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TO: Lois Rossi, Chief  
Reregistration Branch  
Reregistration Division (H7505C)

FROM: Paul Mastradone, Chief  
Environmental Chemistry Review Section #1  
Environmental Fate and Groundwater Branch

THRU: Henry Jacoby, Chief  
Environmental Fate and Groundwater Branch  
Environmental Fate and Effects Division (H7507C)

Attached please find the EFGWB review of:

Reg./File # : Not listed

Chemical Name : Copper Sulfate

Product Type : Fungicide

Product Name : N/A

Company Name : Copper Task Force

Purpose : Review and reassess conclusions made in Science Chapter dated August 21, 1990.

Date Received : 01/03/91 EFGWB #: 91-0309

Time (days): 5.0

Deferrals to :

<input type="checkbox"/> EEB/EFED	<input type="checkbox"/> DEB/HED	<input type="checkbox"/> TB1/HED
<input type="checkbox"/> SIPS/EFED	<input type="checkbox"/> OREB/HED	<input type="checkbox"/> TB2/HED

1.0 CHEMICAL:

Common Name: Copper

Chemical Name: Copper

Chemical Structure: Cu

Chemical/physical properties:

molecular weight: 63.54  
melting point: 1083  
solubility: Insoluble  
vapor pressure: N/A

2.0 TEST MATERIAL: Not applicable since no new studies were submitted.

3.0 STUDY/ACTION TYPE: Generic data reregistration.

4.0 STUDY IDENTIFICATION:

1. Carey, D. O. January 1989. Analytical report for terrestrial outdoor field dissipation studies with copper-containing pesticides. Laboratory Study No. 88-033-02. Unpublished study performed by Biospherics Inc., Beltsville, MD. Submitted by the Copper Sulfate Task Force, c/o Orius Associates, Inc. Frederick, MD. (MRID 41003801)
2. Carey, D. O. January 1989. Method validation report for terrestrial outdoor field dissipation study with copper-containing pesticides. Laboratory study No. 88-003. Unpublished study performed by Biospherics Inc., Beltsville, MD. Submitted by the Copper Sulfate Task Force, c/o Orius Associates, Inc. Frederick, MD. (MRID 41003802)
3. Ravitz, S. February 1989. Interim summary report: Terrestrial outdoor field dissipation study with copper-containing pesticides. File/issue No. 35-COP/89006, Project No. 24086. Unpublished study written by Orius Associates, Inc. Frederick, MD. Submitted by the Copper Sulfate Task Force, c/o Orius Associates, Inc., Frederick, MD. (MRID 41003803)
4. Carey, D. O. December 1988. Analytical report for aquatic outdoor field dissipation studies with copper-containing pesticides. Laboratory Study No. 88-033-02. Unpublished study performed by Biospherics Inc., Beltsville, MD. Submitted by the Copper Sulfate Task

Force, c/o Orius Associates, Inc. Frederick, MD. (MRID 40013804)

5. Ravitz, S. February 1989. Summary of results and conclusions for aquatic and terrestrial field dissipation studies with copper-containing pesticides and the residue and incidence monitoring survey. File/issue No. 35-COP/89020, Project No. 24086. Unpublished study written by Orius Associates Inc. Frederick, MD. Submitted by the Copper Sulfate Task Force, c/o Orius Associates, Inc., Frederick, MD. (MRID 41003805)
6. Gohlke, A. F. November 1988. Literature review to characterize the adsorption potential of copper in the environment. Project No. CSIF0010. Unpublished report prepared by Hydroqual, Inc. Mahwah, NJ. Submitted by the Copper Sulfate Task force, Atlanta, GA. (MRID 40879601)
7. Carey, D. O. December 1988. Method validation report for aquatic outdoor field dissipation study with copper-containing pesticides. Laboratory Study No. 88-003. Unpublished study performed by Biospherics, Inc. Beltsville, MD. Submitted by the Copper Sulfate Task Force c/o Orius Associates, Inc. Frederick, MD. (MRID 40968201)

5.0 REVIEWED BY:

Richard J. Mahler  
Hydrologist, Review  
Section 1, EFGWB, EFED

Signature: *Richard J. Mahler*  
Date:

6.0 APPROVED BY:

Paul J. Mastradone, Chief  
Review Section 1, EFGWB, EFED

Signature: *Paul J. Mastradone*  
Date: MAY 24

7.0 CONCLUSION:

1. Citations No. 1, 2, 4 and 7 listed above under 4.0 "STUDY IDENTIFICATION" were previously reviewed (See attached DERS for MRIDs 41116801 and 41189001) for the Science Chapter dated August 21, 1990; however, the citations were inadvertently omitted from the "STUDY IDENTIFICATION" section in the individual DERS to which they pertain. The studies that were omitted were

method validation and the analytical reports for the terrestrial and aquatic field dissipation studies submitted.

2. Citations No. 3 and 5 listed above under 4.0 "STUDY IDENTIFICATION" were not included in the package with the original studies that were reviewed in the August 21, 1990 Science Chapter. However, both are interim reports and the data contained in them were included in the final reports that were reviewed originally. They also do not provide any additional information that was not included in the final reports.
3. Citation No. 6 above, was not included in the package with the original studies that were reviewed in the August 21, 1990 Science Chapter. The study does not provide any new original data, it is a literature review of 20 references which characterize the adsorption potential of copper in the environment. Specifically the review discusses the partition coefficients of copper in three distinct environmental compartments, i.e., field soils, natural water bodies (streams and lakes) and aquatic sediments.

The literature review stresses that within each compartment there is significant variability in partition coefficients for copper. For example, the range of partition coefficients for soils and streams, lakes and aquatic sediments varied, respectively, from 27 to  $10^5$  and  $10^3$  to  $10^6$ . All of which can be considered as an indication of copper's high tendency to sorb to soils and sediments.

EFGWB notes that partition coefficient ( $K_d$ ) values for soils were derived from the Langmuir equation, which is similar to the Freundlich equation and from which  $K_d$ s can be derived based on equilibrium of soils with various concentrations of copper in solution. Conversely, the partition coefficients reported for streams and lakes were calculated from the amount of copper in the total soluble solids (TSS) and the amount of copper in solution collected from samples at various depths. Sediment partition coefficients were calculated from particulate copper and interstitial water copper and from the Langmuir equation. See Section 10.3.2. for details.

