

COPPER SULFATES

Final Report

**Task 1: Review and Evaluation of
Individual Studies**

Contract No. 68-01-6679

MARCH 28, 1985

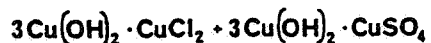
Submitted to:
Environmental Protection Agency
Arlington, VA 22202

Submitted by:
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Enviro Control Division
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COPPER SULFATES

BLUESTONE, BLUE VITROL,
BLUE COPPERAS

COCS, COPRO 53 and 57, COXSUL, CS-56



Cupric sulfate (anhydrous, monohydrate,
pentahydrate)

Copper oxychloride sulfate

Table of Contents

Study

- 1 ✓ Bartley, T.R., and H.J. Cohan. 1967. Progress report on evaluation of copper for aquatic weed control and herbicide residues on irrigation systems: Report No. WC-32. U.S. Dept of the Interior, Bureau of Reclamation, Water Conservation Branch, Div. of Research: Unpublished study; CDL:005528-A. (00099156)
- 2 ✓ Deubert, K. and Demoranville, I. 1970. Copper Sulfate in flooded cranberry bogs. Pestic. Monit. J. 4(1):11-13. Available from: Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402; Published study; CDL: 228173-T. (00099539)
- 3 ✓ Lin, C., A. Nemo, and D. Vedder. 1972. Copper residue in rainbow trout. Hyacinth Control J. 10(May):43-44. Also In unpublished submission received Sep. 14, 1977 under 8959-11; submitted by Applied Biochemists, Inc., Mequon, WI; CDL:231871-C. (00099514)
- 4 ✓ Nelson, J.L., V.E. Bruns, C.C. Coutant, et al.. 1969. Behavior and reactions of copper sulfates in an irrigation canal. Pesticides Monitoring Journal 3(3):186-189. Available from: Superintendent of Documents, U.S. Government Printing Office, published study; CDL:228175-I. (00062074)
- 5 ✓ Riemer, D.N., and S.J. Toth. 1970. Adsorption of copper by clay minerals, humic acid, and bottom muds. J. Am. Water Works Assoc. 62(3):195-197. Also In unpublished submission received Nov. 17, 1970 under 1F1093; submitted by Phelps Dodge Refining Co., New York, NY; CDL:090853-H. (00099262)

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CASE GS0121 COPPER SULFATES STUDY 1

PM PM# 03/28/83

CHEM 024401 Copper Sulfates

BRANCH EFB DISC 30 TOPIC 050515

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 00099262 CONTENT CAT 01

Riemer, D.N., and S.J. Toth. 1970. Adsorption of copper by clay minerals, humic acid, and bottom muds. J. Am. Water Works Assoc. 62(3):195-197. Also in unpublished submission received Nov. 17, 1970 under 1F1093; submitted by Phelps Dodge Refining Co., New York, NY; CDL:090853-H.

SUBST. CLASS = S.

DIRECT RVW TIME = 7 1/2 (MH) START-DATE

END DATE

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CONCLUSIONS:

Mobility - Leaching and Adsorption/Desorption

1. This study is scientifically valid.
2. Copper sulfate is strongly adsorbed onto three lake and pond sediments. Following 5 weekly applications of copper sulfate, totaling 4 mg copper, 1.5-5% of the applied copper was detected in the water. Unextractable copper ranged from 12.5 to 27% of the applied.
3. This study does not fulfill EPA Data Requirements for Registering Pesticides (1983) because the test substance was not characterized, the test substance was not equilibrated with the sediment in a 0.01 M or N Ca ion solution, neither soil/water relationship values (K_d) nor Freundlich K values were reported, and no pretreatment or control samples were submitted.

MATERIALS AND METHODS:

Air-dried sediments (500 g) from Schaedel and Adelpia ponds, and moist sediment (750 g, 456% moisture content) from Carnegie Lake, were added to 1-gallon containers and treated with 5 weekly additions of copper sulfate (copper sulfate pentahydrate, test substance uncharacterized, source unspecified). A total of 4 mg of copper was applied in 2 l of distilled water. Sediment characteristics are presented in Table 1.

After 5 weeks the containers were drained, and the sediments were air-dried. Copper content of the drained water was determined by atomic absorption spectroscopy (AAS). To determine the water extractable copper content of the sediments, 50 g of the air-dried sediments were extracted with distilled water, filtered (size not specified), and the supernatant analyzed for copper by AAS. The acid-soluble fraction of the sediment was determined by extracting 25 g of air-dried sediment with 1 N HCl, filtering the mixture, and analyzing the copper content by AAS. Recovery values and detection limits were not reported.

REPORTED RESULTS:

Copper was strongly bound to the three sediments (Table 2), with a maximum of only 5% of the applied copper being found in solution.

DISCUSSION:

1. Complete sediment characteristics, including the percent sand, silt, and clay, were not submitted.
2. The test substance was not characterized.
3. Recovery values and detection limits were not reported.
4. Desorption tests were not performed.
5. Neither Freundlich K and n values nor soil/water relationship values (K_d) were reported.
6. The test substance was not equilibrated with the sediment in a 0.01 N or M Ca ion solution.
7. Neither control nor pretreatment samples were submitted.

Table 1. Sediment characteristics.

Location	pH	Organic matter content (%)	CEC (meq/100 g)
Carnegie Lake	4.4	13.2	51.5
Schaedel Pond	6.9	2.2	6.8
Adelphia Pond	5.9	1.0	3.5

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Table 2. Distribution of copper in sediments and water following 5 weekly applications of copper sulfate, at 1, 1, 2, 2, and 2 ppm to sediment.

