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Laboratory and Field Investigations of a Potential Selective Algicide, PH4062

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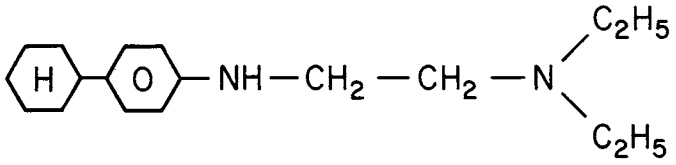
ABSTRACT

Laboratory, greenhouse, and field studies were conducted to evaluate the algicidal activity of PH4062[2] [N-(4 cyclohexylphenol)-N^1, N^1-diethylenediamine]. One-time, 7-day exposure to PH4062 at 0.25 ppmw and above significantly reduced the growth of *Cladophora glomerata* (L.) Kutz. and *Rhizoclonium* sp. Some combinations of copper sulfate ($CuSO_4$) and PH4062 produced an additive, rather than synergistic effect. Growth of *C. glomerata* and *Rhizoclonium* was reduced by 60 to 70%. Control of filamentous algae was obtained after exposure to PH4062 at 2.0 ppmw for 4 hours. Under field conditions, maximum control of filamentous algae was attained 7 days after treatment without any apparent effect on *Chara* sp., phytoplankton, or submersed vascular plants. Bioassays indicated that phytotoxicity of PH4062 persisted for about two days after treatment. The selectivity of PH4062 and its rapid inactivation in water suggests that this componud has excellent potential for practical use as an algicide in small ponds.

Key words: Cladophora glomerata (L.) Kutz. *Rhizoclonium* sp., *Chara* sp., copper sulfate, aquatic macrophyte.

INTRODUCTION

Excessive growth of nuisance algae causes significant economic losses in various agricultural, recreational, potable and fisheries waters (2, 5, 12, 15, 18). However, there are only six active ingredients commonly used to mitigate these pest problems in the U.S.: copper (in several formulations), simazine, endothall, acrolein, diquat and chlorine (EPA "Compendium of Registered Herbicides"). Only copper and diquat have federally established tolerances for potable water (1.0 ppmw and 0.01 ppmw, respectively (45 FR 53459, Aug. 12, 1980; 46 FR 30339, June 8, 1981). Some formulations of copper are toxic to fish (9) and copper has potential for accumulation in soils (12). The effectiveness of copper sulfate is reduced in hard water (12, 20). Diquat is ineffective in water containing high silt or particulate organic loads (30). Acrolein has limited application since it cannot be used in aquaculture or where treated water will enter fisheries habitats (10, 30). Water treated with simazine cannot be used for drinking or irrigation for 12 months (30). Chlorine is used primarily for algae control in swimming pools and municipal water treatment. None of these algicides is highly selective *among* the various algal species and most are phytotoxic to several aquatic vascular plants (19, 22, 29, 30). If one excludes chlorine and the various alkly compounds used in cooling towers, it is clear that there is a critical need for new, selective and environmentally safe algicides. With this need in mind, we have conducted an algicide identification program in which new compounds are examined for algicidal activity against filamentous algae including *Cladophora glomerata* (L.) Kutz, one of the most important algal pests in irrigation conveyance systems in the western U.S. (5, 12). We now report results of laboratory, greenhouse and field investigations on PH4062 (Figure 1), an algicidal compound developed by Duphar, Holland[3]. PH4062 has been tested in Europe (26, 28) and was shown to be effective against various filamentous green algae, at concentrations of 0.25 to 1.0 mg/l, but not unicellular algae or higher aquatic plants.



N—(4 cyclohexylphenyl)—N', N'—diethylenediamine

Figure 1. Structure of PH4062.

METHODS

Laboratory/Greenhouse Treatments. Rhizoclonium sp. was collected from canals near Davis, California, and *Cladophora* was obtained from canals in Dixon, CA. Algae were gently washed with tap water to remove debris and drained briefly to dampness on paper toweling. Subsamples (1 g damp-weight) were used to inoculate 4-liter glass jars containing 3 liters of tap water. After 24 h, PH4062, $CuSO_4 \cdot 5 H_2O$, Cutrine Plus®, or combinations of $CuSO_4 \cdot 5 H_2O$ and PH4062 were added to some of the jars. Treatments were made in six replicates in a greenhouse. Water Temperature was 24 to 26 C; PAR was 400 to 600 $\mu E\ M^{-2}sec^{-1}$. Water quality was: pH 9.0, total alkalinity 224 (ppmw $CaCO_3$), conductivity 543 (μmhos). After one week algal growth was removed to determine fresh and dry weights. In other treatments, the duration of exposure to PH4062 was varied from 1 to 4 hours. After the exposure, the algae were rinsed thoroughly with tap water and placed in another set of jars containing fresh tap water. Seven days after exposure, the amount of algae present was determined as above. Finally, a bioassay was used to determine the dura-

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[2]Trade names and the names of commercial companies are used in this publication solely to provide specific information. Mention of a trade name or manufacturer does not constitute a warranty or a guarantee of the product by the U.S. Department of Agriculture nor an endorsement by the Department over other products not mentioned.

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tion of PH4062 phytotoxicity. Four-liter glass jars containing 3 liters of tap water, and with or without a 3 to 5 cm layer of soil (Yolo clay loam) were treated with PH4062 (1.0 ppmw). *C. glomerata* (1 g fr. wt.) was used to inoculate the jars at 1, 4, 7, 14, 21, and 28 days after treatment. Fresh and dry weights were determined 7 days after inoculation.

Following some treatments, 0.1 g (fresh wt) subsamples were removed for chlorophyll-a analysis. Each subsample was extracted in 90% acetone (v/v) 24 h in dark at 4 C, and then ground 3x with a power-driven teflon pestle. Extractions were pooled and filtered through a 0.45 μ membrane (Millipore®) and the residual was dried and weighed. Chlorophyll-a content in the filtrate was determined by the method of Strickland and Parsons (27).