4. EFGWB concludes that the studies submitted do not provide any additional information that would change any conclusions reached in the original Science Chapter
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dated August 21, 1990. Those conclusions are as follows:

- a. After copper is applied to soil, there is generally very little detectable soluble copper in the water phase of soil extracts; although there may be small quantities of copper dissolved in the soil solution.
- b. The conventional "adsorption constant"  $K_d$  (an indication of the degree of adsorption by soil), as defined in pesticide studies, has been estimated to be approximately 190 for copper<sup>1</sup>. A  $K_d$  value of this magnitude indicates that copper is quite strongly adsorbed to soil and would be expected to be, and in fact is, found in the sediment phase of runoff.
- c. After copper is applied to water and equilibrium is reached with sediments (usually in a few days), there is generally very little detectable soluble copper in the water phase; although there may be small quantities of copper dissolved in interstitial waters of sediments.
- d. Copper applied to soil, sediment and water is complexed with organic compounds, because the formation constants of copper-organic complexes are very high. Other forms of copper are adsorbed to solid phases in soils/sediments by chemisorption or cation exchange processes. Copper is also found adsorbed or occluded in carbonate or oxide minerals and incorporated into the structure of minerals.

In cases where the copper activity in the soil solution or interstitial water of sediments exceeds the solubility products ( $K_{sp}$ ) of copper minerals (e. g. cupric ferrite, tenorite, malachite and azurite, etc.), precipitation of copper will occur as those discrete mineral phases.

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<sup>1</sup>Harter, R. D. 1983. Effect of pH on adsorption of lead, copper, zinc and nickel. Soil Sci. Soc. Am. J. 47:47-51.

McLaren, R. G. and D. V. Crawford. 1973. Studies on soil copper. II. The specific adsorption of copper by soils. J. Soil Sci. 24:443-452.

- e. Under normal conditions that would exist when copper- containing sediments reach an aquatic environment, little if any free copper ions would be expected to be in solution because of the above mentioned factors.
- f. Under normal conditions of copper application to soils or sediments, the leaching data presented, plus general knowledge in the scientific community about copper attenuation by soil and sediments, indicate that copper will not move downward in the soil to any great extent. Thus, ground-water contamination by leaching should not be a problem with copper under the present-day use patterns of copper compounds.

8.0 RECOMMENDATIONS: See conclusions.

9.0 BACKGROUND: Reregistration Division has requested that EFGWB perform the following:

- 1. Review submitted studies and reassess conclusions made in Science Chapter dated August 21, 1990.
- 2. Confer data results to EEB so they may use them to assess their residue and incidence monitoring data.

10.0 DISCUSSION OF INDIVIDUAL STUDIES:

10.1. Four of the submitted studies were previously evaluated during the review of studies for the Science Chapter dated August 21, 1990. The listings of the citations were inadvertently left out of the Science Chapter. The studies that were omitted were method validation and the analytical reports for the terrestrial and aquatic field dissipation studies submitted. They are listed below and immediately follow the original study citation for which they provide the analytical or method validation data.

10.1.1. Original Citation in DER: Guy, S. O. November 2, 1989. Metallic copper environmental fate on citrus in Florida. Prepared by Landis Associates, Inc. Valdosta, GA. Sponsored by Copper Sulfate task force. Frederick, MD. 21701. (MRID 41116801)

1. Carey, D. O. January 1989. Analytical report for terrestrial outdoor field dissipation studies with copper-containing pesticides. Laboratory

Study No. 88-033-02. Unpublished study performed by Biospherics Inc., Beltsville, MD. Submitted by the Copper Sulfate Task Force, c/o Orius Associates, Inc. Frederick, MD. (MRID 41003801)

2. Carey, D. O. January 1989. Method validation report for terrestrial outdoor field dissipation study with copper-containing pesticides. Laboratory Study No. 88-003. Unpublished study performed by Biospherics Inc., Beltsville, MD. Submitted by the Copper Sulfate Task Force, c/o Orius Associates, Inc. Frederick, MD. (MRID 41003802)

10.1.2. Original Citation in DER: Hosmer, A., J. Beaver and T. Brantley. February 8, 1989. An aquatic sediment dissipation study of copper sulfate in the Hillsborough reservoir, Florida. Prepared by Wildlife International, Ltd. Easton, MD. 21601. Sponsored by Copper Sulfate Task Force. Frederick, MD. 21701. (MRID 41189001)

1. Carey, D. O. December 1988. Analytical report for aquatic outdoor field dissipation studies with copper-containing pesticides. Laboratory Study No. 88-033-02. Unpublished study performed by Biospherics Inc., Beltsville, MD. Submitted by the Copper Sulfate Task Force, c/o Orius Associates, Inc. Frederick, MD. (MRID 40013804)

2. Carey, D. O. December 1988. Method validation report for aquatic outdoor field dissipation study with copper-containing pesticides. Laboratory Study No. 88-003. Unpublished study performed by Biospherics, Inc. Beltsville, MD. Submitted by the Copper Sulfate Task Force c/o Orius Associates, Inc. Frederick, MD. (MRID 40968201)

10.2. The following two submissions were not included in the package with the original studies that were reviewed in the August 21, 1990 Science Chapter. However, they are both interim reports and the data contained in them were included in the final reports that were reviewed originally. Need-less-to-state they do not provide any additional information that was not included in the final reports. They are listed below and immediately follow the original study citation for which they provide the interim report. EFGWB notes that citation No. 2 below, contains information for both terrestrial

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and aquatic studies and is included under each original citation listed below.

Submission No. 2 also contains information related to residue and incidence monitoring of aquatic sites treated with copper-containing pesticides. The review of these subjects are the responsibility of Ecological Effects Branch.

10.2.1. Original Citation in DER: Guy, S. O. November 2, 1989. Metallic copper environmental fate on citrus in Florida. Prepared by Landis Associates, Inc. Valdosta, GA. Sponsored by Copper Sulfate task force. Frederick, MD. 21701. (MRID 41116801)

1. Ravitz, S. February 1989. Interim summary report: Terrestrial outdoor field dissipation study with copper-containing pesticides. File/issue No. 35-COP/89006, Project No. 24086. Unpublished study written by Orius Associates, Inc. Frederick, MD. Submitted by the Copper Sulfate Task Force, c/o Orius Associates, Inc., Frederick, MD. (MRID 41003803)

2. Ravitz, S. February 1989. Summary of results and conclusions for aquatic and terrestrial field dissipation studies with copper-containing pesticides and the residue and incidence monitoring survey. File/issue No. 35-COP/89020, Project No. 24086. Unpublished study written by Orius Associates Inc. Frederick, MD. Submitted by the Copper Sulfate Task Force, c/o Orius Associates, Inc., Frederick, MD. (MRID 41003805)

10.2.2. Original Citation in DER: Hosmer, A., J. Beaver and T. Brantley. February 8, 1989. An aquatic sediment dissipation study of copper sulfate in the Hillsborough reservoir, Florida. Prepared by Wildlife International, Ltd. Easton, MD. 21601. Sponsored by Copper Sulfate Task Force. Frederick, MD. 21701. (MRID 41189001)

Ravitz, S. February 1989. Summary of results and conclusions for aquatic and terrestrial field dissipation studies with copper-containing pesticides and the residue and incidence monitoring survey. File/issue No. 35-COP/89020, Project No. 24086. Unpublished study written by Orius Associates Inc. Frederick, MD. Submitted by

the Copper Sulfate Task Force, c/o Orius Associates, Inc., Frederick, MD. (MRID 41003805)

10.3. The following submission was not included in the package with the original studies that were reviewed in the August 21, 1990 Science Chapter. The study does not provide any new original data, it is a literature review of 20 references which characterize the adsorption potential of copper in the environment. Specifically the review discusses the partitioning of copper in three distinct environmental compartments, i.e., field soils, natural water bodies and aquatic sediments.

