ten samples will be analyzed: seven from citrus orchards in a variety of settings and three from tilled agricultural fields. Two settings will be sampled just prior to and after pesticide applications. One pair of citrus orchards and one pair of tilled soils will be sampled from areas

closed in proximity to each other and with similar soil types, but with different histories of copper pesticide application.

The samples will be collected from the 0-1 cm surface layer soil horizon, which is conventionally used in the to characterize pesticide concentrations in soil available for runoff and it is the depth used in runoff models such as SWRRB and CREAMS. Samples to be used in laboratory desorption experiments will be preserved at 4°C (in the field) and then transported to the laboratory.

Laboratory studies: Soils will be characterized for soil moisture content, porosity, bulk density, cation exchange capacity(CEC), percent organic matter, particle size distribution, pH, calcium carbonate, total copper, hydroxylamine-extractable copper, iron, and manganese.

Consecutive desorption experiments will be performed by adding varying amounts of the soil and aqueous phase into 30 mL polycarbonate tubes to a same final volume, but different final concentrations of suspended solids (150-1500 mg/L; total of four levels in each range. The aqueous phase will be a buffered 0.0001 M solution(to simulate ionic strength of runoff). Then, the tubes will be sonicated to disperse the soil particles and agitated for a chosen period of time(typically one hour). After 20 min centrifugation, the aqueous phase will be sampled and analysed for dissolved copper and Cu^{2+} using a copper selective electrode. The supernatant will be removed and replaced with a sufficient amount of metal-free aqueous phase as to maintain a consistent sediment concentration. Again the tubes will be sonicated, sonicated, and sampled; this process will be repeated 3-4 times.

The data obtained will be analyzed mathematically in order to define the resistant and reversibly sorbed fractions of copper bound to soil. The information obtained will be incorporated into the environmental fate analyses of copper in water bodies receiving runoff from treated fields.

D. Approach for Aquatic Sediment Dissipation Field Study

Field program: Reconnaissance sampling will be performed at six sites having known histories of copper pesticide applications (adjacent to agricultural drainage areas or directly to the water). Samples of surficial sediment will be obtained with an Ekman dredge. The samples will be chilled to 4°C and transported to the laboratory for analysis of total copper. Two of the six water bodies will be selected for subsequent sampling and characterization.

Three sites in each of the two selected ones will be sampled for pore water and sediments.

Pore water will be collected using in situ samplers consisting of a plexiglass body having cylindrical cells machined to it on a uniform vertical spacing. The cells are filled with deionized water and covered with a filtration membrane. The samplers are inserted vertically into the sediment, with two or more layers exposed above the sediment-water interface in order to sample the overlying water. Samplers will be kept in place until equilibration between the sediment pore water and the water in the cells is achieved. Sediment core samples will also be collected with plexiglass coring tubes. Surficial sediment samples will be collected at one sample location in each of the two selected sites for subsequent desorption

experiments. Sediment samples will be kept chilled at 4°C.

Laboratory studies:

Interstitial (pore) water will be analysed for: total Cu, Cu²⁺, pH, alkalinity, dissolved organic carbon (DOC), Ca, Mg, dissolved oxygen, H₂S, SO₄²⁻, and conductivity.

Sediment core samples will be sliced (1-in increments) and analysed for porosity, bulk density, particle size distribution, cation exchange capacity, total organic carbon, total and acid soluble copper; copper, iron, and manganese using hydroxylamine extraction and other major copper complexing ligands.

Consecutive desorption experiments will be performed in surficial copper sediments to determine resistant and reversibly sorbed fractions of copper in the sediments. The experimental procedure to be followed is the same as those described for desorption experiments with soils. Data will be analysed mathematically and the results incorporated into the environmental fate modeling.

Speciation modeling will be carried on with one of the available models (FITEQL, MICROQL, MINTEQA1, and MEXAMS). The latter has the advantage of incorporating vertical transport within the sediment and exchange with the overlying water. Simulation of the vertical sediment profiles will provide validation of the speciation modeling. Computation of the copper species (free and complexed) in the pore water and adsorbed as well as mineral forms associated with the solid phase will define the levels of copper species available to organisms.

Environmental fate modeling will be performed with the conventional EXAMS-type simulation together with geochemical equilibrium model and will allow to determine the long term fate of copper in lakes or ponds receiving direct copper treatments or runoffs from treated fields.

Reviewer's comments to soil and aquatic dissipation studies

For desorption studies (soil and sediments), it is recommended that besides analysing the particle size distribution of soils and sediments, the specific surface area (as determined by BET methods, for example) be included. For aqueous phases, it is recommended that pH, E_h, and conductivity be measured. If feasible, other anionic and cationic species besides those related with copper may be monitored.

11. COMPLETION OF ONE-LINER:

Not applicable.

12. CONFIDENTIAL BUSINESS INFORMATION:

Not applicable.