THE EFFICACY OF COPPER-TRIETHANOLAMINE COMPLEX ON WATER NET (*HYDRODICTYON RETICULATUM*)

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SUMMARY

Copper-triethanolamine complex caused a loss of buoyancy and arrested growth of water net in a greenhouse trial at concentrations above 0.25 mg copper/litre water. Ten mg/litre was required for complete control. In a field trial at Lake Aniwhenua, a surface application, applied to give 0.3 mg copper/litre (total water column) controlled surface mats of water net and water net growing on macrophytes, but did not affect water net growing on the floor of the lake or accumulate in the sediments. The algicide was also herbicidal for macrophytes, but no toxic effects were observed on fauna.

Keywords: copper triethanolamine complex, algicide, water net, *Hydrodictyon reticulatum*

INTRODUCTION

Since 1986 when water net was first found in New Zealand it has spread rapidly through much of the Bay of Plenty and Waikato regions and become a major public nuisance, particularly in Lakes Rotorua, Rotoiti and Aniwhenua (Hawes *et al.* 1991). As part of the search for a solution, a wide range of algicides were screened for their potential to control water net. Most had little or no effect at recommended dose rates (Wells and Clayton 1993) but copper was one exception. Copper has been used for more than 50 years as a standard chemical for control of algal problems in reservoirs in the USA although concerns have been raised regarding the long term use and accumulation of copper in the environment (Cooke *et al.* 1993). A number of summaries exist on the impact of copper in aquatic ecosystems (McKnight *et al.* 1983; Demayo *et al.* 1982; Cooke *et al.* 1993).

To keep the amount of copper used to a minimum, copper triethanolamine (K-Tea, Griffin Corporation) was chosen in preference to copper sulphate as it produces higher concentrations of Cu^{+2} ions in the water column and therefore has greater efficacy per weight of copper applied, particularly in alkaline or hard water (Anderson and Docheretz 1985).

The objective of this study was to determine the efficacy of copper triethanolamine on water net under controlled greenhouse conditions and then determine its effectiveness in a field trial and evaluate its impacts in an aquatic ecosystem.

METHODS

Greenhouse efficacy test

About 50 g wet weight (c. 0.4 g d.wt.) water net was exposed to six different concentrations of copper triethanolamine: 0.01, 0.1, 0.25, 0.5, 7.5, and 10 mg copper/litre and an untreated control. Six, 5 g samples of water net (wet weight) were removed from each treatment after a 1 hour exposure and transferred to separate 4 litre tanks filled with tap water plus a 0.5% hydroponic growers mix. Changes in appearance of the water net were recorded daily for 2 weeks, then the water net was harvested, dried at 70°C for 48 h and weighed. Water net remaining in the herbicide tanks was subjected to continuous exposure to copper. After 2 weeks the continuous treatments were compared subjectively with respective 1 hour exposure treatments. Water net was kept in the herbicide tanks for a further 2 weeks (4 weeks total) before final assessment of effects.

Proc. 47th N.Z. Plant Protection Conf. 1994: 373-378

Field trial

A backwater at the head of Lake Aniwhenua (on the Rangitaiki River, Bay of Plenty Region) with a history of water net infestations was selected for this study. In January 1994, a one ha plot was surface sprayed, from an airboat, with 30 litres copper triethanolamine (3 kg/ha) to give a calculated 0.3 mg copper/litre total water column. The site had a slow, variable current flow (< 0.01 m/sec), an average depth of 1.5 m, and a high (90%+) cover of water net present on the sediments and covering macrophytes. About 10% of the site was covered by floating mats of water net. Areas of oxygen weed (*Elodea canadensis* c. 10% cover), pondweeds (*Potamogeton ochreatus* and *Potamogeton crispus* c. 20% cover) and bare sediment without water net ($< 5\%$), were also present. The margins were dense bullrush (*Typha orientalis*). The site had numerous rainbow and brown trout (*Salmo gairdnerii* and *S. trutta*), goldfish (*Carassius auratus*), eels (*Anguilla dieffenbachii*) and a few bullies (*Gobiomorphus cotidianus*). Invertebrates were abundant amongst the water net and included: daphnia (*Ceriodaphnia dubia*), cyclopoid copepods, blood worms, snails (*Potamopyrgus antipodarum*, *Limnaea tomentosa*, and *Planorbis kuhuica*), leeches (*Hirudinea* sp.) and a wide variety of insects including waterboatmen and backswimmers (*Sigara* sp. and *Anisops* sp.), the diving beetle (*Liodes plicatus*), *Oxythera albiceps*, a damselfly (*Ischnura aurora*) and the aquatic moth larva (*Hygraula nitens*). The control site was similar to the treated site and positioned upstream to avoid interference from chemical drift.