10.3.1. Study Identification: Gohlke, A. F. November 1988. Literature review to characterize the adsorption potential of copper in the environment. Project No. CSIFO010. Unpublished report prepared by Hydroqual, Inc. Mahwah, NJ. Submitted by the Copper Sulfate Task Force, Atlanta, GA. (MRID 40879601)

10.3.2. Conclusions:

10.3.2.1. General Conclusions: EFGWB concludes that this submission provides supplemental information related to the adsorption/desorption of copper in soils, streams and lakes and aquatic sediments, since it is only a literature review and not an original study.

10.3.2.2. Soils and Aquatic Sediments: The partition coefficient values reported in this review for soils and aquatic sediments varied significantly from 27 to  $10^6$  and are affected by the mineral and organic matter content of the sorbent material, the solution pH and other physical and chemical characteristics of the sorbent material. These high partition coefficient values all manifest the high tendency of copper to sorb to soils and sediment.

The effect of these physical and chemical characteristics as reported in the review can be summarized as follows:

1. There is an inverse relationship between the partition coefficient and particle size of the material studied. In regards to soils, the larger size weight fractions have a partition coefficient generally 10 to 40 percent of the partition coefficient of the smaller sized fractions (silts

and clays). For sediments, after normalizing the data to the surface area/g of solids, the two order of magnitude range in partition coefficients is reduced to approximately a factor of four.

2. Removal of the organic matter from the soil materials with hydrogen peroxide produces more than an order of magnitude reduction in the partition coefficient.

Some of the variability in the partition coefficients of sediments can be explained by variations in the organic matter content. By calculating the  $K_{oc}$  of the sediments, some of the variability is eliminated; although the variation still exhibits a two order of magnitude range in  $K_{oc}$ .

3. Increasing the pH of the equilibrium solutions of soils from 5.0 to 7.0 resulted in a two-fold order of magnitude increase in the partition coefficient in pure clay systems; while increases of about a factor of 2 would be expected in natural field soils.

4. Pure clay systems have generally low partition coefficients of 56 to 375, in comparison to >17,000 for organic matter and >250,000 for manganese oxide.

10.3.2.3. Streams and Lakes: Much less information was reported in the review about factors effecting the partitioning of copper in natural water systems as compared to soils and aquatic sediments. Generally, the partition coefficients of copper in water columns are quite variable and are inversely related to the suspended solids concentration (TSS). At TSS concentrations <10 mg/l (which are representative of allowable suspended solids in drinking water), partition coefficients are in the  $10^5$  to  $10^6$  range. At TSS levels of 100 mg/l or more (which may be encountered during significant runoff events from treated fields), the partition coefficients can be significantly lower, by as much as an order of magnitude or more. This implies that a greater concentration of copper would be in solution relative to particulate bound copper. No other information related to other factors affecting the partitioning of copper in streams and lakes was presented in the literature review.

10.3.2.4. Summary: All measures of sorption of copper to soil, sediments or suspended solids indicate that copper has a high tendency to bind to these solids and that very little copper would be in solution once equilibrium is attained.

11.0 COMPLETION OF ONE-LINER: N/A

12.0 CBI APPENDIX: Some data from past reviews was claimed to be CBI by the registrant; therefore, it must be treated as such.

DATA EVALUATION RECORD

STUDY IDENTIFICATION:

Guy, S. O. November 2, 1989. Metallic copper environmental fate on citrus in Florida. Prepared by Landis Associates, Inc. Valdosta, GA. Sponsored by Copper Sulfate Task Force. Frederick, MD. 21701. (MRID # 411168-01).

REVIEWED BY:

Richard J. Mahler, Hydrologist  
Review Section I, EFGWB

Signature: Richard J. Mahler

Date: AUG 21 1990

APPROVED BY:

Paul J. Mastradone, Chief  
Review Section I, EFGWB

Signature: Paul J. Mastradone

Date: AUG 21 1990

TYPE OF STUDY: Terrestrial Field Dissipation--164-1

CONCLUSIONS:

1. EFGWB concludes that this study is scientifically valid; however the study does not satisfy the data requirements for Field Dissipation For Terrestrial uses because there was too much variation in the recovery data for the various forms of copper determined in the total suspended solids-aqueous suspension phase.
2. Total copper at the site did not change significantly during the length of the study, and the copper application of 12.7 lb/A did not significantly increase the total copper level in the 0-5 cm soil depth (154 and 160 ppm, respectively, before and after application).

This is not unexpected since the citrus orchard where this study was performed has been in existence for at least 75 years and has had historical applications of copper compounds. Pesticide use records kept from 1974 to 1988 show at least one yearly application of a copper containing compound to the citrus orchard. This historical use of copper accounts for the high concentration of copper in the soil.

3. The data showed that, while copper has leached in the soil as a result of long-time copper applications, little copper movement was detected below the 45 cm soil depth.

4. Since only small amounts of copper (all  $\leq 0.190$  ppm with most concentrations  $< 0.079$  ppm) and  $\text{Cu}^{++}$ , cupric ion (one determination was 0.100 ppm while the others were generally  $< 0.040$  ppm), were released during the simulated run-off/desorption cycles, the resulting dissolved copper concentrations would be low if copper is moved off-site via mass movement of soil. However, as mentioned above under "1", the extreme variation in the recovery of  $\text{Cu}^{++}$  in the spiked samples probably does not allow these small amounts of  $\text{Cu}^{++}$  in solution to be quantified.
5. EFGWB concludes that the study as presented provides supplemental data towards the dissipation of copper in the environment. However, resolution of the problems related to recoveries of copper as noted above, is unlikely to alter the conclusions related to the fate of copper transported to off-site aquatic environments via mass movement of soil. Therefore, EFGWB concludes that sufficient data has been submitted so that the environmental fate of copper sulfate and group II copper compounds can be sufficiently elucidated from the limited information in this submission plus what is known in the scientific community in regards to copper in the environment and that the registrant does not need to submit any further information.