Location	Total copper added (mg)	Water Total copper in solution (mg)	Sediment		
			Extractable copper (mg/100 g)		
			Water	Acid	
				Extraction 1	Extraction 2
Carnegie Lake	4.00	0.06	0.00	2.33	0.52
Schaedel Pond	4.00	0.06	0.00	2.50	0.40
Adelphia Pond	4.00	0.20	0.00	2.90	0.40

CASE GS0121

COPPER SULFATES STUDY 2

PM PM # 03/28/83

CHEM 024401

Copper Sulfates

BRANCH EFB

DISC 30 TOPIC 051025

GUIDELINE 40 CFR 163.62-10C

FORMULATION 90 - FORMULATION NOT IDENTIFIED

FICHE/MASTER ID 00099539

CONTENT CAT 01

Deubert, K., and I. Demoranville. 1970. Copper Sulfate in flooded cranberry bogs. Pestic. Monit. J. 4(1):11-13. Available from: Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402; Published study; CDL: 228173-T.

SUBST. CLASS = S.

DIRECT RVW TIME = 7 1/2 (MH) START-DATE

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CONCLUSIONS:

Field Dissipation - Aquatic and Aquatic Impact Uses

1. This study is scientifically valid.
2. Copper sulfate, at 4 lb/acre-foot of water, dissipated from the flood waters of two cranberry bogs in Massachusetts with half-lives of 1-6 days.
3. This study does not fulfill EPA Data Requirements for Registering Pesticides (1983) because the test substances were not characterized, soil and water were not characterized, complete field test data were not provided, copper sulfate was not applied at the highest registered application rate, the application method was not representative of actual use conditions, and soil samples were not analyzed.

CuSO₄ applied to bog water in a dump bag, without cranberry bushes, instead of spraying on cranberry foliage. Only 1:20 analyzed instead of 1:2000.

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MATERIALS AND METHODS:

Copper sulfate (test substance uncharacterized, source unspecified), was applied at 4 lb/acre-foot of water (~0.4 ppm copper) to two cranberry bogs (2-acre treated size) located in Massachusetts in the spring of 1969. One site (Bog 1) was flooded with water (not described) taken from a nearby pond; the other site (Bog 2) received river water (not described). The bogs remained flooded during the experiment. The water depth in the bogs ranged from 4 to 13 inches. Copper sulfate was applied by adding it to a burlap bag and dragging the bag through the bog water.

Surface and subsurface water samples were taken pretreatment, and at 1, 3, 6, 8, 10, and 28 days posttreatment. Samples were filtered (Whatman No. 44), mixed with bathocuproine (used to form an orange-colored bisphenanthroline chelate with cuprous ions), acidified with HCl to pH ~4.5, and extracted with chloroform. The organic phase, following separation, was then filtered through glass wool into an absorption cell and analyzed for copper colorimetrically. Recovery of copper from flood water samples fortified with 0.3 ppm Cu was $94 \pm 0.3\%$. Detection limits were not reported.

REPORTED RESULTS:

Copper concentrations declined with half-lives of 1-3 days and 3-6 days from the subsurface and surface water, respectively, of two cranberry bogs treated with copper sulfate at 4 lb/acre-foot of water (Table 1). After 28 days, surface and subsurface water samples had declined to the pretreatment water concentrations of copper (0.02 ppm).

DISCUSSION:

1. Soil and water were not characterized. In addition, soil samples were not analyzed.
2. The test substance was not characterized.
3. Water samples were taken from only two collection sites at each bog, representing ~1 acre per sample. With so few samples taken, it's not possible to ascertain if the data were representative of the whole bog.
4. Rainfall and irrigation data were not reported.
5. Copper sulfate was not applied at the highest registered rate (5.3 lb ai/A).
6. Copper sulfate was applied by dragging a burlap bag, containing the test substance, through the bogs. This method of application is not representative of actual use conditions.

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Table 1. Dissipation of copper sulfate (ppm copper) in cranberry bog flood water following application of copper sulfate, at 4 lb/acre-foot of water (~0.4 ppm copper), to two bogs located in Massachusetts.

Sample Location	Pretreatment	Sampling interval (days)					
		1	3	6	8	10	28
<u>Bog 1</u>							
Surface	0.02	0.84	0.52	0.10	0.08	0.04	0.02
Subsurface	0.02	0.92	0.10	0.06	0.06	0.04	0.02
<u>Bog 2</u>							
Surface	0.02	0.78	0.50	0.10	0.06	0.05	0.02
Subsurface	0.02	0.96	0.06	0.06	0.06	0.03	0.02

CASE GS0121 COPPER SULFATES STUDY 3

PM PM# 03/28/83

CHEM 024401 Copper Sulfates

BRANCH EFB DISC 30 TOPIC 101050

FORMULATION 90 - FORMULATION NOT IDENTIFIED

FICHE/MASTER ID 00099156 CONTENT CAT 01
Bartley, T.R., and H.J. Cohan. 1967. Progress report on evaluation of copper for aquatic weed control and herbicide residues on irrigation systems: Report No. WC-32. U.S. Dept of the Interior, Bureau of Reclamation, Water Conservation Branch, Div. of Research: Unpublished study; CDL:005528-A.

SUBST. CLASS = S.

DIRECT RVW TIME = 20 (MH) START-DATE END DATE

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CONCLUSIONS:

Field Dissipation - Aquatic and Aquatic Impact Uses

1. The data pertaining to Experiments 2 and 3 in this study are scientifically invalid because the sampling protocol was inadequate to accurately assess the dissipation of copper sulfates from water. The data generated from the Farmer's Ditch Irrigation Canal in Colorado (Experiment 1) are scientifically valid.
2. Maximum copper concentrations in irrigation water, following yearly copper sulfate pentahydrate applications of ~8100, 3900, and 5900 lb during the 1966, 1967, and 1968 irrigation seasons, were 0.19, 0.05, and 0.50 ppm, respectively. Sediment copper concentrations, at most sampling sites, increased during the 1967 and 1968 irrigation seasons. Copper concentrations in soil, from agricultural fields irrigated with the treated water, did not increase during any of the years.
3. This study does not fulfill EPA Data Requirements for Registering Pesticides (1983) because the test substance was not characterized (Experiments 2 and 3), water and sediment were not completely characterized, and detection limits and recovery values were not reported.

