Effectiveness of a Chelated Copper Algicide on Algae Grown Under Differing Water Column Phosphorus Regimes

A Summary Report Submitted to Diversified Waterscapes Incorporated

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INTRODUCTION

The algicide F-30 (copper sulfate pentahydrate; Diversified Waterscapes, Inc., Laguna Niguel, CA) is a chelated copper formulation that can be applied to control a broad spectrum of filamentous and planktonic algal species as well as some macrophytes. The chelated copper formulation contains 10.94% copper sulfate, which is equivalent to 0.032 kg ai L^{-1} of elemental copper. Chelated formulations tend to stay in solution longer, give better control, and are generally less toxic to fish species than traditional copper sulfate (Watson 1989). Chelated copper formulations have shown success in controlling a variety of algal species (Fitzgerald and Jackson 1979, Hallingse and Phlips 1996, Murray-Gulde et al. 2002).

The long-term success of algal control in a given water body may depend on the availability of nutrients to initiate regrowth after an initial algicide application. A major cause of algal blooms in surface waters throughout the United States is anthropogenic nutrient loading (Carpenter et al. 2000, Çelik and Ongun 2006). The response of these algal blooms appears to be driven by the amount of available nutrients in the water column; in particular, phosphorus (Notestein et al. 2003). To our knowledge little attention has been directed to the control of algae using a chelated copper algicide under differing water column phosphorus concentrations. The objective of this study was to evaluate the control of algae grown under three different water column phosphorus concentrations using F-30 algicide. These results should indicate the ability of this chelated copper product to control algae at different levels of phosphorus loading, in addition to the length of time before algal regrowth occurs after an initial treatment.

MATERIALS AND METHODS

The study was conducted in an outdoor mesocosm facility at the R. R. Foil Plant and Soil Science Research Center, Mississippi State University, Starkville, Mississippi for six weeks beginning in August 2006 and concluding September 2006. The experimental design consisted of a randomized complete block with three concentrations of water column phosphorus that were treated with the chelated copper algicide and identical rates of phosphorus that were not treated with algicide to serve as reference (experimental control) units. Each rate was replicated four times in 24 378-L tanks. Phosphorus as potassium phosphate monobasic (KH_2PO_4) was added to designated units at the rates of 60 µg/L, 90 µg/L, and 150 µg/L to simulate eutrophic to hypereutrophic water (Wetzel 2001). Experimental units were also amended with 1.80 mg/L of nitrogen as ammonium nitrate (NH_4NO_3, 99% nitrogen) to ensure that nitrogen would not be a limiting factor. Aeration was supplied to each unit using a regenerative air blower. Two 30.50

cm air stones and a PVC lift pipe were used to constantly agitate the water column to prevent filamentous algae growth. Algae were allowed to grow for approximately 14 days prior to algicide application. Natural inocula of algae were used to establish algae populations in all experimental units. We did not attempt to characterize algae species in this study, as we were only interested in the efficacy of the product on a general algal bloom.

After the 14-day growth period, the chelated copper algicide was applied to the water column as a submersed treatment at a rate of 0.4 mg/L as elemental copper. Chlorophyll *a* (*in vivo* ppb) was measured at pre-treatment (prior to application) 7, 14, 21, and 28 days after treatment (DAT) to assess algae growth using a hand held fluorometer. To assess water clarity, transparency was measured using a transparency tube at the time of chlorophyll measurements. At the conclusion of 28 days, data were analyzed using a one-way Analysis of Variance using a Fisher's LSD for comparison of the means to detect differences of chlorophyll *a* and water transparency between the algicide treatments and their respective untreated reference. All analyses were conducted within a given time interval and not between time intervals. Separate analyses were conducted for chlorophyll *a* and water transparency data for a given time interval. Also, a Pearson's Correlation was conducted to assess the relationship between chlorophyll *a* and water transparency over the 28 days of the study. All analyses were conducted using Statistix 8.0 software at an a = 0.05 (Analytical Software 2003).

RESULTS AND DISCUSSION

The goal of this study was to simulate different water column phosphorus concentrations representing eutrophic to hypereutrophic conditions. We expected to have a significant difference in the pretreatment chlorophyll *a* measurements, having lower concentrations in the 60 µg/L phosphorus experimental units and greater concentrations in the 150 µg/L phosphorus experimental units; and the application of a chelated copper product would result in a reduction in chlorophyll *a* concentrations to similar levels across all phosphorus concentrations (Table 1). Indeed, the algicide was effective in reducing the chlorophyll *a* concentrations and in most instances increasing water transparency in this study. A significant difference was detected between the reference experimental units and the algicide treated units for all time intervals Table 1). Chlorophyll *a* concentrations were reduced in all of the algaecide treated units within each time interval regardless of phosphorus availability.