#### MATERIALS AND METHODS:

The test site was located near Haines City, Florida. The site was located in a mature citrus grove that has been under citrus cultivation for 75 years before the study was commenced. From June, 1974 to April 1988 at least one application of a copper compound was applied to the citrus grove at a rate of 20 pounds material/acre. The most recent use of copper before the study was started was on April 11, 1988. While no historical records were maintained, it was assumed that there was copper usage on this grove prior to 1974, since it has been in existence for the past 75 years.

A 250' x 300' area (1.72 acres) of a mature citrus grove was sprayed with an air-blast sprayer containing tri-basic copper sulfate (53% metallic copper equivalent) at the recommended label rate (12.0 lb copper sulfate/A) in each of two applications (May 23, 1988 and June 7, 1988). The soil sampled from the 0-1' depth at the treated area had the following characteristics (Table 5): pH = 6.0, organic matter = 1.2, CEC = 1.9 meq/100g soil, total copper = 123 ppm, sand = 94% and clay = 6%.

A non-treated area was located about one mile from the treated area on non-citrus land in order to sample from an area that had not received previous copper applications. The non-treated area was 50' x 50' (0.057 acres). The non-treated area was divided into 100, 5' x 5' sub-plots to facilitate sampling. All sub-

plots were clearly identified (method of identification of each sub-plot was not specified). The soil sampled from the 0-1' depth at the non-treated area had the following characteristics (Table 5): pH = 6.1, organic matter = 1.6, CEC = 2.2 meq/100g soil, total copper = 2 ppm, sand = 93%, silt = 2% and clay = 5%.

The sprayed area was subdivided into 100, 25' x 30' sub-plots that contained one tree within each sub-plot. All sub-plots, treated and non-treated, were randomly sampled according to a predetermined randomization plan. Where applicable, the soil was sampled to depth of 30 cm before and after the first application using a soil probe. For the remainder of the soil sampling, a 0-5 cm soil depth was excavated and then sampled with a soil probe from 5-35 cm. The final sampling at 147 days after the second application was taken to a soil depth of 105 cm. Soil sampling commenced prior to treatment and on the following dates in 1988: May 24, June 7, June 13, June 21, July 5, August 2, September 25, and November 1. These dates represent -15, -14, -0, 0, 1, 6, 14, 28, 56, 110 and 147 days after the second treatment.

Soil samples were sectioned into 0-5 cm, 5-15 cm and 15-25 cm intervals for the first two sampling intervals and 5-15 cm, 15-25 cm and 25-35 cm intervals for the rest of the study. The last sample interval (147 days after the last treatment) was sectioned into 10 cm intervals from the 5 to 105 cm soil depth. These soil samples were analyzed for total copper and hydroxylamine hydrochloride extractable copper, manganese and iron by use of atomic absorption spectroscopy.

Soil samples were also collected at the 0-1 cm depth and composited over three plots. Aqueous suspensions (called total suspended solids-aqueous suspensions) of these composited samples were analyzed for dissolved copper, total copper and cupric ion by use of atomic absorption spectroscopy or an electrode that was specific for  $\text{Cu}^{++}$  ion.

#### REPORTED RESULTS:

##### Recovery Data

Table 7 shows the recovery data obtained for the soil analyzed for total copper and extractable copper, manganese and iron, and for the total suspended solids-aqueous suspension analyses.

The study author reported recoveries of total copper spiked at 420 to 500 ug/g ranged from 73 to 108% with an average value of 88.1% for 23 spiked samples. Recoveries for extractable copper spiked at 240 and 250 ug/g ranged from 72 to 109% with an average value of 96.2% for 20 spiked samples. Recoveries for extractable manganese and iron were within acceptable limits and averaged 93.4 and 90.9%, respectively.

The recovery data for the total suspended solids-aqueous suspension analyses reported by the study author showed that recoveries of cupric ion analyses after copper spiking ranged from 99 to 140% with an average of 112.2%. The copper spike recoveries for dissolved copper analyses varied from 48 to 133% with an average of 89.2%. Total copper spike recoveries in the aqueous suspensions ranged from 26 to 94% with an average of 63.7%.

The author concluded from this recovery data that there were not any compounds in the aqueous extract suspensions that interfered with copper analysis.

#### Data For Non-treated Samples

Tables 1-4 and 12 present a summary of the residue data for total copper in the soil samples collected from the non-treated plots. The data show that the level of indigenous copper was low. The average total copper level in the 0-5 cm soil depth ranged from 7.1 to 19.0 ug/g during the length of the study. The total copper in the soil profile decreased as soil depth increased at all sample intervals.

#### Data For Treated Samples

Tables 1-4 present the residue data for total and extractable copper for the treated plots. Total copper ranged from 105 to 230 ug/g and averaged 158.3 ug/g. Extractable copper ranged from 112 to 227 ug/g and averaged 160.0 ug/g. The amount of copper decreased with depth down to the 25-35 cm depth, at which point the copper values in the treated soil were not significantly different from the copper concentrations in the non-treated soil at or below that depth (Table 12).

The study author noted that during collection of the samples from the 0-35 cm depth, the tubes did not fill to the full depth that was probed. Therefore when the tubes were sectioned, the resulting samples at the 25-35 cm depth and, at times, the 15-25 cm depth, represented only the upper part of those sample depths. When this happened, the actual concentration in those depths would be over-estimated since the copper concentration in the soil decreased with depth.

The study author noted that the residues of total copper were not always greater than the amount of extractable copper. It was speculated that this occurred because the samples were not homogenous and/or were not corrected for moisture content in the total copper analysis while extractable copper was preformed with dry soil.



### Half-life Estimation

The study author noted reported that since copper is elemental compound it will not dissipate in situ. Therefore, determination of half-life decomposition for any form of copper measured in the present study is not appropriate.

### Leaching Data for Copper

The samples collected at 147 days after the last copper application were taken in 10 cm increments down to the 105 cm depth for total copper analysis (Table 17). The results show that copper levels were below the 2.0 ug/g detection level below the 55 cm depth and averaged only 2.8 ug/g at the 45-55 cm depth. The study author noted that these results show that in spite of the high levels of copper from past applications to the soil surface, the movement of copper has been confined to top 45 cm of the soil profile.

The author reported that the leaching data indicate that copper will not move downward in the soil to a great extent despite the highly mobile conditions of this low organic matter sand soil. Thus, ground water contamination by leaching should not be a problem with copper under the use patterns of the present study.