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MATERIALS AND METHODS:

Experiment 1

Copper sulfate (copper sulfate pentahydrate, commercial grade, 25% copper, source unspecified) was applied by a gravity box to the Farmer's Ditch Irrigation Canal near Loveland, Colorado during the 1966, 1967, and 1968 irrigation season. The irrigation water (Table 1), fed by the Big Thompson River, flowed through an earthen bottom irrigation canal which was ~12 miles long, tapering from a bottom width of 12 feet for the first 6 miles to ~2 feet at its terminus. At normal operating capacity (20.30 cfs) the water depth of the canal varied between 2 and 3 feet, and the flow velocity approached 1 ft/sec. The sediment was described as gravel to silty in the upper one-third of the canal, and clay-like in the remainder of the canal (sediments not further characterized).

The total seasonal application rate of copper sulfate was 8100, 3900, and 5900 lb in 1966, 1967, and 1969, respectively (Table 2). Sediment (0- to 6-inch depth) samples were taken twice yearly at sampling stations located downstream from the application site. Agricultural fields, which had received the treated irrigation water, were sampled (0- to 6-inch depth) on the same dates as the sediment. Water samples were taken periodically at 13 sampling stations along the canal (Table 3). Control samples were taken upstream (distance not reported) from the application site. Figure 1 illustrates the sampling locations.

Air-dried, sieved (0.25 mm) soil and sediment samples (2 g), after organic matter removal, were acid digested in HNO_3 , mixed with HF and concentrated H_2SO_4 , and evaporated to dryness. The residue was then combined with a mixture of water and HNO_3 , and filtered (Whatman No. 42). The filtrate was analyzed for copper by atomic absorption spectroscopy (AAS). Water samples were directly analyzed by AAS.

Experiment 2

In a similar experiment conducted in Washington, copper sulfate (test substance uncharacterized, source unspecified) was added to the water in a 7-mile earthen bottom irrigation canal, at 1 lb/cfs, for 133 days between June 17 and October 28, 1966. A total of 3200 lb of copper sulfate, equivalent to 0.185 ppm (0.046 ppm copper) was added. The canal water characteristics are given in Table 1. The sampling protocol is presented in Table 4. Sampling locations are illustrated in Figure 2.

Sediment and water samples were analyzed as described previously (Experiment 1).

Experiment 3

Copper sulfate (test substance uncharacterized, source unspecified), was added to irrigation water at 1 lb/cfs, as a slug application once

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biweekly to the Friant-Kern canal in California during the 1966 irrigation season. Sediment and water (pH 7.1) were incompletely characterized. Following a slug application on May 17, water samples were taken every 5 minutes for 45 minutes at locations downstream from the application site. Sampling locations are illustrated in Figure 3. Sediment samples were taken on June 14 and July 14 at 120 and 40.2 miles, respectively, from the application site.

Water and sediment samples were analyzed for copper colorimetrically (analytical methodology not further described).

REPORTED RESULTS:

Experiment 1

Mean weekly water temperatures varied between 60 and 72 F during the test period. No data, however, were presented for July water temperatures.

The concentrations of copper in irrigation water and sediment, and agricultural soil irrigated with the treated water, are presented in Table 4. Maximum copper concentrations in irrigation water, following yearly copper sulfate pentahydrate applications of ~8100, 3900, and 5900 lb during the 1966, 1967, and 1968 irrigation seasons, were 0.19, 0.05, and 0.50 ppm, respectively. Sediment copper concentrations, at most sampling sites, increased during the 1967 and 1968 irrigation seasons. The maximum copper concentration in sediment was 209 ppm. Copper concentrations in soil did not increase during any of the years.

Experiment 2

The concentrations of copper in irrigation water and sediment, and agricultural soil irrigated with the treated water, are presented in Table 5.

Experiment 3

The copper concentrations in the water of the Friant-Kern irrigation canal in California following a slug application of copper sulfate, at 1 lb/cfs, are presented in Table 5. Copper concentrations in the sediment, and in soil from agricultural fields irrigated with treated canal water, are reported in Table 6.

DISCUSSION:

General (Experiments 1, 2, and 3)

1. Sampling protocol was inadequate to provide useful data for accurately assessing the aquatic dissipation of copper sulfates from treated canals at the Friant-Kern Canal in California (Experiment 3), and an unidentified canal in Washington State (Experiment 2).

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2. Sediment characteristics were not submitted. Additionally, soil characteristics from the agricultural fields irrigated with the treated water, were not reported.
3. Water characteristic data did not include dissolved oxygen contents (Experiments 1 and 2).
4. No detection limits or recovery values were reported.

Experiment 2

The test substance was not characterized.

Experiment 3

1. The test substance was not characterized.
2. Water characteristics were not submitted.
3. The colorimetric method, used to determine copper concentrations in sediment and water, was not described in sufficient detail.