Copper levels in water were monitored by collecting three surface water samples, from within the treated plot (one from each transect) prior to treatment and again at 0.5, 1, 3, 6, 12 and 24 h thereafter, for analysis of total copper. Copper levels were also monitored from the Rangitaiki River below Rabbit Bridge and in the untreated control plot at the same times. Three sediment samples were collected from within the treated and untreated plots prior to treatment and again 2 weeks post treatment for analysis of total copper.

The abundance of water net and submerged aquatic macrophytes was measured on three 50 m transects, evenly spaced in the treated plot, and one in the untreated plot using the quantitative line transect method of Clayton (1983). The depth of water and heights and cover of each species were recorded in a 0.1 m^2 quadrat every metre along each transect line and then vegetation profiles drawn. The transects were selected and measurements made prior to treatment and at 1, 2, 4, and 8 weeks after treatment.

A quantitative measure of the effects of copper on the biomass of water net was undertaken using a bioassay technique. Thirty grams wet weight water net was added to three fine meshed 0.3 m^3 floating cages in the treated plot prior to application of copper and also to three cages in the untreated plot. The cages were harvested 48 h later and water net transferred to tanks filled with tap water at NIWA, Hamilton, to observe subsequent changes over the balance of a 2 week period, after which dry weights were determined by drying samples in a forced air drying oven (at 70°C) to constant weight.

Impacts on invertebrates were monitored by adding an additional cage within treated and untreated plots, to enclose ten snails (*Potamopyrgus antipodarum*), three mussels (*Hyridella menziesii*), twenty daphnia (*Daphnia magna*) and six damselfly larvae (*Ischnura aurora*), for 96 h following treatment and recording any mortalities. Fish surveillance was maintained, by observation above water and on SCUBA, over a 48 h period in and near the treated plot, to note avoidance, changes in behaviour, stress reactions and mortalities.

RESULTS

Glasshouse trial

Water net biomass after 2 weeks was markedly reduced by additions of copper at concentrations from 0.1 to 0.25 mg/litre (Figure 1). At 0.25 mg/litre and above water net biomass was reduced to less than the pre-trial level of 0.44 g dry weight. In the 0.25 and 0.5 mg/litre treatments, water net fragmented and produced many daughter nets, but none were present at 7.5 mg/litre or above. After 2 weeks the degree of control in the continuous exposure treatments was the same as that in the respective 1 hour

treatments. After 1 month none of the water net in the 10 mg/litre treatment was viable, but at 7.5 mg/litre and lower, water net remained green although it had not recovered.

Figure 1: Mean dry weights of water net 14 days after a 1 hour exposure to copper triethanolamine at concentrations shown. Copper concentrations raised to the 0.25 power were plotted using a bayesian smoother (Wheeler and Upsdell 1994) with log link and an asymptotic covariance function. Shaded area = 95% confidence interval.

Figure 2: Copper concentrations in water sampled from treated (circles and solid line) and untreated (triangles and lower dotted line) plots and in the Rangitaiki River (squares and upper dotted line) below Rabbit Bridge. The graph is an analysis of the log of the copper concentrations using an asymptotic covariance function and a bayesian smoother (Wheeler and Upsdell 1994). Shaded area = 95% confidence intervals for treated plot copper concentrations.

Figure 3: A. Transect 3, pre-spray; B. Transect 3, 2 weeks post-spray, showing loss of surface water net and macrophytes; C. Control transect, as it appeared both pre-and 2 weeks post-spray. T.o.= bullrushes; L.m.= duckweeds and azolla; P.o.= pondweeds; H.r.= water net; E.c.= Canadian pondweed.

Field trial

The application of copper triethanolamine to the trial plot resulted in maximum levels up to c. 0.6 mg copper/litre (but with considerable variance) in surface waters with concentrations dropping to background levels within 6 to 12 h (Figure 2). Downstream, copper levels remained low in the river due to considerable dilution and no impacts on macrophytes or algae were noted there. Sediment copper levels ranged from 5.5 - 26 mg/kg sediment in the untreated plot and were not elevated in the treated

plot following copper application, with mean levels of 11.5 mg copper/kg sediment prior to treatment and 10 mg/kg 2 weeks after treatment.