The cupric ion (extracted with 0.01 M  $\text{Ca}(\text{NO}_3)_2$  concentrations (Tables 22-24) determined on 25, 60 and 100 mg samples of soil excavated from the surface one cm of soil at the test site were usually below the detection limits reported (i.e.  $<0.040$  ppm  $\text{Cu}^{++}$ ).

### Environmental Fate of Copper

The study author concluded that total copper levels (154 ppm background levels before the start of the study, due in part to the historical application of copper compounds to the orchard) at this site did not significantly change during the length of the study, nor did the application of 12.7 lb/A of metallic copper significantly increase the total copper level in the soil. Deep sampling of the soil at 147 days after the last treatment showed little copper movement below the 45 cm depth even though conditions were favorable for copper leaching. Analyses for dissolved copper and cupric ion resulted in only low amounts being released during the desorption cycles in spite of a worst case condition found on the test site. Therefore, if copper is moved off-site via mass movement of soil, the dissolved copper concentration would be low.

## DISCUSSION:

1. EFGWB concludes that this study is scientifically valid and provides supplemental information about the fate of copper sulfate salts when applied to soils.
2. The data presented in this study is supported by data from other researchers who have found basically the same results. In these other studies (see selected list of copper literature references on pages 1.6 and 1.7), the general consensus of the scientific community is that:
  - a. Since copper does not metabolize under field conditions and form degradation products, the amount of copper at a particular site depends on the indigenous copper level present in the soil (it can range from 10 to 100 ppm), the number of years of copper application, if any, and the amount of soil loss.
  - b. After copper is applied to soil, there is generally very little detectable soluble copper in the water phase of soil extracts; although there may be small quantities of copper dissolved in the soil solution or interstitial waters of sediments.
  - c. The portion of copper in soil and sediment is complexed with organic compounds, because the formation constants of copper-organic complexes are very high. Other forms of copper are adsorbed to solid phases in soils by chemisorption or cation exchange processes. Copper is also found adsorbed or occluded in carbonate or oxide minerals, incorporated into the structure of minerals.

In cases where the copper activity in the soil solution exceeds the solubility products ( $K_{sp}$ ) of copper minerals (e. g. cupric ferrite, tenorite, malachite and azurite, etc.), precipitation of copper will occur as those discrete mineral phases.
  - d. The conventional "adsorption constant"  $K_d$  (an indication of the degree of adsorption by soil), as defined in pesticide studies, has been estimated to be approximately 190 for copper<sup>1</sup>. A  $K_d$  value of this magnitude indicates that copper is quite strongly

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<sup>1</sup>Harter, R. D. 1983. Effect of pH on adsorption of lead, copper, zinc and nickel. Soil Sci. Soc. Am. J. 47:47-51.

<sup>1</sup>McLaren, R. G. and D. V. Crawford. 1973. Studies on soil copper. II. The specific adsorption of copper by soils. J. Soil Sci. 24:443-452.

adsorbed to soil and would be expected to be, and in fact is, found in the sediment phase of runoff. It has been suggested that copper should behave like paraquat ( $K_d$  ranges between 200<sup>2</sup> and 960<sup>3</sup>), DDT ( $K_d$  of 14000<sup>4</sup>) and other pesticides that are tightly bound to soil particles. In the case of DDT and paraquat, the amount in soil solution is extremely small, which may contribute to the resistance to degradation of both compounds when encountered in soil. As a contrast to these elevated  $K_d$ s, atrazine, a chemical which has been detected in ground water, has reported  $K_d$ s ranging from 1.46 to 2.44<sup>5</sup>.

3. The data showed that, while copper has leached in the soil as a result of long-time copper applications, little copper movement was detected below the 45 cm soil depth. As can be seen in Tables 12 and 17, the average copper concentration in the surface 5 to 45 cm in the citrus orchard was at least 10 to 30 times greater than the copper concentration in the non-treated soil. In general, the copper concentration was greatest in the surface horizons and decreased with depth.

The high concentration of copper in the soil is not unexpected since the citrus orchard where this study was performed has been in existence for at least 75 years and has had historical applications of copper compounds. Pesticide use records kept from 1974 to 1988 show at least one yearly application of copper containing compounds to the citrus orchard.

4. Under normal conditions that would exist when copper-containing sediments reach an aquatic environment, little if any free copper ions would be expected to be in solution.
5. Although the authors had some problems with recovery data for  $Cu^{++}$ , EFGWB concludes that resolution of the problems would not necessarily change any of the results presented, given the large amount of published studies that, in general, support this study.

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<sup>2</sup>Burns, R. G. and L. J. Audus. 1970. Weed Res. 10:49.

<sup>3</sup>Damanikis, M., D. S. Drennan, J. D. Fryer and K. Holly. 1970. Weed Sci. 10:264.

<sup>4</sup>Shin, Y., J. J. Chodan, and A. R. Walcott. 1970. J. Agr. Food Chem. 18:1129.

<sup>5</sup>Walker, A. and D. V. Crawford. 1968. Isotopes and Radiation in soil organic matter studies. Intern. Atomic Energy Agency, Vienna, p. 91.

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DATA EVALUATION RECORD

STUDY IDENTIFICATION:

Hosmer, A., J. Beaver and T. Brantly. February 8, 1989. An aquatic sediment dissipation study of copper sulfate in the Hillsborough reservoir, Florida. Prepared by Wildlife International Ltd. Easton, MD. 21601 Sponsored by Copper Sulfate Task Force. Frederick, MD. 21701. (MRID # 411890-01).

REVIEWED BY:

Richard J. Mahler, Hydrologist  
Review Section I, EFGWB

Signature: Richard J. Mahler

Date: AUG 21 1990

APPROVED BY:

Paul J. Mastradone, Chief  
Review Section I, EFGWB

Signature: Paul J. Mastradone

Date: AUG 21 1990

TYPE OF STUDY: Field Dissipation for Aquatic Uses and Aquatic Impact--164-2

CONCLUSIONS:

1. EFGWB concludes that this study is scientifically valid; however the study does not satisfy the data requirements for Field Dissipation For Aquatic Uses and Aquatic Impact because:
  - a. There was too much variation in the recovery data for the various forms of copper determined and in total copper values determined in the sediments with depth.
  - b. There was no adequate explanation of the variation in total copper concentrations in the sediment with depth.
  - c. Only one site was chosen for the aquatic dissipation study. According to Subdivision N Guidelines § 164-2, Field Dissipation for Aquatic Uses, at least two sites are to be used or a justification for using only one site should be given.
2. EFGWB concludes that the study as presented provides supplemental data towards the dissipation of copper in the environment. However, resolution of the problems related to recoveries and variation of copper as noted above, is unlikely to alter the conclusions related to the fate of copper applied to aquatic systems. Therefore, EFGWB concludes that the environmental fate of copper sulfate and

group II copper compounds can be sufficiently elucidated from the limited information in this submission plus what is known in the scientific community in regards to copper in the environment. The registrant does not need to submit any further information.