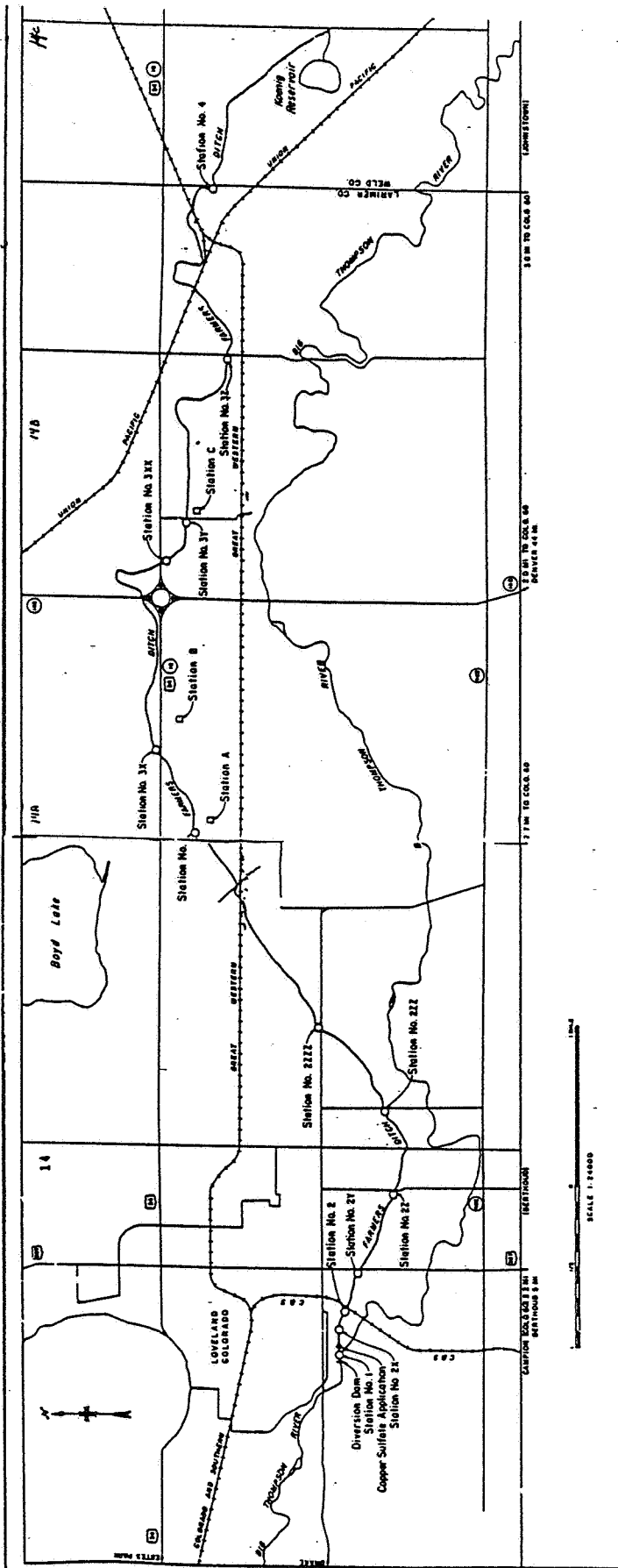


Figure 1. Sampling stations along the Farmers Ditch canal located near Loveland, Colorado.

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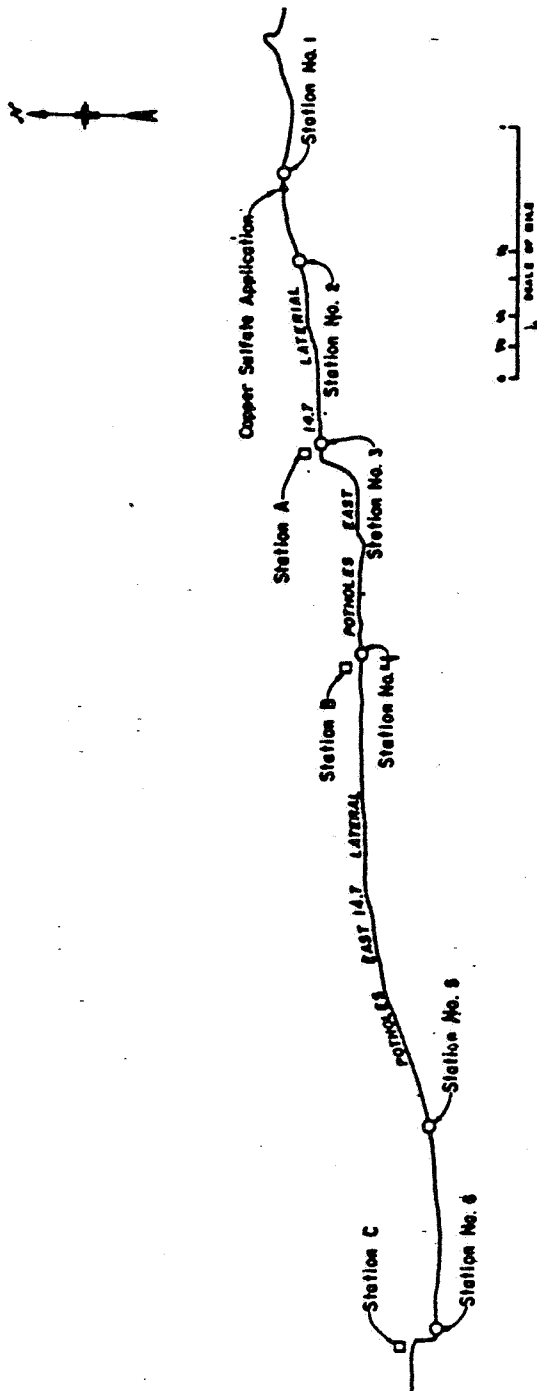


Figure 2. Sampling stations along the East 14.7 Lateral canal in Washington.