Within 48 h of treatment, all water net floating on the surface and amongst macrophytes in the treated plot had become chlorotic and later could not be found. In the untreated plot, surface mats of water net persisted and increased in occurrence by 14% over 2 weeks (Table 1). There was little change in benthic water net in the treated plot with a near complete cover and average heights of c. 0.4 metres persisting. Submerged macrophytes in the treated plot collapsed after 1 week and most remaining stalks sank beneath the benthic water net within 2 weeks as shown in Profile 3 (Figure 3). There was little change in treated profiles over the following 6 weeks. Bullrushes around the treated plot were not affected.

TABLE 1: Frequency data (number of 0.1 m² quadrats with particular species present) for untreated control and treated transects, pre-spray and 2 weeks post-spray with percent change in frequency for surface water net (H.r.) and all water net (benthic and that on macrophytes) and submerged macrophytes.

	Untreated (n=50)			Treated 1 (n=43)			Treated 2 (n=50)			Treated 3 (n=50)		
	pre	post	Δ%	pre	post	Δ%	pre	post	Δ%	pre	post	Δ%
surface H.r.	14	16	+14	6	0	-100	8	0	-100	26	0	-100
all H.r.	50	50	0	43	43	0	50	50	0	37	37	0
sub. macr.	50	50	0	28	25	-9	20	3	-85	17	8	-53

Water net within the floating cages in the treated plot lost its net structure and sank within 3 days of treatment and by 2 weeks (in culture) had produced numerous daughter nets, but without an increase in dry weight. In contrast, water net from cages in the untreated plot grew from 0.94 g to 2.82 g. d.wt. and remained as a surface floating mat.

Invertebrates caged in the treated and untreated plots all remained alive during the 96 h test. The same diversity of invertebrates was seen in the treated plot pre- and post-spray. No toxic symptoms were noted in any fish species, even though they remained in the area throughout the trial. Several trout were observed feeding on surface insects in the treated plot within 15 minutes of treatment.

DISCUSSION

In the greenhouse trial the lowest concentration at which surface water net lost buoyancy was noted at 0.25 mg/litre copper. A total water column concentration of 0.3 mg/litre (3 kg/ha or 0.3 g/m²) was elected for the field trial to test whether this concentration would also control nuisance surface growths of water net. The lowest rate of copper likely to provide control was selected to minimise any possible toxicity effects and accumulation in sediments. The results confirmed that all surface floating and near surface water net was effectively controlled. A surface water copper concentration of 0.57 mg/litre was recorded (Table 1) shortly after spraying and higher concentrations would have resulted amongst mats of floating water net as the copper was sprayed directly onto the surface. This would account for the observation that much of the floating water net was killed rather than just lost buoyancy, and corresponds with results in the glasshouse trial at 10 mg/litre copper. Copper concentrations would have been rapidly diluted with depth and no effects on benthic water net were noted. Sediment copper levels were within the normal natural range for New Zealand sediments (Smith 1986) and were not elevated following treatment.

Environmental impacts were minimal with invertebrates and fish showing no signs of toxicity though they would have lost habitat with the loss of surface water net. It was demonstrated that copper can be applied, given adequate dilution, without accumulating in the sediments. The macrophytes, however, were as susceptible to the

copper as the water net. The potential loss of macrophytes must be considered with future applications.

Overall these results suggest that surface applications of copper triethanolamine at about 3 kg/ha could be very useful in controlling surface accumulations of water net on a larger scale. For example, the technique may prove useful for removing/controlling shoreline accumulations along Lake Rotorua or in Lake Aniwhenua against the dam. The effects of decaying water net on water quality will need to be assessed and effects on biota and accumulation in sediments would need to be monitored as they are likely to be site specific.

ACKNOWLEDGEMENTS

Environment BoP, Cyanamid (NZ) Ltd, and BoP Electricity funded most of this work. Environment BoP staff and Aleki Taumoepeau (NIWA) assisted in the field and Graeme Bourdôt (referee) and John Clayton (NIWA) suggested useful changes to the manuscript. Martin Upsdell (AgResearch) was the consulting biometrician.

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