## MATERIALS AND METHODS:

### Introduction

The study was conducted at the Hillsborough reservoir located in Tampa, FL during the Spring and Summer of 1988 (Figure 1). The total impoundment is approximately 175 acres (700 million gallons).

The Hillsborough Reservoir management routinely controls algae blooms with copper sulfate to minimize the foul taste and odor associated with *Anabaena* sp. and *Synura* sp. During seasons in which algae blooms occur, water samples are collected to monitor algal abundance and copper sulfate is applied to those zones with the highest algal densities.

Records of copper sulfate application have been kept for the past 30 years. As an example, from 1985 to 1987, an annual average of nearly 40,000 pounds of copper sulfate was applied to the reservoir (Table 1).

Sediments in the reservoir are mainly sand with a thin layer (1-2 inches) of overlying organic matter. Clay occurs at a depth of about three to five feet. Mean alkalinity values during the period of copper sulfate use ranged from 44 to 94 mg/L and the mean pH ranged from 6.80 to 7.60 (see Table 5, pages 48-52 for a complete characterization of the sediments with depth).

### Experimental Design

The reservoir was divided into three replicates (Figures 2 and 3) along its length that corresponded with Zones 1, 2 and 3 of the Tampa Water Department's eight application zones.

Within each of the three plots, an approximately 240 foot transect oriented parallel to the shoreline was located 50 feet from the shore line. The three transects were divided into thirteen subplots spaced about 20 feet apart and marked with numbered buoys. Each subplot was sampled only once with the most downstream subplot sampled first, and then the next upstream subplot. This sequence was used to prevent contamination of future subplots by sediment disturbance during sampling operation.

## Application Procedures

Approximately 10.8 lb/A of copper sulfate was applied on April 7, 1988, about one month prior to the start of the normal algae control season, utilizing the procedures normally used at the reservoir (i.e., an airboat equipped with a 100-gallon tank and gasoline powered pump). Dual six foot spreader poles were mounted at the front of the boat with spray nozzles attached through which the copper sulfate solution was applied.

Zones 1 through 6 were selected for treatment to allow the treated water to flow through the sampling plots. Due to the variable size of the river zones, copper ion concentrations were calculated, based on water volumes, to range from 0.9 to 1.25 ppm in the upper two feet of the water column. This application rate was approximately twice the Tampa Water Department's target concentration of 0.5 ppm metallic copper. Throughout the rest of the algae control season, a total of 91.6 lb/A (8.6 tons) copper sulfate was applied to the reservoir.

## Sample Collection

### Water Column Samples

Water column samples were collected approximately two feet from the surface, two feet from the bottom and about midpoint between the other two samples.

Three 1-liter samples were taken at each depth and composited in a bucket. Water temperature and dissolved oxygen were determined immediately after compositing. The composited sample was then divided into 6 subsamples for determination of various chemical and physical properties of the water.

### Interstitial (Pore) Water Samples

Pore water samples in the sediments was collected with in situ samplers (Figure 4) that consisted of an acrylic body with uniformly spaced cylindrical cells (4 cm apart) which utilized a semi-permeable membrane to pass ions into a cell containing deionized water. After equilibration with the outside environment and retrieval of the samplers, the concentration of ions in the cell water was measured.

Five samplers were placed in each subplot by a scuba diver who hammered or pushed the sampler in to the sediment to a depth of 32 cm. After 14 days equilibration, the samplers were brought to the surface and immediately assayed or preserved for various physical and chemical properties.

Pore water samples were collected prior to copper sulfate application and 15 and 31 days after application.

### Sediment Cores

After the pore samplers were removed, six sediment cores were taken with six, two-inch diameter and 40 cm long cellulose acetate butyrate tube that was driven into the sediment to a depth of 32 cm. After capping the tubes, they were brought to the surface and the sediment was removed from the tube in 4 cm increments and composited and thoroughly mixed with sediment from corresponding depths of the other five cores. One third of the composite sample was sent to the analytical laboratory for residue analysis, while the rest was sent to another laboratory for sediment characterization.

### Surficial Sediment Samples

Before removal of the pore water samplers and collection of sediment cores, a duplicate surface sediment samples were collected from an adjacent sequential subplot with a Ponar dredge. Samples were placed into polyethylene bottles and sent to the laboratories for residue analysis and/or soil characterization.

Total copper, dissolved copper, and  $\text{Cu}^{++}$  residue analysis was determined on the total suspended solids aqueous suspension in order to simulate leaching of copper from the sediment.

### Residue Sample Collection Schedule

Water column samples were collected from one subplot in each of the three replicates before the copper sulfate was applied, immediately after application (Day +0), and additionally on 1, 2, 4, 7, 15, 31, 62 and 112 days after application. Pore water, sediment cores, and surficial sediments were collected from each replicate 3 days before and 15 and 31 days after application on April 7, 1988.

### Handling of Samples

Samples that were not assayed immediately in the field were stored at 4°C within two hours after collection prior to packaging with "blue ice" to maintain temperature at 4°C and subsequent shipment to the analytical laboratories .

### Monitoring

Water flow into and out of the reservoir was measured daily by the Tampa Water Department by measuring river elevation , dam discharge and water flow into the reservoir. Meteorological information was obtained from the NOAA National Weather Service in Ruskin, FL, located 30 miles south of the reservoir.



## Statistical Analyses

Analysis of variance (ANOVA) was performed using Duncan's multiple range test and was deemed to be statistically significant if  $p < 0.05$ . If ANOVA indicated no significant difference within a sample unit for a given parameter, then the data within that sample unit was pooled for further statistical comparison by ANOVA.

## REPORTED RESULTS:

### Recovery Data

There was no discussion of copper recovery data by the study author in the text of the report. Discussion was limited to one or two paragraphs in the analytical report that was included in the study report with at least 15 tables that showed the percent copper recovery from spiking the various material sampled (i.e., sediment, reservoir water, etc.).

Table A, prepared by the reviewer, lists the summary of copper recoveries as reported in the study.