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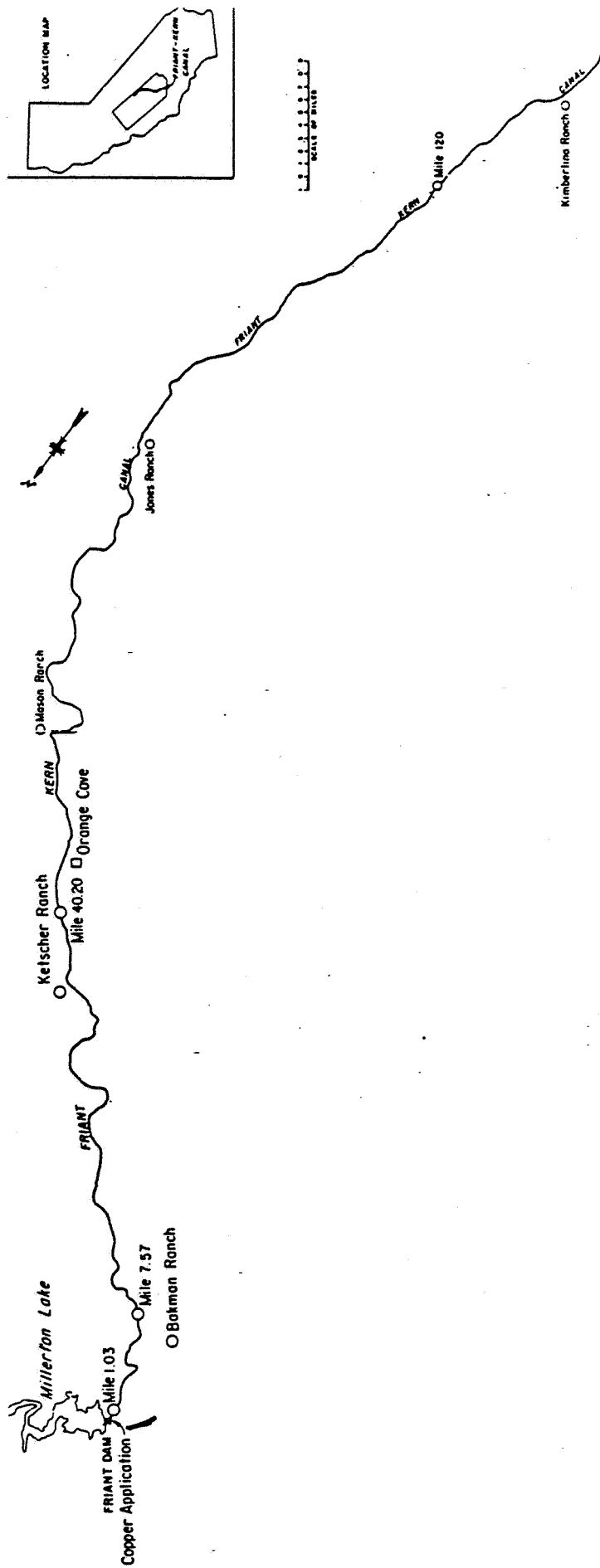


Figure 3. Sampling stations along the Friant-Kern canal in California.

Table 1. Water characteristics.

Location	Sampling date	pH	Hardness as CaCO ₃ (ppm)
Farmers Ditch, Loveland, CO	May 24, 1966	8.2	314
	Aug. 23, 1966	7.8	150
Potholes E. 14.7, WA	Sep. 12, 1966	7.8	137

Table 2. Copper sulfates application schedule at the Farmers Ditch irrigation canal near Loveland, Colorado during the 1966, 1967, and 1968 irrigation seasons.

Sample period	Average flow rate (ft ³ /sec)	Days applied	Hours applied per day	Copper sulfates applied (lb/hr)	Average concentration ^b (ppm Cu)
Jun. 3-14, 1966	24.9	12	16	2.6	0.08
Jun. 15-19, 1966	21.7	5	24	2.5	0.13
Jun. 20 - Aug. 22 1966	25.0	64	12	8.3	0.19
Aug. 23 - Sep. 24 1966	12.5	18	6	8.3	0.19
1966 ^a	22.5	--	--	--	0.17
May 22 - Aug. 27 1967 ^a	23.0	70	24	2.3	0.11
May 15 - July 11 1968	--	90	7	4.9	--
July 12-31, 1968	--	20	4.75	8.9	--
Aug. 1-26, 1968	--	26	6	8.9	--
Aug. 27 - Sept. 13 1968	--	18	3.5	8.7	--
1968 ^a	24.2	--	--	--	0.10

^a Yearly averages.

^b Average concentration (ppm Cu) = $\frac{\text{Total mg copper applied}}{\text{Total liters of water}}$

$$\text{Total mg Cu applied} = (\text{total lb Cu applied}) \times \frac{(0.454 \text{ kg})}{\text{lb}} \times \frac{(10^6 \text{ mg})}{\text{kg}}$$

$$\text{Total lb Cu applied} = \left(\frac{\text{lb}}{\text{hr}}\right) \times \left(\frac{\text{hr}}{\text{day}}\right) \times \text{days} \times \left(\frac{63.54 \text{ Cu}}{(249.64 \text{ CuSO}_4 \cdot 5\text{H}_2\text{O})}\right)$$

$$\text{Total liters water} = \left(\frac{\text{ft}^3}{\text{sec}}\right) \times \left(\frac{24 \text{ hours}}{\text{day}}\right) \times \text{days} \times \left(\frac{3600 \text{ sec}}{\text{hr}}\right) \times \left(\frac{28.32 \text{ l}}{\text{ft}^3}\right)$$

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Table 3. Copper concentrations (ppm) in the water, sediment, and soil of an irrigation canal in Colorado treated daily with copper sulfates^a during the 1966, 1967, and 1968 irrigation seasons.