Field Treatments. Studies were conducted in two locations: two cement-lined canals (w = 3.5 m, l = 56 m, depth = 0.8 m) maintained under static water conditions and located at the USDA Aquatic Weed Control Laboratory, Davis, CA, and six earthen ponds (average: w = 8.5 m, l = 114, depth = 1.3 m) operated by the Sutter-Yuba Mosquito Abatement District, CA. One of the cement-lined canals was treated with PH4062 at a concentration of 1.0 ppmw on 8/13/81; two earthen ponds were treated similarly on 9/14/81. Two other earthen ponds were treated with $CuSO_4 \cdot 5\ H_2O$ to produce 1.0 ppmw Cu on 9/14/81. Two earthen ponds and one cement-lined canal were left untreated as controls. At the time of treatments, the cement-lined treated and control canals had 75 and 50% of their surfaces covered with filamentous algae, respectively (visual observation). Both canals had extensive growths of Eurasian watermilfoil (*Myriophyllum spicatum* L.). Filamentous algae covered the surface of about 25% of the earthen ponds, all of which had dense populations of chara. In addition, several of the earthen ponds contained mixed populations of sago pondweed (*Potamogeton pectinatus* L.), horned pondweed (*Zannichellia palustris* L.), and southern naiad (*Najas guadalupensis* [Spring]).

Effect on Aquatic Vegetation. The effects of treatments on aquatic vegetation were observed over several weeks to determine the percent water surface covered with filamentous algae and the appearance of the algae. Samples of floating algal mats were collected at various times by placing a 20 X 20 cm PVC quadrat over the algae at five randomly selected points within the infestation. All algae within the quadrat were removed and fresh and dry weights were determined. Attached algae in the cement-lined canals was sampled pretreatment and 14 days posttreatment by placing the 20 X 20 cm PVC quadrat over five randomly selected sites on the sides at a 0.2 m depth. Algae in the quadrat were carefully removed with a 15 cm steel blade. In each pond, the biomass (dry weights) of chara within 20 X 20 cm quadrats was obtained at five randomly located sites on the bottom.

Effects of PH4062 on phytoplankton were determined by collecting three 1-liter samples from each treatment site. Samples were preserved immediately with 10% formalin. Four 50-ml aliquots from each 1-liter sample were centrifuged at low speed (ca. 1500 rpm) for 25 minutes. The supernatant was decanted and the concentrated phytoplankton from each subsample was evenly distributed throughout 1.0 ml of distilled water and placed on a hemacytometer. The number of cells per liter was based on the average of 40 grids per sample (10 grids per subsample). The relative abundance of genera present was determined.

Water Quality. Dissolved oxygen, pH and conductivity was determined at midday at three sites within each earthen pond with a Hydrolab Model 8000. Standard methods were used to determine total alkalinity and hardness of water from each pond. (Changes in water quality were not determined in the cement-lined canals.)

Bioassay for Persistence of PH4062 Phytotoxicity. To obtain an estimate of the duration of algicidal acitvity, four 3-liter water samples from each earthen pond were collected 0, 1, 2, 4 and 7 days posttreatment, returned to the laboratory and bioassayed using *C. glomerata* as an indicator species. Dry weight of the alga in the pond water was determined seven days after inoculation as described previously (see "Laboratory/Greenhouse").

RESULTS

Laboratory/Greenhouse Efficacy Studies. PH4062 caused a significant reduction in growth of *C. glomerata* at concentrations at or above 0.25 ppmw, which is approximately the same algicidal range for $CuSO_4$ and Cutrine Plus® (Figure 2). *Rhizoclonium* sp., another filamentous alga, was similarly affected by all three algicides at 0.25 ppmw, but appeared to be more susceptible than *C. glomerata* at 1.0 ppmw (Figure 3). PH4062 was algistatic to *Rhizoclonium* sp. at 0.1 ppmw, though there was considerable variability among replicate treatments at this concentration.

Chlorophyll-a content in *C. glomerata* was reduced by about 25% after exposure to 0.5 ppmw PH4062 for 7 days ($2.14 \pm .16$ vs $1.59 \pm .16$ $\mu g\ mg^{-1}$ dry wt.). This is not a large decline, but indicates that chlorophyll is affected. Chlorosis was seen occasionally after exposure to PH4062 in the greenhouse but was much more apparent in the field treatments.

Results of short-duration exposure of *C. glomerata* or *Rhizoclonium* sp. to 1, 2, or 4 ppmw $CuSO_4$ and PH4062 are presented in Table 1. Duncan's Multiple Range analyses at 5% level showed that none of the exposures to PH4062 or $CuSO_4$ at 1 ppmw completely arrested growth, although 4 h exposure to PH4062 was sufficient to reduce dry weight of *C. glomerata* to aproximately 70% of the control weight. Two to four h exposure to 2 or 4 ppmw PH4062 was algicidal to *C. glomerata* and reduced dry weight more than similar concentrations of $CuSO_4$.

The response of *C. glomerata* to a 7-day exposure to combinations of PH4062 and copper sulfate is presented in Table 2. Growth of untreated *C. glomerata* was greater in the first experiment compared to the second experiment, but phytotoxicity based on % reduction in dry weight was similar in both experiments.

Most combinations of $CuSO_4$ and PH4062 were not significantly more phytotoxic than PH4062 alone. For example, the dry weight of *C. glomerata* treated with PH4062 at 1.0 ppmw plus $CuSO_4$ at 1.0 ppmw averaged 0.23 g, while that treated with PH4062 alone was 0.24 g. Based on Duncan's Multiple Range Analysis four combinations