The study report discussed the following in regards to the variation in recovery data:

1. Total copper: For replicate 5 (Table on page 89) in the low level spike, we suspect the sample was not fortified and that the 20 % recovery is due to the varying levels in the background deviation of the unfortified sample.
2. Hydroxylamine hydrochloride extractable copper: For the low level spike, we suspect the high percent recovery (Table on page 91) is due to the fact that the fortification level is so close to the initial background of the unfortified sample.
3. Calcium nitrate extractable copper: It is suspected that the low percent recovery for cupric ion and dissolved copper in the aqueous suspensions (Tables on pages 100-105) is due to incomplete matrix disruption and ion exchange. The extraction method uses a weak ion exchange reagent to extract the copper. It does not use a reagent that would serve as a matrix disrupter which would be necessary to extract all the copper. A higher reagent concentration coupled with more severe conditions such as low pH and/or heat might have effected better recoveries, but these conditions are not amenable to cupric ion analysis by the specific ion electrode.

Quality control samples and spiked reagent blank samples (Tables on page 86 and 87, respectively) for the analyses of cupric ion and dissolved copper verify the validity of the method. Results for total and extractable copper, which use methods that disrupt the sample matrix, gave acceptable results. It was stated that this also seems to indicate that for dissolved copper and cupric ion, the low percent recovery is due to inefficient matrix disruption.

It was also stated that the variable recoveries for total, dissolved and cupric copper was due in part to the extremely small sample weights (100, 60 and 25 mg) used in the analyses.

Similarly, for total copper, the method calls for 10 ml of the calcium nitrate-suspended sample to be withdrawn from the tube. Because the sample is well flocculated, some settling of the suspension occurred before the aliquot could be withdrawn, which could result in an inconsistent sample size and subsequent variability in concentration.

#### Interstitial Water

Pore-water total copper concentrations were variable within and between plots on a given sampling day (Table 8). Total copper concentrations ranged from <0.012 to 0.110 ppm. Although not statistically significant, mean total copper concentrations were highest in pore water collected from the middle of the sediment profile at the 12-16 cm depth. There were no significant differences between plots.

Cupric ion ( $\text{Cu}^{++}$ ) concentration in pore water was below the detection limits (<0.006 ppm) in plots II and III sampled 3 days before copper sulfate application, and it was also <0.006 ppm in all three plots on sampling days 15 and 31 (Table 9). However, in plot I, although the  $\text{Cu}^{++}$  concentration in the top 16 cm level was <0.006 ppm, the  $\text{Cu}^{++}$  ion in the 16-20 cm and lower depths ranged from 0.086 to 1.177 ppm.

#### Sediments

Total copper in the sediments display a trend toward decreasing concentration with increasing depth (Table 10). The concentration of copper in the top 12 cm of sediments was frequently >100 ppm.

#### Surficial Sediments

The method used to determine total and dissolved copper, including  $\text{Cu}^{++}$ , measured in the surficial sediments was intended

to simulate desorption of copper from the sediment. Total copper (Tables 30-32) in the suspensions ranged from 0.082 to 0.33 mg/l. The majority of dissolved copper (Tables 33-35) in the suspensions were <0.012 mg/l, with some concentrations varying from 0.012 to 0.28 mg/l. The concentration of Cu<sup>++</sup> in the suspensions were all <0.040 mg/l (Tables 36-38).

### Water Column

#### Total Copper

Three days prior to copper sulfate application, total copper concentrations in the water column were <0.012 ppm in the surface, middle and bottom regions sampled (Table 11). The concentration of total copper in water samples collected on the day of application contained between <0.012 to 0.170 ppm. One day after application total copper values ranged between 0.100 to 0.150 ppm, and by seven days after application, the total copper concentrations in the water samples were between <0.012 to 0.040 ppm. One month after application (T1+31) total copper concentration was <0.012 ppm in all regions of the water column sampled.

The Tampa Water Department commenced normal copper sulfate spray applications. From May 31, 1988 (T1+54) to June 8, 1988 (T1+112), between 100-400 lb/zone of copper sulfate was applied in order to meet the Department's target concentration of 0.5 ppm. During the remainder of June and July approximately 100 to 600 lb/zone of copper sulfate was applied. As a result of these applications, total copper concentration at 62 days after the initial application ranged between 0.040 to 0.320 ppm.

#### Dissolved Copper

The dissolved copper concentrations (Table 12) closely paralleled those reported for total copper. Dissolved copper was not detected before copper sulfate application. The concentration varied from 0.110 to 0.170 ppm in water samples on the day of application. Subsequent to this day, the concentration of dissolved copper varied from <0.012 to 0.100 ppm on the second day after application to near or below the detection limit on the 31st day after application. After the Tampa Water Department commenced copper sulfate applications in May, subsequent sampling again revealed elevated concentrations of copper in the water varying from <0.012 to 0.170 ppm.

#### Cupric Ion

The Cu<sup>++</sup> ion concentration in the reservoir water remained below the detection limit (<0.006 ppm) throughout all sampling periods.

DISCUSSION:

1. EFGWB concludes that this study is scientifically valid and provides supplemental information about the fate of copper sulfate salts when applied to aquatic systems.
2. Before this study can satisfy the data requirements for a field dissipation for aquatic uses and aquatic impact study the following points should be expanded upon by the registrant:
  - a. EFGWB notes that the study authors did not discuss why, in plot I (Table 10) sampled 3 days before application, the total copper concentration throughout the profile sampled was <2.0 ppm. Nor did they attempt to explain why the total copper concentration with increasing depth in plots I and III (Tables 10) sampled 31 days after application varied from 18 to 140 ppm, decreased to <2.0 ppm and then increased to as high as 140 ppm before decreasing to <2.0 to 16 ppm.
  - b. EFGWB notes that the study author did not attempt to calculate a half-life for copper applied to the reservoir. After considerable time and effort, this reviewer determined that the half-life of copper in the reservoir water averaged 10 days. The data used to calculate the half-life was taken from Tables 11 and 12. This information is needed because the purpose of aquatic field dissipation studies for pesticides for aquatic uses is to determine the extent of dissipation and mobility of pesticide residues under actual use conditions. These studies will generate data for evaluating potential hazards of a pesticide to aquatic organisms under actual use conditions and will provide information with respect to mechanisms of dissipation in various aquatic environments.

EFGWB strongly suggests that the registrant follows the Subdivision N Guideline § 164-2 for future field dissipation studies for aquatic uses and aquatic impact.
  - c. EFGWB notes that there were numerous other physical and chemical determinations made in this study and except for sulfur, there was little discussion of these other determinants.
3. In the original copper sulfate Registration Standard issued March 1986, the following Environmental Fate Data Requirements were not satisfied and were needed:

Aerobic Soil Metabolism--162-1

Anaerobic Soil Metabolism--162-2  
Anaerobic Aquatic Metabolism--162-3  
Aerobic Aquatic Metabolism--162-4  
Leaching and Adsorption/Desorption--163-1  
Field dissipation for Terrestrial Uses--164-1  
Field Dissipation for Aquatic Uses--164-2

In 1987, by way of a memorandum from Richard Mountfort, PM 23 to Arthur Gohlke, Chairman of the Copper Sulfate Task Force, the Agency advised the Copper Sulfate Task Force members of changes in the data requirements in the Copper Sulfate Registration Standard. The changes were an attempt to establish consistency with the Copper (II) Compounds Registration Standard that was to be issued in the near future (and in fact was issued April 1987), and to reflect additional information evaluated by the Agency since the Copper Sulfate Registration Standard was issued in March 1986.