Sampling station ^b	Sampling date											
	1966						1967			1968		
	May 24 ^c	Jun. 15	Jul. 7	Jul. 26	Aug. 23	Sep. 29	May 17 ^c	May 24	Sep. 28	May 7 ^c	Jul. 11	Oct. 29
<u>Water</u>												
1	0.00	0.00	0.00	0.00	0.00	-- ^d	--	0.00	--	--	0.00	--
2x	--	0.09	--	--	--	--	--	0.05	--	--	0.50	--
2	0.00	0.10	0.13	0.18	0.19	--	--	0.02	--	--	0.47	--
2y	--	0.08	--	--	--	--	--	--	--	--	--	--
2z	--	0.07	--	--	--	--	--	0.02	--	--	0.40	--
2zz	--	0.06	--	--	--	--	--	--	--	--	--	--
2zzz	--	0.07	--	--	--	--	--	0.02	--	--	0.35	--
3	0.00	0.06	0.08	0.08	0.09	--	--	0.02	--	--	0.31	--
3x	--	0.04	--	--	--	--	--	0.02	--	--	0.26	--
3xx	--	0.03	--	--	--	--	--	--	--	--	--	--
3y	--	--	--	--	--	--	--	0.02	--	--	0.19	--
3z	--	0.01	--	--	--	--	--	0.02	--	--	0.17	--
4	0.00	0.01	0.01	0.01	0.02	--	--	0.02	--	--	0.07	--
<u>Sediment</u>												
1	46.7	--	--	--	--	18.7	24.0	--	21.5	22.5	--	18.0
2x	--	--	--	--	--	40.3	40.0	--	43.5	82.0	--	50.5
2	30.0	--	--	--	--	32.0	116.5	--	123.5	65.0	--	96.5
2z	--	--	--	--	--	51.3	52.0	--	209.0	56.0	--	93.0
3	40.0	--	--	--	--	33.7	42.5	--	59.0	49.5	--	66.0
3y	--	--	--	--	--	24.7	25.0	--	34.0	39.0	--	52.0
4	40.0	--	--	--	--	28.7	66.0	--	38.5	60.0	--	104.0
<u>Soil</u>												
A	40.0	--	--	--	--	23.7	24.0	--	21.0	24.5	--	24.0
B	30.0	--	--	--	--	19.7	19.0	--	19.0	21.5	--	21.5
C	43.3	--	--	--	--	22.7	20.5	--	19.5	21.5	--	22.0

^a Total copper sulfate added in 1966, 1967, and 1968 was ~8100, 3900, and 5900 lb, respectively.

^b See Figure 1.

^c Pretreatment.

^d Not sampled.

Table 4. Copper concentrations (ppm) in water, sediment, and soil of an irrigation canal in Washington treated daily^a with copper sulfate at 1 lb/cfs during the 1966 irrigation season.

Sampling station ^b	Treatment	Sampling date				
		May 24	Aug. 3	Sep. 12	Oct. 21	Nov. 4
<u>Water</u>						
1	Untreated	0.07	0.00	0.00	0.00	--
2	Treated	-- ^c	0.05	0.10	0.14	--
3	Untreated	0.02	--	--	--	--
	Treated	--	0.05	0.10	0.07	--
4	Treated	--	0.04	0.29	0.02	--
6	Treated	--	0.03	0.03	0.01	--
<u>Soil</u>						
A	Untreated	30.0	--	--	--	--
	Treated	--	--	--	--	26.7
B	Untreated	20.0	--	--	--	--
	Treated	--	--	--	--	20.0
C	Untreated	20.0	--	--	--	--
	Treated	--	--	--	--	23.3
<u>Sediment</u>						
1	Untreated	23.3	--	--	--	30.0
2	Untreated	20.0	--	--	--	--
	Treated	--	--	--	--	123.3
3	Untreated	23.3	--	--	--	--
	Treated	--	--	--	--	120.0
4	Untreated	23.3	--	--	--	--
	Treated	--	--	--	--	106.7
6	Untreated	20.0	--	--	--	--
	Treated	--	--	--	--	80.0

^a Treated for 133 days between June 17 and October 28, 1966.

^b See Figure 2.

^c Not sampled.

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Table 5. Copper concentrations (ppm) in irrigation water from the Friant-Kern Canal following a slug application of copper sulfate, at 1 lb/cfs, on May 17, 1966.

Sampling station ^a	Initial sampling time	Sampling time (minutes after initial)									
		0	5	10	15	20	25	30	35	40	45
Mile 1.03	8:55 a.m.	0.00	2.35	3.91	2.52	1.31	0.77	0.30	0.11	0.02	--
Mile 7.57	12:15 p.m.	0.21	1.19	2.41	2.25	1.57	0.77	0.32	0.16	0.07	0.06
Bakman Ranch	2:30 p.m.	0.08	0.31	0.91	1.41	1.35	0.83	0.47	0.29	0.18	0.14

^a See Figure 3.

Table 6. Copper concentrations (ppm) in sediment and soil from the Friant-Kern Canal following bi-weekly slug applications of copper sulfate at 1 lb/cfs, during the 1966 irrigation season.

Sampling station	Treatment	Sampling date									
		May		Jun.				Jul.	Nov.		
		17	25	6	8	10	14	14	22	23	24
<u>Sediment</u>											
Mile 40.2	Untreated	--	--	--	--	--	--	40	--	--	--
	Treated	--	--	--	--	--	--	48	--	--	--
Mile 120	Untreated	--	--	--	--	--	24	--	--	--	--
	Treated	--	--	--	--	--	27	--	--	--	--
<u>Soil</u>											
Backman Ranch	Untreated	32	--	--	--	--	--	--	--	20	--
	Treated	32	--	--	--	--	--	--	--	25	--
Ketscher Ranch	Untreated	--	--	22	--	--	--	--	--	--	23
	Treated	--	--	22	--	--	--	--	--	--	23
Mason Ranch	Untreated	--	84	--	--	--	--	--	--	--	91
	Treated	--	62	--	--	--	--	--	--	--	60
Jones Ranch	Untreated	--	--	--	33	--	--	--	--	37	--
	Treated	--	--	--	35	--	--	--	--	35	--
Kimberlina Ranch	Untreated	--	--	--	--	18	--	--	--	--	--
	Treated	--	--	--	--	19	--	--	--	--	--

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CASE GS0121 COPPER SULFATES STUDY 4 PM PM# 03/28/83

CHEM 024401 Copper Sulfates

BRANCH EFB DISC 30 TOPIC 05050043

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 00099514 CONTENT CAT 01
Lin, C., A. Nemo, and D. Vedder. 1972. Copper residue in rainbow trout. Hyacinth Control J. 10(May):43-44. Also In unpublished submission received Sep. 14, 1977 under 8959-11; submitted by Applied Biochemists, Inc., Mequon, WI; CDL:231871-C.

SUBST. CLASS = S.