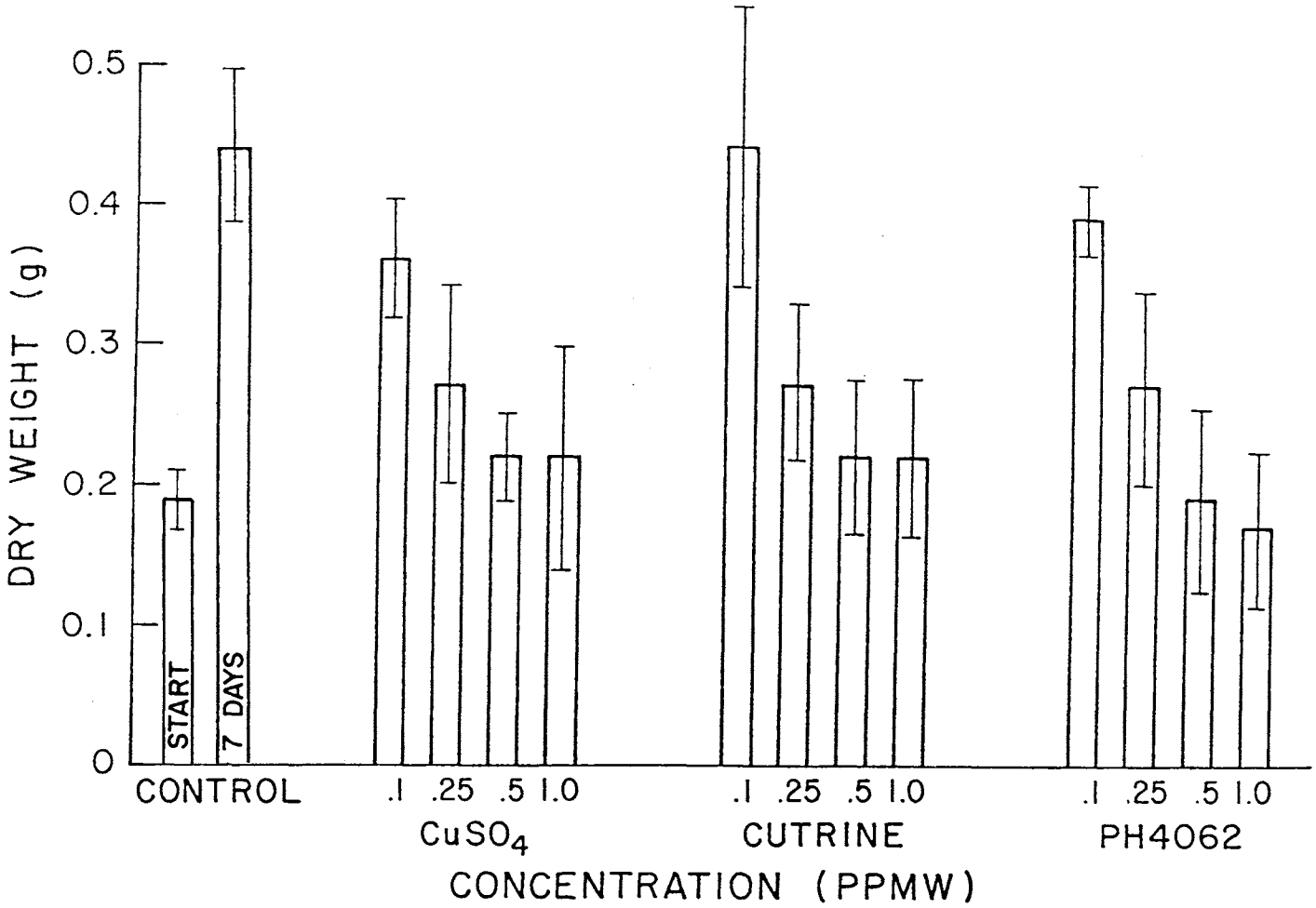

Figure 2. Effect of PH4062, Cutrine Plus and copper sulfate on growth of *Cladophora glomerata*. Bars are means ± s.e. dry weight determined after 7-day exposures. Starting dry weights were 0.20±01 g.

caused significantly greater reduction in dry weight compared to single treatments: Exp. 1, 0.5 or 1.0 ppmw $CuSO_4$ + 0.5 ppmw PH4062 and Exp. 2, 0.1 ppmw $CuSO_4$ + 0.25 or 1.0 ppmw PH4062. However, when results of Exp. 1 and 2 were averaged, none of the combination treatments produced a significant increase in phytotoxicity. Therefore, it is not likely that the compounds interact synergistically since the decrease in biomass at low, equal concentrations (e.g., 0.25 + 0.25) is approximately equal to the *expected* reduction caused by the *added* effect of each when used together. At higher, equal concentrations, the effect was less than additive.

When soil was not present during exposure, PH4062 significantly reduced growth of *C. glomerata* for up to seven days (Fig. 4). However, when soil was present in bioassay jars, phytotoxicity persisted less than four days. Growth of algae inoculated into 14-day-old controls was also reduced. This was consistently observed in 1981 and 1982 and might be associated with a reduction of available nutrients by soil-borne algae and other micro organisms, and/or release of substances which may inhibit growth of *C. glomerata*. Such algal growths were observed on the soil surface and as suspensions in the jars held 14 days. It is clear, however, that the presence of unsterilized soil decreased the duration of algicidal activity by at least 10 days under these conditions.

Field Treatments. One week after treatment the water surface previously covered by filamentous algae in the treated cement-lined canal had been reduced by 60% based on visual observations. The algae in the treated canal was chlorotic, a symptom previously associated with PH4062 activity in some greenhouse exposures. However, 14 days after treatment the floating filamentous algae in the treated canal was similar in color to the algae in the untreated canal.

Pretreatment dry weight of the floating filamentous algae was very similar in the two canals (Table 3). Dry weight of algae in the untreated canal remained essentially the same while the dry weight of the floating algae decreased 35% (significant between 5 to 10% level) in the treated canal. PH4062 did not appear to have a detrimental effect on the algae attached to the side of the canal or on the phytoplankton (Table 3). In fact, biomass of attached algae doubled in the treated canal during and after the treatment period.

In the earthen ponds, chlorosis of floating filamentous algae occurred two days after all treatments. No change was observed in the physical condition of filamentous algae

