COPPER SULFATE TREATMENT
OF LAKES AND RESERVOIRS:
CHEMICAL AND BIOLOGICAL CONSIDERATIONS

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Technical Note No. 24

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SUMMARY

Since 1905, copper sulfate has been widely used as a means of controlling nuisance algae in drinking water reservoirs. Reservoir managers, relying on experience, have developed procedures which are generally successful in combatting summer blooms of these algae. In some cases, however, treatment programs fail to prevent blooms or may exacerbate the problem. Furthermore, at least two states have issued regulations which effectively prohibit the use of copper in drinking water reservoirs.

This report reviews the recent scientific advances in this laboratory and elsewhere on the subject of interactions between copper and lake organisms. The report concludes that algicide treatments are often a necessary part of water quality management and that copper sulfate is still the safest and most effective algicide in most reservoirs.

Alternatives to copper, such as organic algicide, are ecological "unknowns" and have determined effects on human health. By contrast, copper, when properly used, is safe for both humans and the environment, as evidenced by nearly eighty years of experience in the field.

Part of the report discusses practical techniques for determining the optimal treatment strategy for a given reservoir. This is especially important in lakes or reservoirs that have experienced difficulties in controlling nuisance algae. Using the procedures developed in this laboratory, reservoir managers can design copper treatment programs that will effectively eliminate undesirable algae, with minimal environmental side effects and with a cost effective dosing of copper sulfate.

INTRODUCTION

Copper sulfate has been used to control algal blooms in lakes and reservoirs in the United States since the turn of the century and is still considered to be the algicide of choice for most nuisance algal blooms (Appendix I). The chemical and biological processes controlling the effect and fate of copper added to a reservoir are outlined in the following chapter. An experimental procedure is presented which may be used in the future to determine the copper speciation in a reservoir and the copper sensitivity of the phytoplankton. Based on scientific analysis of these results, changes in algal control strategies may be indicated.

Processes important in $CuSO_4$ treatment. From the initial use of copper sulfate as an algicide, the free cupric ion has been thought of as the toxic copper species. Water supply operators have also been aware of the differences in sensitivity to copper among algal species. However, the simple formulas that prescribe copper sulfate dosages based on pH, alkalinity, and nuisance algal species have not in general been very useful. These prescriptions were mostly based on data from copper sulfate treatment episodes in a given locality (e.g. New York State for (Hale 1954); and their empirical nature is the probable cause of their failure in other geographic regions. A more general formula for effective copper sulfate dosages would calculate the cupric ion activity as a function of total copper sulfate added from the relevant chemical characteristics of the reservoir and compare that with the cupric ion activity that is toxic to the resident nuisance algal species. Research on the environmental chemistry of copper and the

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toxicity of copper to phytoplankton has made significant progress in
the past decade. As will be seen in the following discussion,
experimental and computational methodologies have been developed which
yield the data necessary for computing optimal copper sulfate
dosages (e.g. Morel et al. 1979).