A correlation of -0.70 was observed between chlorophyll *a* and water transparency. Water transparency was also significantly different between the reference experimental units and the algicide treated units from 14 DAT to the conclusion of the study (Table 1). Water transparency was not significantly different ($F = 0.85$, d.f. = 23, $p = 0.533$) 7 DAT for any of the experimental units. Water transparency increased in all of the algicide treated units and were significantly different when treated units were compared to their respective reference units with the exception of the 90 µg/L phosphorus level. The 90 µg/L phosphorus units treated with algicide did have a slight increase in water transparency however significance was only observed 21 DAT. The lack of a statistical difference in water transparency in the treated 90 µg/L phosphorus units was attributed to the large amount of dead algae being re-suspended by the aeration in these treatment units. In a natural system the dead algal cells would have settled to the bottom of the water-body resulting in an increase in water transparency. In this study the dead algal cells were continuously being resuspended in the water column by the air lift pipes which made it difficult to detect differences among treatments.

Phosphorus concentrations in this study were selected to simulate a range of phosphorus concentrations that could result in nuisance algal growth under field conditions. Nutrient gradients in shallow lakes have major effects on the density of phytoplankton (Çelik and Ongun 2006) with phosphorus being the limiting nutrient (Notestein et al. 2003). After 28 days the initial algicide application was effective at controlling algal growth as indicated by chlorophyll *a* measurements. Furthermore, there was no regrowth of algae and water transparency increased from pre-treatment over the duration of the study. Based on data from this study the algicide is effective at controlling and maintaining control of algae under a range of nutrient availability. However, these results were obtained from a static exposure with copper continuously being resuspended in the water column that represents a worst-case scenario for copper exposure and efficacy. Caution should be taken when extrapolating these data to field conditions due to the fact that in large scale lake applications copper would become biologically unavailable very rapidly in some instances. Therefore, further research may be needed to determine contact and exposure times, how long this algicide can maintain control, and to determine if a lower application rate can achieve the same level of control. The 0.4 mg/L rate is the maximum-labeled rate for this algicide; a trial using the minimum recommended rate of 0.2 mg/L might offer further insights on the effectiveness of this product.

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Table 1. Mean (± 1 SE) chlorophyll *a* and water transparency measurements over 28 days of the study. Means followed by the same letter are not statistically significant at an $\alpha = 0.05$. Analyses were conducted within a given time interval and not between time intervals. Separate analyses were conducted for chlorophyll *a* and water transparency for a given time interval.

		Days After Treatment			
F-30 + Phosphorus (µg/L)	**Pre-Treatment**	**7**	**14**	**21**	**28**
		Chlorophyll *a* [1]			
0.40 + 60	7.86 ± 1.53 b	1.40 ± 0.32 b	0.63 ± 0.14 c	0.69 ± 0.16 b	0.78 ± 0.17 c
0.40 + 90	13.14 ± 2.67 ab	3.46 ± 1.34 b	1.44 ± 0.82 c	1.53 ± 0.68 b	1.22 ± 0.28 c
0.40 + 150	14.27 ± 2.76 ab	2.03 ± 0.25 b	1.09 ± 0.22 c	0.94 ± 0.24 b	1.48 ± 0.53 c
0.00 + 60	10.22 ± 1.34 ab	8.70 ± 0.92 a	9.03 ± 1.02 b	10.80 ± 1.04 a	11.00 ± 2.22 bc
0.00 + 90	12.31 ± 1.01 ab	10.99 ± 1.40 a	12.36 ± 1.74 ab	12.83 ± 0.75 a	17.01 ± 1.38 ab
0.00 + 150	16.57 ± 3.45 a	11.81 ± 2.03 a	14.41 ± 3.38 a	17.76 ± 5.81 a	25.33 ± 7.99 a
		Transparency (cm) [2]			
0.40 + 60	32.56 ± 3.76 a	35.75 ± 3.12 a	35.00 ± 3.17 a	33.00 ± 3.81 a	31.75 ± 4.88 a
0.40 + 90	22.56 ± 1.82 b	29.53 ± 3.26 a	26.95 ± 4.02 ab	29.00 ± 5.90 ab	28.60 ± 4.02 ab
0.40 + 150	22.93 ± 1.96 b	30.33 ± 1.62 a	33.65 ± 1.48 a	33.15 ± 2.19 a	36.65 ± 10.53 a
0.00 + 60	31.66 ± 2.41 a	30.15 ± 2.17 a	23.75 ± 2.53 bc	16.55 ± 1.16 c	15.05 ± 1.24 b
0.00 + 90	29.10 ± 3.33 ab	27.10 ± 5.05 a	18.15 ± 2.68 bc	16.50 ± 1.19 c	15.05 ± 0.92 b
0.00 + 150	23.25 ± 2.60 b	28.20 ± 3.22 a	20.25 ± 1.84 c	19.65 ± 6.11 bc	14.75 ± 3.49 b

[1] F = 14.6, d.f. = 23, p = 0.001, 7 DAT; F = 14.2, d.f. = 23, p = 0.001, 14 DAT; F = 9.02, d.f. = 23, p = 0.001, 21 DAT; F = 8.74, d.f. = 23, p = 0.001, 28 DAT

[2] F = 6.34, d.f. = 23, p = 0.001, 14 DAT; F = 4.25, d.f. = 23, p = 0.012, 21 DAT; F = 3.52, d.f. = 23, p = 0.021, 28 DAT