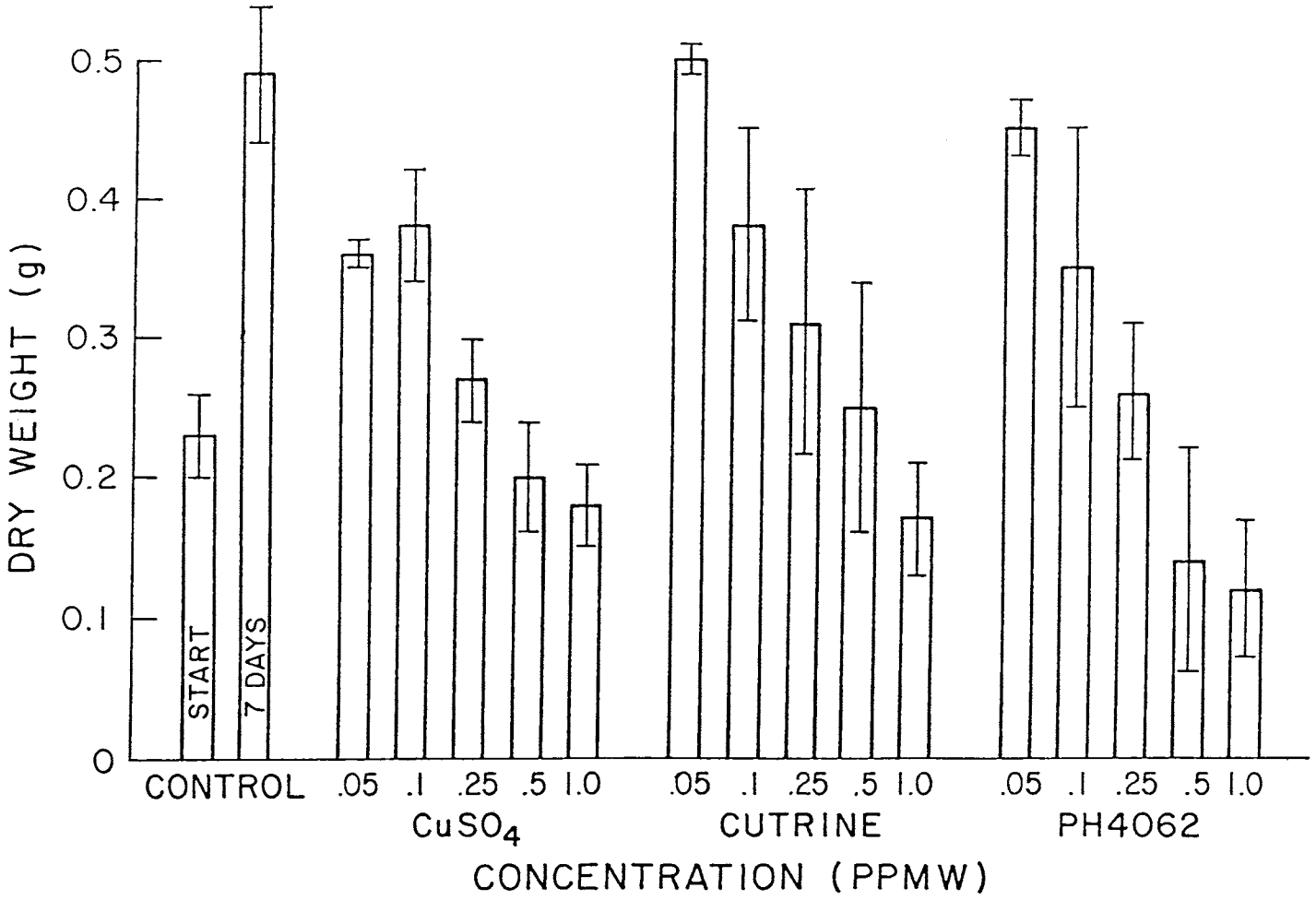

Figure 3. Effect of PH4062, Cutrine Plus and copper sulfate ($CuSO_4 \cdot 5H_2O$) on *Rhizoclonium* sp.—Bars are means ±s.e. dry weight determined after 7-day exposures. Starting dry weights were 0.2±01 g.

TABLE 1. RESPONSE OF *Cladophora glomerata* AND *Rhizoclonium* SP. TO VARIOUS EXPOSURE PERIODS AND TO CONTRATIONS OF PH4062 AND $CuSO_4$ ONE WEEK AFTER TREATMENT.

Concentration in ppmw	Exposure period (hr)	Dry Wt. of Algae (g x 10^{-2})[1]			
		Cladophora glomerata[2]		*Rhizoclonium*[3]	
		PH4062	$CuSO_4$	PH4062	$CuSO_4$
Control	1	43 a		44 a	
	2	49 a		45 a	
	4	43 a		45 a	
1.0[4]	1	34(79)[5] bcde	44(102) ab	40(91) a	39(88) a
	2	35(71) abcde	41(84) abc	35(55) bc	26(58) bc
	4	30(69) de	39(91) abcd	25(55) bc	29(64) b
2.0	1	35(75) cde	38(88) abcd	26(59) bc	24(55) bc
	2	16(32) fg	30(61) de	31(47) bcd	22(49) bcd
	4	17(39) fg	31(71) de	14(32) de	24(53) bc
4.0	1	19(43) f	32(75) cde	19(44) cd	30(67) b
	2	07(15) g	24(50) ef	10(21) e	20(44) cd
	4	16(37) fg	22(51) ef	11(24) e	23(47) bc

[1]Values followed by the same letter are *not* significantly different at 5% level as determined by Duncan's Multiple Range Test. Each value is the mean of three replicates.
[2]Initial weight = 22 x 10^{-2}g.
[3]Initial weight = 23g.
[4]$CuSO_4$ concentration expressed as ppmw Cu^{+2}.
[5]Number within parentheses is % of control.

or macrophytes in the control ponds nor in chara or other macrophytes in the PH4062 treated ponds two days posttreatment. However, 10% to 50% of the chara was chlorotic in ponds that had been treated with $CuSO_4$. Chlorosis of filamentous algae became progressively more pronounced in all treated ponds up to four days posttreatment, except that chara did not develop any symptoms in the PH4062 treated ponds. Areal coverage of floating filamentous algae in one control pond (Pond 10) increased over 100% by seven days after treatment, however, it did not increase in the other control pond. No increase in areal coverage of filamentous algae was seen in any of the treated ponds.

Twenty-eight days after treatment, less than 1% of Pond 9 ($CuSO_4$) was covered with filamentous algae. The chara was decomposing or completely chlorotic. In contrast, new growth of chara was observed in Pond 1 ($CuSO_4$). Filamentous algae in control Pond 10 covered almost 75% of the water surface. Areal coverage in PH4062 ponds was approximately the same as at seven days posttreatment. Neither PH4062 or $CuSO_4$ had any noticeable effect on the vascular plants present in the ponds.

The quantitative data from the plant samples generally correspond well with the visual observations described above. Dry weight of filamentous algae decreased in all the

TABLE 2. RESPONSE OF *Cladophora* TO VARIOUS COMBINATIONS OF PH4062 AND $CuSO_4$ AFTER SEVEN DAYS OF TREATMENT.