Toxicity of copper to phytoplankton. The toxicity of copper to two
species of Spirogyra, a freshwater green alga, was studied by Nageli
(1893, as cited in Moore and Kellerman 1904), who coined the term
"oligodynamic" to express the toxic effect of low concentrations of
some metal ions. The ecology of freshwater algae in relation to the
management of reservoirs was thoroughly discussed by Lund (1955). He
pointed out the importance of monitoring algal populations regularly
to anticipate nuisance algal blooms and also the importance of organic
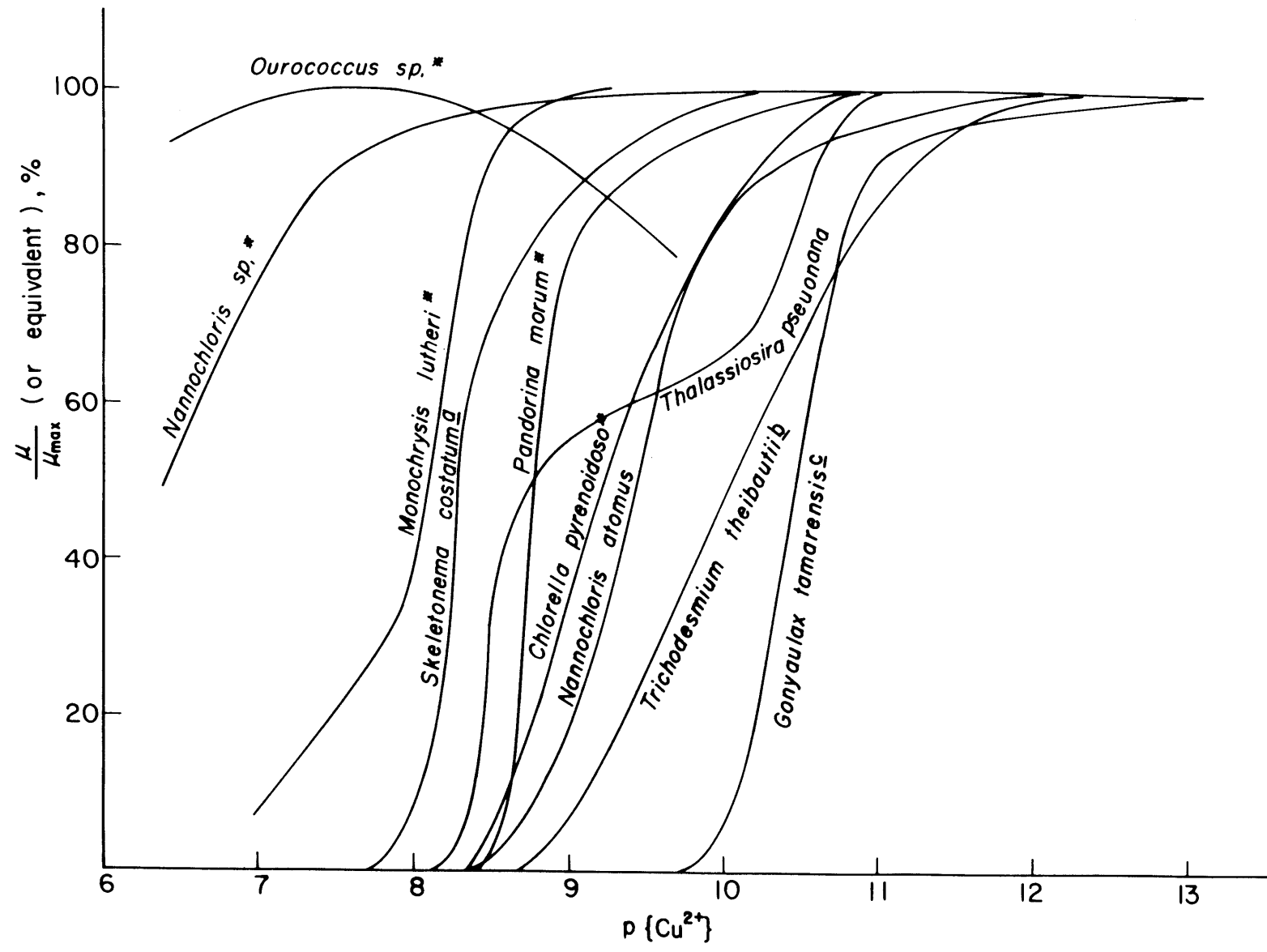substances in controlling metal toxicity.

Complexation of copper by natural and synthetic organic compounds
has been shown to detoxify copper. Fogg and Westlake (1955) demon-
strated that extracellular polypeptides produced by Anabaena cylindrica
complexed copper and reduced the toxicity of copper to A. cylindrica
when added to culture medium. The addition of a synthetic chelating
agent, EDTA, was shown to have the same detoxifying effect in cultures
of two freshwater algae, Chlorella pyrenoidosa and Microcystis
aeruginosa (Fitzgerald and Faust 1963). The reduction in the toxicity
of copper to several estuarine and marine algal species by addition of
synthetic chelating agents has been shown by Erickson et al. (1970),
Martin and Olander (1971) and (Davey et al. 1973). The complexing
capacity of lake water was measured using anodic stripping voltametry

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and its relationship to the toxicity of copper to _Chlorella pyrenoidosa_
was shown (Gatcher et al. 1973). They concluded that ionic copper
is most likely toxic to planktonic algae at concentrations of 10^{-10}M,
and that the high organic content of lake water necessitates the use
of copper dosages in the range of 1 mg/l.