DIRECT RVW TIME = 7 1/2 (MH) START-DATE END DATE

REVIEWED BY: W. Frantz
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DATE: Feb. 12, 1985

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CONCLUSION:

Laboratory Accumulation - Fish

This study is scientifically invalid because the sampling protocol and experimental design were inadequate to determine the accumulation of copper sulfates in fish. Additionally, this study would not fulfill EPA Data Requirements for Registering Pesticides (1983) because the test substances were not characterized, the fish were not fractionated into edible and visceral portions, no depuration period was included, concentrations of copper sulfates in water were not determined, recovery values and detection limits were not reported, and it could not be determined whether a flow-through or static exposure system was used.

MATERIALS AND METHODS:

Rainbow trout (Salmo gairdneri; length 30-45 cm, weight 2.2-4.2 g) were maintained under unspecified conditions in nursery tanks for 6 months prior to initiation of the study. Spring water (pH 8.0, total hardness 291 ppm, dissolved oxygen 11.0 ppm, alkalinity 274 ppm, temperature 12 ± 2 C) was continuously delivered to epoxy-coated nursery tanks ($\sim 1 \text{ m}^3$), containing either copper sulfates pentahydrate (test substance uncharacterized and source unspecified), or copper triethanolamine (Cutrine, test substance uncharacterized, and source unspecified) at 0.000, 0.125, 0.250, 0.375, 0.500, 0.625, 0.750, 1.000, 2.000, 4.000, 6.000, and 8.000 ppm.

Rainbow trout (20) were sampled at 24, 48, 72, and 96 hours of exposure, and frozen. Fish (2) were thawed, dried, weighed, and mascerated, and ashed at 500 C in a muffle furnace for 12 hours. The residue was dissolved in 4 M HNO_3 , and copper determined by atomic absorption spectroscopy, at 324.6 nm, using a H_2 flame. Recovery values and detection limits were not reported.

REPORTED RESULTS:

Cumulative fish mortality prior to and during the test period was not reported. Fish exposed to a wide range of copper concentrations did not accumulate copper (Table 1). Copper sulfate formulation did not affect fish accumulation of copper.

DISCUSSION:

1. Water samples were not analyzed to confirm copper application rates or the concentration of copper in water during the exposure period. It could not, therefore, be determined whether fish were exposed to a constant copper concentration during the study.
2. The description of the experimental design was inadequate to determine whether a static or flow-through system was used.
3. Fish were not fractionated into edible and visceral portions for analysis.
4. Data were not presented illustrating the copper concentration in fish at each sampling interval. It could not be determined from what sampling interval(s) the data were taken.
5. The exposure period was too short (4 days). Additionally, no depuration period was included.
6. The test substances were not characterized.
7. Recovery values and detection limits were not presented.

Control info see Table 1

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8. Fish mortality data were not provided; however, it was stated that "Fish treated with copper sulfate pentahydrate at concentrations above 1.000 ppm of copper showed acute toxicity during a 24-hour exposure."

Table 1. Copper concentrations^a (ppm) and bioconcentration factors^b in whole-body tissues of rainbow trout during exposure to copper sulfates pentahydrate (CuSO₄·5H₂O) or copper triethanolamine (Cutrine).

Treatment rate (ppm Cu)	Cutrine		CuSO ₄ ·5H ₂ O	
	Concentration ^c	BCF	Concentration ^c	BCF
0.125	-- ^d	--	0	0
0.250	1.7	6.8	0	0
0.375	1.5	4.0	1.1	2.9
0.500	0.4	0.8	1.0	2.9
0.625	1.1	1.76	--	--
0.750	1.2	1.6	--	--
1.000	<0 ^e	--	0	0
2.000	<0	--	<0	--
4.000	7.5	1.9	2.6	0.6
6.000	<0	--	--	--
8.000	--	--	9.6	1.2

^a It could not be determined what sampling interval(s) these data represent.

^b Bioconcentration factor (BCF) = $\frac{\text{concentration in fish}}{\text{concentration in water}}$.

^c Concentrations are corrected for copper concentrations in the control fish of 2.8 ppm.

^d Not determined.

^e Concentration in fish was less than the concentration in the control.

2c

CASE GS0121 COPPER SULFATES STUDY 5

PM PM# 03/28/83

CHEM 024401 Copper Sulfates

BRANCH EFB DISC 30 TOPIC 051025 GUIDELINE 40 CFR 163.62-10c

FORMULATION 90 - FORMULATION NOT IDENTIFIED

FICHE/MASTER ID 00062074 CONTENT CAT 01

Nelson, J.L., V.E. Bruns, C.C. Coutant, et al.. 1969. Behavior and reactions of copper sulfates in an irrigation canal. Pest. Monit. J. 3(3):186-189. Available from: Superintendent of Documents, U.S. Government Printing Office, published study; CDL: 228175-I.

SUBST. CLASS = S.

DIRECT RVW TIME = 8 (MH) START-DATE END DATE

REVIEWED BY: W. Frantz
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APPROVED BY:
TITLE:
ORG:
TEL:

SIGNATURE: DATE:

CONCLUSIONS:

Field Dissipation - Aquatic and Aquatic Impact Uses

1. This study is scientifically valid.
2. Within ~3 days following copper sulfate pentahydrate application, at 1 lb/cfs, to water (411 cfs) in a concrete irrigation canal in Washington, copper concentrations in the water and suspended sediment at four sampling stations, located 0.5, 5.9, 11.5, and 23.5 miles downstream from the application site, returned to pretreatment levels (<0.001 ppm). As the distance from the site of application increased, peak concentrations of copper in water and suspended sediment decreased. In water, peak copper concentrations ranged from 1.610 (0.5 mile) to 0.015 ppm (23.5 miles). Peak copper concentrations in suspended sediments ranged from 0.292 (0.5 mile) to 0.015 ppm (23.5 miles).
3. This study does not fulfill EPA Data Requirements for Registering Pesticides (1983) because the test substance was not characterized, sediment and water characteristics were not reported, and bottom sediments were not sampled after treatment.