	Treatment (ppmw)	Dry Wt. of Algae[1] (g x 10^{-1}) Exper. 2[2]	Exper. 2[2]
Control		69 a	40 e	55
PH4062	0.10	73(105)[3] a	40(100) e	57(104)
	0.25	56(81) b	33(83) f	45(88)
	0.50	42(61) c	25(63) g	34(62)
	1.00	26(38) d	21(53) g	24(44)
$CuSO_4$[4]	0.10	64(93) a	36(90) f	50(91)
	0.25	53(77) b	32(80) f	43(78)
	0.50	38(55) c	23(58) g	31(56)
	1.00	40(58) c	27(68) fg	34(62)
PH4062 + $CuSO_4$	0.10 + 0.10	57(83) b	34(85) f	46(84)
	0.25 + 0.10	54(78) b	26(65) fg	40(72)
	0.50 + 0.10	48(70) bc	23(58) g	36(65)
	1.00 + 0.10	38(55) c	14(35) h	24(44)
PH4062 + $CuSO_4$	0.10 + 0.25	50(73) bc	26(65) fg	38(69)
	0.25 + 0.25	48(69) bc	25(63) fg	37(67)
	0.50 + 0.25	35(51) c	21(53) g	28(51)
	1.00 + 0.25	28(41) d	17(43) b	23(42)
PH4062 + $CuSO_4$	0.10 + 0.50	40(58) c	23(58) g	32(58)
	0.25 + 0.50	36(53) c	21(53) g	29(52)
	0.50 + 0.50	28(41) d	23(58) g	26(47)
	1.00 + 0.50	25(36) d	19(48) gh	22(40)
PH4062 + $CuSO_4$	0.10 + 1.0	33(49) c	23(58) g	28(51)
	0.25 + 1.0	30(43) cd	23(58) g	27(49)
	0.50 + 1.0	28(41) d	20(50) g	24(44)
	1.00 + 1.00	26(38) d	10(48) gh	23(42)

[1]Value in a column followed by the same letter are not significantly different at 5% level as determined by Duncan's Multiple Range Test. Each value is the mean of three replicates.
[2]Initial dry weight = 22 x 10^{-2}.
[3]Numbers within parentheses are percent of control weight.
[4]Concentration expressed as ppmw copper ion.

treated ponds seven days after treatment (Figure 5). A slight increase in dry weight of filamentous algae occurred in the PH4062 treated ponds between 14 and 28 days. The dry weight of filiamentous algae in $CuSO_4$ ponds was relatively constant after seven days posttreatment. Dry weight of chara was reduced 80% in the ponds treated with $CuSO_4$ seven days posttreatment (Figure 6). Dry weight of chara in the control ponds and PH4062-treated ponds remained relatively constant over the 28 day sampling period.

Phytoplankton cell numbers declined only in one $CuSO_4$-treated pond and one control pond on posttreatment day 7 (Figure 7). Phytoplankton concentration in the other ponds gradually increased through day 14; however, concentrations in PH4062-treated pond No. 2 and the two control ponds continued to increase through day 28. Analysis of variance showed that PH4062 significantly affected the relative abundance of 18 genera identified (F = 20.7) (Table 4). Genera which changed most over time were: *Chondrocystis, Chroococcus, Coconeis* and *Scenedesmus.* The lack of *Chondrocystis* in PH4062-treated ponds 4 and 7 days posttreatment suggests that this alga is susceptible to the algicide, since it comprised 18 to 42% of the genera present in control ponds.

Results of bioassays for persistence of PH4062 are presented in Figure 8. By four days posttreatment, growth of *C. glomerata* in water from PH4062-treated ponds was not

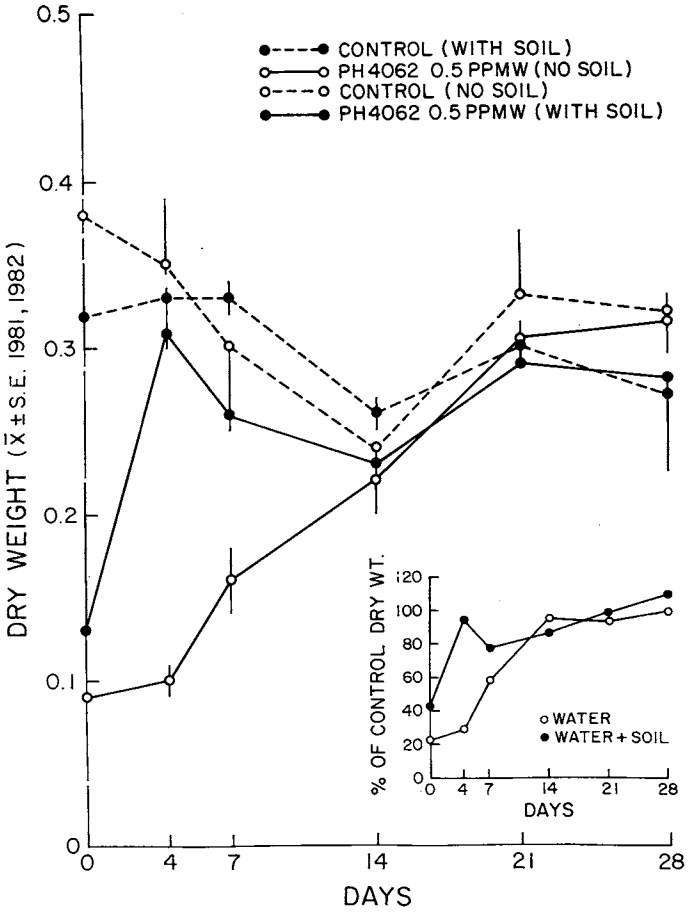

Figure 4. Duration of PH4062 algicidal activity in 4-liter jars with or without a 3-5 cm layer of soil. Treated jar contained 3-1 water and were inoculated with 1.0 g fresh wt. *Cladophora glomerata* at the times indicated.—Values are means ± s.e., 4 replicates;—insert shows results expressed as percent of control.

significantly different from that in water from the control ponds. When this is expressed as % of control growth (Figure 8 inset) it is clear that most of the algicidal activity is lost within 24 to 48 h. The data are very similar to the re-

TABLE 3. DRY WEIGHT[1] OF FLOATING AND ATTACHED ALGAE AND PHYTOPLANKTON IN CANAL TREATED WITH PH5063 FOR THE CONTROL OF FILAMENTOUS ALGAE.

Canal	Sample	Floating filamentous algae Dry weight (g)	Attached algae Dry weight (g)	Phytoplankton Population (plankton/liter)
Untreated Canal 2	Pretreatment	20.0 a[2]	7.1 a	1352 ab
	14 day post-treatment	23.2 a	6.8 a	1568 a
Treated Canal 1	Pretreatment	19.8 a	6.5 a	916 b
	14 day post-treatment	12.8 a	15.1 b	1068 b
		(LSD 12.8)	(LSD 6.4)	(LSD 421)

[1]Weight of algae in 400 cm^2 area.
[2]Values in a column followed by the same letter are not significantly different at 5% level as determined by Duncan's Multiple Range Test. Each value is mean of five replicates.