It had been hypothesized by Steeman Neilsen (1970) that _Nitzschia
palea_ released copper complexing agents in response to copper stress.
Several bioassay experiments have also suggested that extracellular
algal metabolites can "condition" the medium (Lange 1973; Davey et al.
1973) and that copper stress can result in increased concentrations of
"detoxifying" algal metabolites (Foster 1979). Using potentiometric
methods, the copper complexing capacity of extracellular products
released by freshwater phytoplankton has been characterized (Swallow
et al. 1978, Chapter I and II). Most eucaryotic species were found to
produce low concentrations of weak copper complexing organic compounds
and several blue-green algal species produced strong copper-complexing
agents, which have been identified as siderophores. The concentrations
of algal produced copper-complexing agents in freshwater ecosystems are
probably too low to control the speciation of copper except
during or after algal blooms. If a reservoir is treated with copper
sulfate before an algal bloom has developed, complexation of the added
copper by algal metabolites will probably not be significant.

Although it had long been believed that the toxic
agent was the free cupric ion, it was not until recently that research-
ers have quantified the toxicity of the free copper ion to phytoplankton.
Using EDTA to buffer the cupric ion activity, Manaham and Smith (1973),
found that copper concentrations less than 90 ppb were limiting to

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Figure 1. Inhibition of growth as a function of cupric ion activity for species of freshwater, estuarine and marine algae. All the data is as in percent of maximum growth rate except: a) is the inverse of the length of the lag phase, b) is percent of maximum ^{14}C uptake, and c) is percent motile cells.

Ourococcus sp. *

100

$\frac{\mu}{\mu_{max}}$ (or equivalent) , %

Nannochloris sp. *

80

Monochrysis lutheri *

60

Pandorina morum *

Skeletonema costatum $\underline{a}$

Thalassiosira pseuonana

40

Chlorella pyrenoidoso *

Nannochloris atomus

Trichodesmium theibautii $\underline{b}$

Gonyaulax tamarensis $\underline{c}$

20

6   7   8   9   10   11   12   13

p {Cu^{2+}}

Oocystis and those greater than 200 ppb were toxic. By using

different concentrations of chelating agents and copper, the toxic

response was shown to be a unique function of the cupric ion activity

for four species of marine algae (Sunda and Guillard 1976; Anderson

and Morel 1978; Sunda and Lewis 1978). Determination of toxicity

in terms of the cupric ion activity is useful for comparison of the

sensitivity of different algal species. Data from several researchers

(Sunda and Guillard 1976; Anderson and Morel 1978; Morel et al. 1978;

Sunda and Lewis 1978; Rueter et al. 1979; and Chapter III) is

presented in Figure 1. We see that toxic cupric ion activities range

from greater than 10^{-6}M to 10^{-11}M for species of green algae, diatoms,

dinoflagellates and blue-green algae. A weakness in this comparison

is that the response to copper stress was evaluated using different

algal growth parameters, including ^{14}C uptake, cell motility, optical

density and chlorophyll a. However the conclusion that there are

significant differences in copper sensitivity among algal species is

supported by earlier experimental results (Mandelli 1969; Steeman

Neilsen et al. 1969; Steeman Neilsen and Wium-Anderson 1970; Steeman

Neilsen and Brunn Larsen 1976) and by observations of copper sulfate

treatment episodes.

Further experiments have shown that cellular uptake of copper is

controlled by the cupric ion activity in the external medium (Sunda

and Guillard 1976; Chapter III). This mechanism is responsible for the

observed relationship between toxicity and cupric ion activity. Table

I summarizes data on the uptake of copper on a per cell basis for

freshwater and marine algal species. Anabaena flos-aquae was shown by

Gibson (1972) to take up more copper per cell weight at a given copper

concentration than Scenedesmus quadricauda, but toxicity occurred at
the level of 1% of dry weight for both species. S. quadricauda has
been observed to replace A. flos-aquae as the dominant alga after
copper treatment. Foster (1977) also found that toxicity occurred at
the same concentrations of cellular copper in copper-tolerant and
copper-sensitive species of Chlorella vulgaris. In experiments with a
marine diatom, Rueter and Morel (1979) have found that copper uptake
is also dependent on silicon nutrition, with more copper being assimi-
lated by silicon-limited cells. This result has interesting implica-
tions for the copper sulfate treatment of spring diatom blooms of
nuisance species such as Synedra and Asterionella, which may become
silicon limited.