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MATERIALS AND METHODS:

Sieved (2 mm) copper sulfate crystals (copper sulfate pentahydrate, test substance uncharacterized, source unspecified) were applied at 1 lb/cfs to a 5-mile section of the concrete-lined Roza Main Canal located north of Sunnyside, Washington in June, 1966. A total of 411 lb of copper sulfate was applied rapidly (<1 minute) to the canal water (pH 7.0-7.3; alkalinity as CaCO₃, 90-100 ppm). The flow of water in the canal was 411 cfs. Sediment characteristics were not reported. Water and sediment samples were taken pretreatment upstream from the site of application, and up to 218 hours after treatment at 0.5, 5.9, 11.5, and 23.2 miles downstream. An indicator dye, applied with the copper sulfate, was used to signal the beginning of sampling at the downstream sites.

Water samples were analyzed for copper by measuring 400 ml of filtered (0.3 μm) canal water into a 16-oz glass bottle, and adding 10% hydroxylamine hydrochloride. The pH of the solution was buffered to 4.0-5.0 with 1 M sodium acetate. Cuproine, in isoamyl alcohol, was added, the solution shaken, separated, and the organic phase transferred to a cuvette. The copper concentration in the organic phase was determined by absorbance at 545 nm using a spectrophotometer and comparing the absorbance to a standard curve. Recovery values were not reported. The detection limit was 0.001 ppm.

Bottom sediment samples (20 g) were extracted with 0.1 N HCl, filtered (Whatman #40), and transferred to a 250-ml volumetric flask. The filter was then rinsed with 0.1 HCl and added to the extract until the 250-ml flask was brought to volume. The combined extracts were analyzed as described above for water.

Suspended sediments were collected on a 0.3 μm filter. The filters and sediment were air-dried, the sediment was scraped off the filter surface, weighed, and analyzed for copper in the same manner as described above for bottom sediment. Recovery values were not reported. Detection limit was 0.001 ppm.

REPORTED RESULTS:

Prior to treatment, copper concentrations in water were 0.001 ppm and in bottom sediments ranged from 3.9 (0.5 miles) to 8:1 (23.2 miles) ppm.

Within ~3 days following copper sulfate pentahydrate application, at 1 lb/cfs, to the water in the irrigation canal in Washington, copper concentrations in the water and sediment at four sampling stations, located 0.5, 5.9, 11.5, and 23.5 miles downstream from the application site, returned to pretreatment levels (Tables 1-4). As the distance from the site of application increased, peak concentrations of copper in water and suspended sediment decreased. In water, peak copper

concentrations ranged from 1.610 (0.5 mile) to 0.038 ppm (23.5 miles). Peak copper concentrations in suspended sediments ranged from 0.292 (0.5 mile) to 0.015 ppm (23.5 miles).

DISCUSSION:

1. The test substance was not characterized.
2. Sediment characteristics were not submitted. Additionally, complete water characteristics, including temperature and dissolved oxygen content, were not reported.
3. Recovery values were not reported for water or sediment.

Table 1. Copper concentrations (ppm) in water and suspended sediment sampled 0.5 miles downstream of an irrigation canal in Washington treated with copper sulfate pentahydrate, at 1 lb/cfs.

Sampling interval (hours)	Water	Suspended sediment
0.00	0.001	0.001
0.15	0.001	0.003
0.22	0.013	0.007
0.25	0.740	0.073
0.28	1.610	0.179
0.32	1.150	0.292
0.45	0.835	0.215
0.58	0.560	0.167
0.73	0.475	0.053
0.88	0.186	0.011
1.50	0.008	0.011
6.00	0.010	0.004
22.00	0.003	0.002
30.42	0.002	-- ^a
77.50	0.001	0.000
99.83	0.001	0.002
122.83	0.001	--
170.00	0.001	0.000

^a Not reported.

Control?

Table 2. Copper concentrations (ppm) in water and suspended sediment sampled 5.9 miles downstream of an irrigation canal in Washington treated with copper sulfate pentahydrate, at 1 lb/cfs.

Sampling interval (hours)	Water	Suspended sediment
3.13	0.004	0.001
3.75	0.002	0.002
4.00	0.128	0.027
4.25	0.359	0.255
4.50	0.236	0.238
4.75	0.110	0.025
5.50	0.016	0.017
6.33	0.008	0.003
7.00	0.005	0.005
9.50	0.003	0.004
22.75	0.001	0.002
30.88	0.002	0.001
76.75	0.001	0.002
99.33	0.002	0.001
127.83	0.003	--a
169.33	0.001	0.001
216.00	0.001	0.001

a Not reported.

Table 3. Copper concentrations (ppm) in water and suspended sediment sampled 11.5 miles downstream of an irrigation canal in Washington treated with copper sulfate pentahydrate, at 1 lb/cfs.

Sampling interval (hours)	Water	Suspended sediment
7.08	0.001	0.001
8.42	0.006	0.003
8.83	0.065	0.008
9.25	0.231	0.208
10.25	0.022	0.019
11.35	0.012	0.006
12.83	0.005	0.005
14.85	0.007	0.002
23.33	0.003	0.002
31.25	0.004	0.001
76.00	0.002	0.002
97.83	0.001	0.002
127.16	0.002	-- ^a
167.25	0.001	--
215.50	0.001	0.003

^a Not reported.

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Table 4. Copper concentrations (ppm) in water and suspended sediment sampled 23.5 miles downstream of an irrigation canal in Washington treated with copper sulfate pentahydrate, at 1 lb/cfs.

Sampling interval (hours)	Water	Suspended sediment
14.25	0.002	0.002
17.00	0.002	0.001
21.75	0.018	0.015
21.00	0.038	0.014
22.75	0.007	0.006
23.75	0.007	0.004
26.75	0.005	0.002
29.75	0.004	0.002
75.50	0.002	0.001
97.00	0.001	0.001
126.50	0.001	0.001
168.17	0.002	0.001
218.50	0.001	0.001