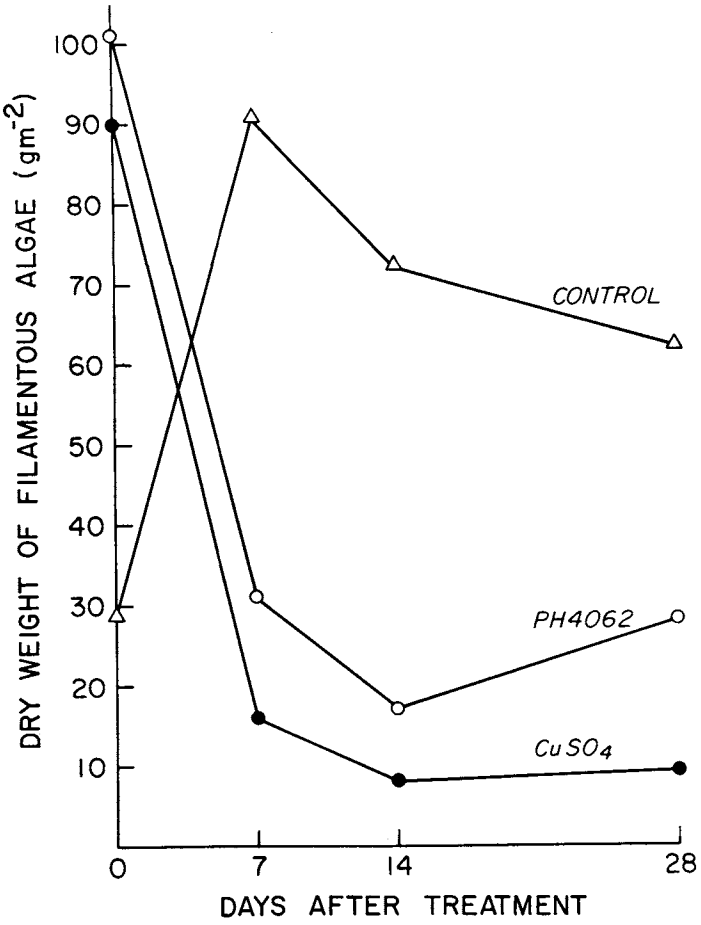

Figure 5. Effect of field treatments of 1.0 ppmw PH4062 or $CuSO_4 \cdot 5H_2O$ on filamentous algae. Values are means of two ponds, 5 replicate samples per pond.

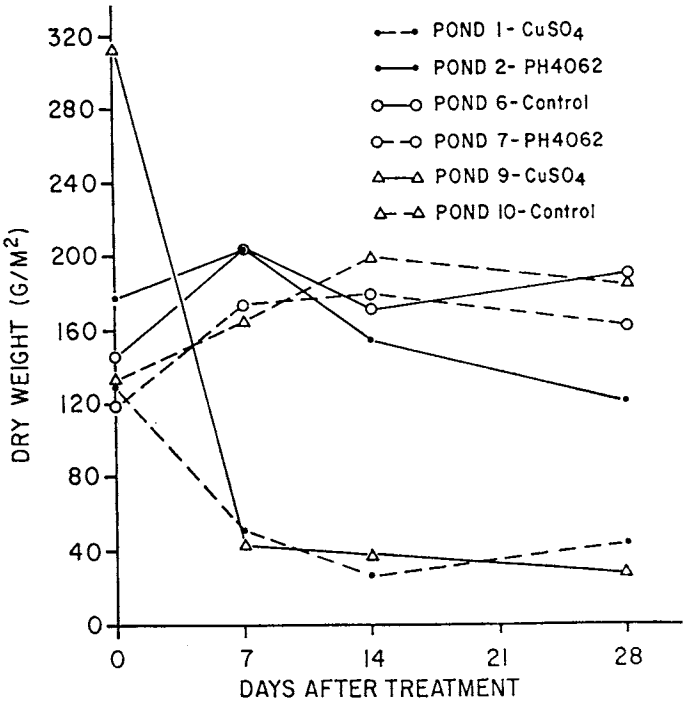

Figure 6. Effect of 1.0 ppmw PH4062 or $CuSO_4 \cdot 5H_2O$ on dry weight of *Chara* sp. in earthen ponds. Values are means of 6 replicate samples in each of two ponds.

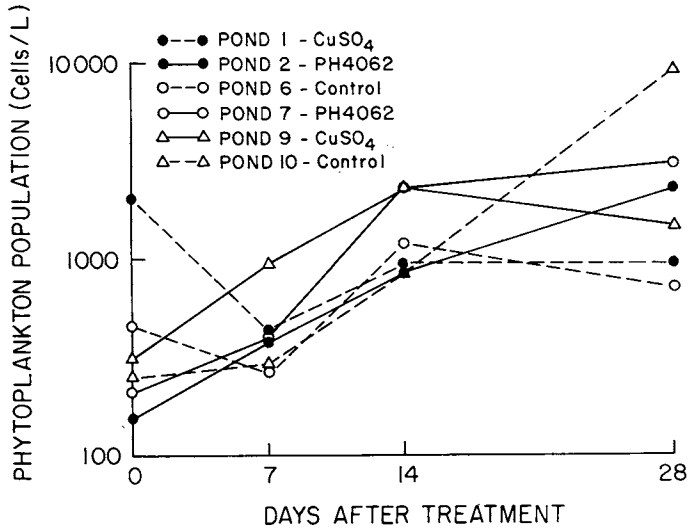

Figure 7. Effect of 1.0 ppmw PH4062 or $CuSO_4 \cdot 5H_2O$ on phytoplankton abundance in earthen ponds. Values are means of 3 replicate spamples.

sults obtained in the 3-liter jar treatments when a soil layer was included (Figure 4 inset). Although water from the $CuSO_4$-treated ponds was not bioassayed, analysis of copper by atomic absorption spectroscopy showed that algicidal concentrations remained through 7 days after treatment (Figure 9).

With the exception of dissolved oxygen and pH, water quality did not change significantly following algicide treatments. Four days after treatment both PH4062 and $CuSO_4$ caused precipitous drops in midday dissolved oxygen to 0.5 to 1.5 ppm (Figure 10). Dissolved oxygen concentration 28 days after treatment was similar to pretreatment concentration. In the control ponds dissolved oxygen generally remained constant. The pH followed the same pattern, decreasing from 9.4 to 9.7 to 7.3 to 8.2 by day 7 (Figure 11).