As a result of the Agency decision, the following Environmental Fate Data were the only studies required for both the Copper Sulfate and Copper (II) Compounds Registration Standards:

Leaching and Adsorption/Desorption--163-1  
Field dissipation for Terrestrial Uses--164-1  
Field Dissipation for Aquatic Uses--164-2

The above three data requirements are needed in order to clarify:

1. If copper ions would leave treated fields via runoff or other mechanisms and enter aquatic systems.
2. Once in the aquatic system, will the copper ion remain in solution or will it become unavailable, by adsorption to sediment or precipitation, for impact on aquatic organisms.

Included in the memorandum was a notation suggesting that additional details regarding test materials and procedures for the Environmental Fate testing were to be discussed in a followup meeting with the Copper Sulfate Data Task Force and EPA representatives. The meeting was held on October 29, 1987 and the following points were discussed in the meeting based on protocols submitted for dissipation studies:

- a. Dissipation field work will involve 1 site for soil sampling and 1 site for aquatic sediment sampling. A justification for this deviation from multiple site sampling will be included. EAB (now EFGWB) will

provide suggestions for conduct of the laboratory portions of the studies.

- b. The literature review for adsorption/desorption and aquatic dissipation will supplement information gained from studies in #2 above, such that Ecological Effects Branch (EEB) will be provided a detailed fate analysis to use in their risk assessment.

It appears that the registrants have misunderstood the essence of the meeting, and the conclusions reached at the meeting regarding the need to use certain models programs such as MEXAMS, SWRRB, CREAMS, etc. to determine the environmental fate of copper in the environment (see attached memorandum from Emil Regelman, EFGWB to Richard Mountfort PM 23 dated 1/28/88 in regards to a review of protocols submitted in response to copper sulfate/copper (II) Registration Standards). This information is needed so that EEB will have sufficient information for their use for risk analysis.

4. The data presented in this study is supported by data from other researchers who have found basically the same results. In these other studies (see selected list of copper literature references on page 2.11), the general consensus of the scientific community is that:
  - a. Since copper does not metabolize under field conditions and form degradation products, the amount of copper at a particular site depends on the indigenous copper level present in the soil/sediment (it can range from 10 to 100 ppm), the number of years of copper application, if any, and the amount of soil/sediment loss.
  - b. After copper is applied to water and equilibrium with sediments is reached (usually in a few days), there is generally very little detectable soluble copper in the water phase; although there may be small quantities of copper dissolved in interstitial waters of sediments.
  - c. The portion of copper in soil/sediment is complexed with organic compounds, because the formation constants of copper-organic complexes are very high. Other forms of copper are adsorbed to solid phases in soils/sediments by chemisorption or cation exchange processes. Copper is also found adsorbed or occluded in carbonate or oxide minerals, incorporated into the structure of minerals.

In cases where the copper activity in the soil solution exceeds the solubility products ( $K_{sp}$ ) of copper

minerals (e. g. cupric ferrite, tenorite, malachite and azurite, etc.), precipitation of copper will occur as those discrete mineral phases.

- d. The conventional "adsorption constant",  $K_d$  (an indication of the degree of adsorption by soil/sediment), as defined in pesticide studies, has been estimated to be approximately 190 for copper<sup>1</sup>. A  $K_d$  value of this magnitude indicates that copper is quite strongly adsorbed to soil/sediment and would be expected to be, and in fact is, found in the sediment phase of runoff. It has been suggested that copper should behave like paraquat ( $K_d$  ranges between 200<sup>2</sup> and 960<sup>3</sup>), DDT ( $K_d$  of 14000<sup>4</sup>) and other pesticides that are tightly bound to soil/sediment particles. In the case of DDT and paraquat, the amount in solution is extremely small, which may contribute to the resistance to degradation of both compounds when encountered in soil/sediment. As a contrast to these elevated  $K_d$ s, atrazine, a chemical which has been detected in ground water, has reported  $K_d$ s ranging from 1.46 to 2.44<sup>5</sup>.
5. Under normal conditions that would exit when copper-containing sediments reach an aquatic environment, little if any free copper ions would be expected to be in solution.
6. Although the authors had some problems with recovery data for the various forms of copper determined, EFGWB concludes that resolution of the problems would not necessarily change any of the results presented, given the large amount of published studies that, in general, support this study.

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<sup>1</sup>Harter, R. D. 1983. Effect of pH on adsorption of lead, copper, zinc and nickel. Soil Sci. Soc. Am. J. 47:47-51.

McLaren, R. G. and D. V. Crawford. 1973. Studies on soil copper. II. The specific adsorption of copper by soils. J. Soil Sci. 24:443-452.

<sup>2</sup>Burns, R. G. and L. J. Audus. 1970. Weed Res. 10:49.

<sup>3</sup>Damanikis, M., D. S. Drennan, J. D. Fryer and K. Holly. 1970. Weed Sci. 10:264.

<sup>4</sup>Shin, Y. J. J. Chodan, and A. R. Walcott. 1970. J. Agr. Food Chem. 18:1129.

<sup>5</sup>Walker, A. and D. V. Crawford. 1968. Isotopes and Radiation in soil organic matter studies. Intern. Atomic Energy Agency, Vienna, p. 91.

Copper Sulfate DER

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TABLE A. SUMMARY OF COPPER RECOVERIES REPORTED BY STUDY AUTHOR.

MATERIAL SPIKED	-----SPIKING LEVEL-----		
	Low	Medium	High
	-----Percent Recovery (Range)-----		
Reagent Blank Total	115 (112-124)	115 (104-129)	111 (100-120)
Reservoir Water1 Total	116 (None)	116 (112-118)	108 (None)
Sediment2 Total	99 (20-120)	100 (84-120)	93 (83-109)
Extractable	111 (84-176)	95 (78-108)	100 (84-119)
Ca(NO <sub>3</sub> ) <sub>2</sub> Extractable Total	212 (90-287)	124 (67-225)	47 (7-88)
Cu <sup>++</sup> ion	2 (0-33)	32 (0-82)	53 (17-92)
Dissolved	74 (0-449)	45 (9-108)	47 (17-77)

1. Pretreatment sample.
2. Average of three depths.

2.23

Copper Substrate DER

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