DISCUSSION

The dose/response results from the laboratory studies

TABLE 4. RELATIVE ABUNDANCE OF PHYTOPLANKTON GENERA WHICH OCCURRED >1% RELATIVE FREQUENCE IN CONTROL AND PH4062 TREATED PONDS.[1]

	Days Posttreatment					
	4		7		28	
	Control	PH4062	Control	PH4062	Control	PH4062
Genera:						
Anomoeneis	—	—	—	—	1.3	0.3
Chondrocystis	18.7	—	42.0	—	49.7	1.8
Chroococcus	76.4	93.0	56.8	86.2	5.6	48.1
Closteriopsis	0.2	—	—	—	6.1	15.4
Coconeis	1.1	5.6	—	9.4	3.5	12.7
Diatomella	—	0.3	—	—	20.7	6.9
Hydroseros	1.3	0.6	—	0.1	0.4	—
Navicula	1.1	0.1	0.8	—	8.0	3.6
Scenedesmus	0.8	0.3	—	3.5	0.2	9.8
Staurastrum	—	—	—	—	1.0	0.1
Unidentified A	—	—	—	0.1	1.5	0.3

[1]Values are means from 3 samples per pond, 2 replicate subsamples per sample.

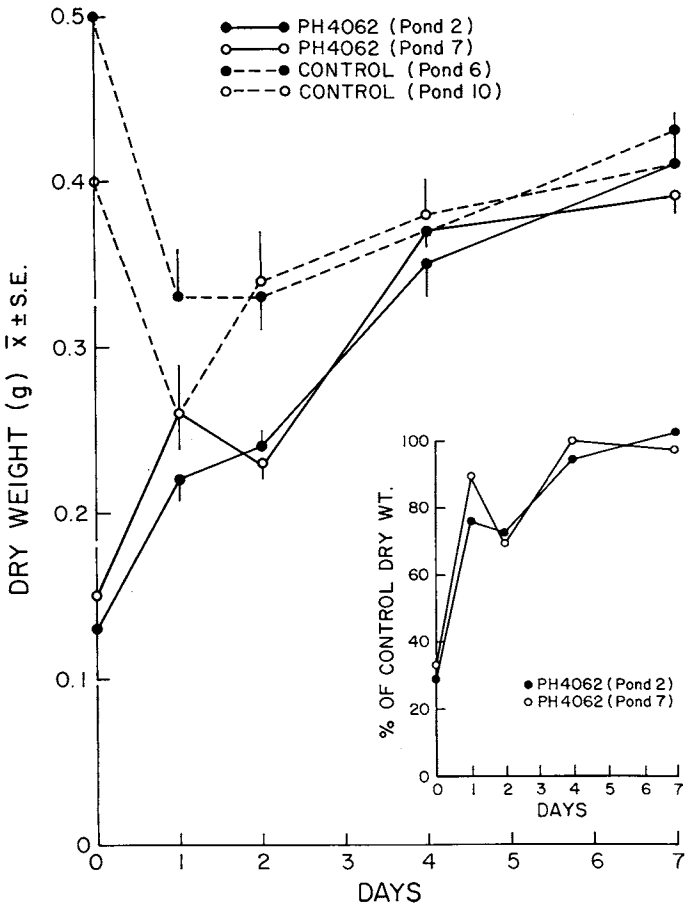

Figure 8. Duration of PH4062 algicidal activity after application in earthen ponds at 1.0 ppmw. On the days indicated, water was removed from treated ponds and inoculated with *Cladophora glomerata*. Values are means ± s.e. dry weight 7 days after inoculation; insert shows results expressed as percent of control.

indicate that PH4062 is as phytotoxic as copper sulfate to *Cladophora glomerata* (L.) Kutz, and *Rhizoclonium* sp. when administered as one-time, "slug" type applications at 0.25 to −1.0 ppmw. At low concentrations, e.g., 0.25 to 0.5 ppmw, both compounds were algistatic since growth was not completely arrested. With short duration exposures, e.g., four hours, PH4062 appeared to be more effective than copper sulfate. The difference may result from more uptake of PH4062 and/or differences in the modes of action of the two compounds. The chlorosis of the filamentous algae observed within a day or two after PH4062 treatments indicates a rapid effect on synthesis and/or degradation of chlorophyll. This was confirmed by chlorophyll-a analysis seven days posttreatment. Little is known about the site or mode of action of PH4062, while copper is known to affect respiration and photosynthesis (11, 21), and may be less phytotoxic in some algae in which it is bound to the cell wall (18).

The minimum phytotoxic concentration of PH4062 (0.25 ppmw) is similar to that reported by Tooby et al. (28) for *Vaucheria dichotoma* Vauch, *Cladophora* sp., and *Spirogyra* sp. However, they stated that *Enteromorpha intestinalis* (L.) Grev. was more resistant, requiring >0.5 ppmw for control.

Phytoplankton numbers were not significantly reduced

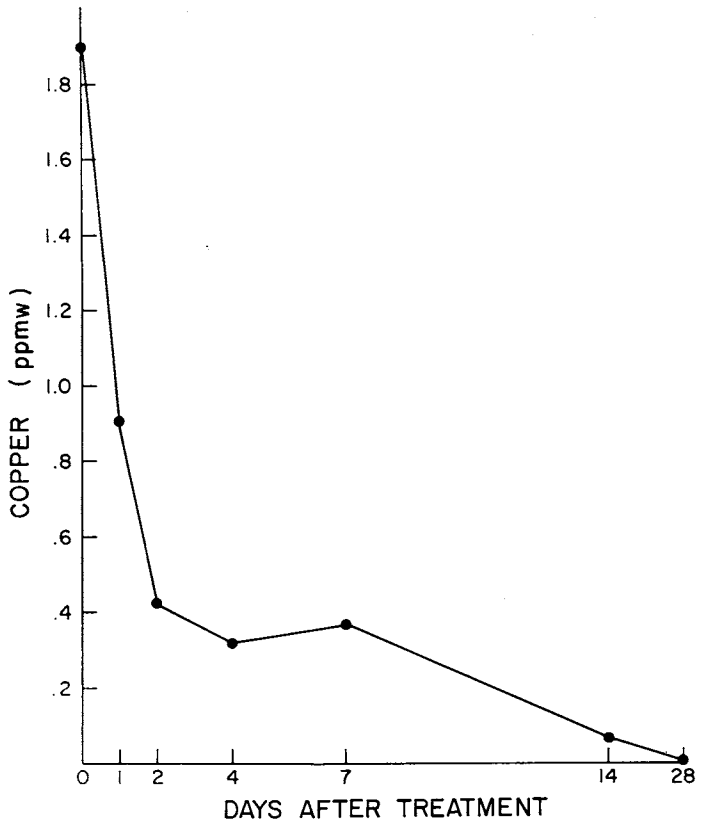

Figure 9. Concentration of copper in earthen ponds treated with for each sampling time. Sample on day 0 was taken .5 h after treatment. $CuSO_4 \cdot 5H_2O$. Values are means from 3 samples in each of two ponds

by PH4062 in the field applications, although the relative abundance of some genera appeared to have been altered. Such shifts in phytoplankton and periphyton have been reported following herbicide treatments (1, 3, 4, 29) and this suggests that some non-filamentous algae may be susceptible to PH4062.

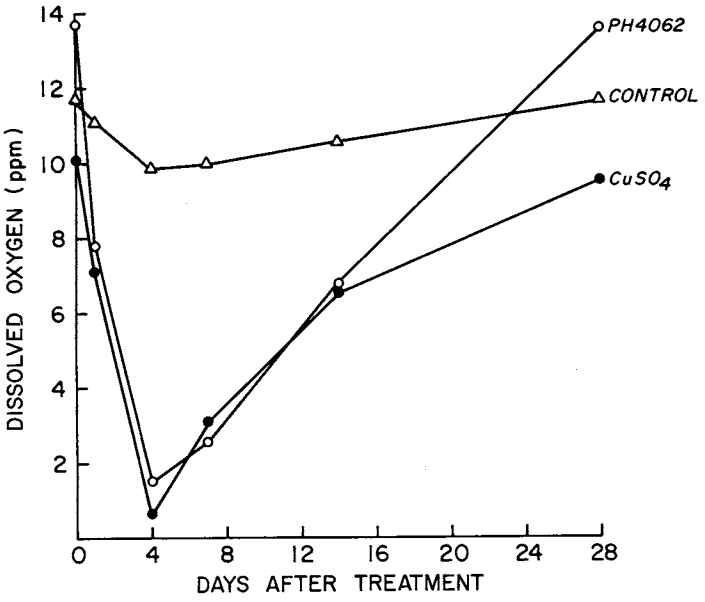

Figure 10. Effect of 1.0 ppmw PH4062 or $CuSO_4$ on dissolved oxygen at midday in small ponds. Values are means of two ponds.

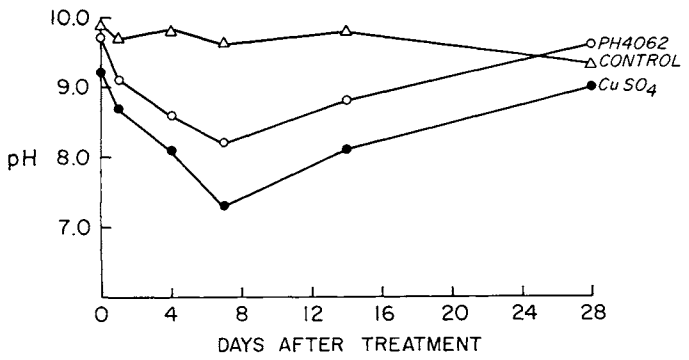

Figure 11. Effect of field treatments of 1.0 ppmw PH4062 or $CuSO_4 \cdot 5H_2O$ on pH in earthen ponds. Values are means of two ponds.

Chara was apparently unaffected by PH4062. In fact, none of the rooted macrophytes in the PH4062-treated ponds exhibited any phytotoxic symptoms. Furthermore, no significant effects have been observed on *Potamogeton nodosus* Poir.; *P. pectinatus* (L.), *Myriophyllum spicatum* (L.) or rice (*Oryza sativa* L. M101) in replicated, static greenhouse trials (unpublished USDA/ARS Annual Report, 1981). Spencer-Jones et al. (26) also found no effects on chara, *Ceratophyllum demersum* L., or *Callitriche stagnalis* Scop. after exposure to PH4062.

Bioassays for algicidal activity from both greenhouse and field-scale treatments indicate consistently that PH4062 is not effective beyond 2 to 4 days after application. These results correlate well with unpublished data on the fate and dissipation of PH4062 in water/soil systems (unpublished data, Duphar, Holland). For example, initial concentrations of 0.5 ppmw decreased to ca. 0.13 ppmw within 24 hours and to ca. 0.05 ppmw in 48 hours in small, artificial ponds. Also, when ^{14}C-PH4062 was applied to a soil/water system, 95% of the label was associated with the soil phase within two weeks. This suggests that the compound is metabolised in the soil, or otherwise bound to soil and particulates in the water.

The rapid inactivation of PH4062 means that both field and seven-day greenhouse treatments were, in fact, short term, pulse-type exposures. This also suggests that the 2 to 4 hour greenhouse treatments provided a more accurate comparison of PH4062 and copper acute toxicity. Under these conditions, initial concentrations of PH4062 may be nearly sustained for the four hours, and it would appear that $CuSO_4$ is less effective in reducing dry weight (see Table 1).

Aside from a depression of dissolved oxygen and pH PH4062 had little effect on water quality parameters measure in this study. Perturbations in water quality following aquatic herbicide treatments are not unusual (1, 3, 14, 24, 25). The reduction in pH is generaly attributed to the release of organic acids and to a decline in photosynthesis. Godshalk and Wetzel (13) demonstrated that decomposing *M. heterophyllum* Michx. lowered the pH in small flasks containing lake water, particularly under anaerobic conditions. The magnitude and duration of the changes perhaps has the most impact on the practicality of using a particular algicide. Generally, the changes in water quality resulting from the $CuSO_4$ or PH4062 were transient with pretreatment conditions being re-established after four weeks.

The characteristics of PH4062 reported here and by European researchers suggest that this compound has excellent potential for practical use. Its algicidal activity toward many filamentous forms equals or surpasses copper, which is non-degradable. The selectivity of PH4062 is highly desirable. Copper, on the other hand is phytotoxic to many filamentous and unicellular algae, and aquatic vascular plants (9, 29). The resistance of chara is particularly significant since this species can be beneficial in small ponds (6, 7). Finally, phytotoxicity of PH4062 to filamentous algae lasts only 2 to 4 days. Since field treatments sometimes result in non-uniform exposure to algae, the duration of phytotoxicity may not be sufficient for complete control. However, the effective life of the compound might be extended by altering the formulation. The fact that PH4062 is fast acting partly compensates for its ephemeral nature. In this respect, it is similar to algicidal and herbicidal activity of hydrogen peroxide reported by Quimby (16, 17, 23) and this laboratory (8).

More work is needed to better characterize the specificity of PH4062. If the mode of action were known, a new understanding of physiological and biochemical differences between filamentous and unicellular algae could emerge.

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