In the context of control of algal blooms in freshwater reservoirs,
the copper sensitivity of blue-green algae is especially important.
The ecology of freshwater blue-green algae is complicated by their
unique physiology, which includes formation of gas vesicles for
buoyancy, fixation of atmospheric nitrogen, and excretion of sidero-
phores which can complex copper. Blue-green algae appear to be more
sensitive to copper than some eucaryotic algae, but this generalization
needs further experimental support. Nitrogen fixation by Anabaena and
Aphanizomenon was suppressed significantly at copper additions of 5 to
10 μg/l in lake water containing a far greater complexing capacity
(Horne and Goldman 1974). Maintenance of sufficient copper concentra-
tions to prevent nitrogen fixation was suggested as an alternative
control strategy to prevent blue-green algal blooms. In a later study
in the same lake, during a spring bloom of Aphanizomenon, copper
concentrations greater than 10 μg/l were found to inhibit nitrogen

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Table I

$p(Cu_T)$	$p(Cu^{2+})$	Thalassiosira pseudonana(3H)[a]	
4.7-5.4	9.3-10.6	19-2 x 10^{-17} moles/cell	
4.7-5	8.84-9.2	32-23	
4.5	8.6	40	
4	8.5	85	
		Nannochloris sp.[b]	
7	9.8	1.5 x 10^{-17} moles/cell	
6.4	8.1	1.0	
6	7.4	3.7	
5.7	6.6	15.0	
		Ourococcus sp.[b]	
7	9.5	1.0 x 10^{-17} moles/cell	
6.4	8.1	1.7	
6	7.3	9.9	
5.7	6.6	21.4	
		Chlorella vulgaris(non-tolerant)[c]	
no addition		9 x 10^{-19} moles/cell	.0004 % dry weight
6.4		1.6 x 10^{-18}	.0012
6.1		5.9	.002
5.9		2.4 x 10^{-17}	.009
5.8		4.5	.017
5.6		1.3 x 10^{-16}	.05
5.5		1.8	.06
5.4		3.9	.12

Table I   (continued)

$p(Cu_T)$	$p(Cu^{2+})$	Chlorella vulgaris(tolerant)[c]	
no addition		2×10^{-18} moles/cell	.002 % dry weight
5.8		4	.004
5.4		1.8×10^{-17}	.015
5.1		5.2	.047
4.9		2.3×10^{-16}	.083
		Scenedesmus quadricauda[d]	
5.8		.2 % dry weight	
5.3		.4	
5.1		.5	
4.9		.7	
4.8		1.0	
		Anabaena flos-aquae[d]	
6.1		.6 % dry weight	
5.8		1.1	
5.2		2	
5.1		2.6	
5.0		3.2	

a- data from Sunda and Guillard 1976

b- data from Chapter III

c- data from Foster 1979

d- data from Gibson 1973

fixations, photosynthesis, and pigment accumulation (Elder and Horne
1977). A stimulatory effect at additions of 2 µg/l were also observed.

Toxicity of copper to zooplankton and fish. One important feature of
an ideal algicide is that it be nontoxic to zooplankton and fish
at the acute and chronic concentrations resulting from treatment. As
was stated previously there is little field data on the survival of
zooplankton and fish after copper sulfate treatment. There are
laboratory studies which show that the cupric ion activity is again
the critical parameter determining toxicity (Pagenhoff et al. 1974;
Andrew et al. 1977; and Waiwood and Beamish 1978). Their data for
rainbow trout and Daphnia magna, a cladoceran, are compared with copper
toxicity data for freshwater phytoplankton (Chapter III) in Figure 2.
It is not apparent from this figure that herbivores and planktivores
are generally more sensitive to copper than phytoplankton; however more
laboratory experiments are clearly needed.

The important question here is how does copper sulfate treatment
effect the different compartments of the aquatic food web. The best
way to answer this question is to study co-occurring species of phyto-
plankton, zooplankton and nekton in laboratory and field experiments.
In the field study of copper sulfate treatment of Mill Pond the
abundance of the zooplankton community decreased and an obvious change
in species composition was not observed. The decrease in the
zooplankton may effect the success of the copper sulfate treatment;
removing grazing pressure may allow surviving phytoplankton populations
to increase more rapidly than if the herbivores were present.

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Figure 2. Inhibition of growth as a function of cupric ion activity for several freshwater algae (data from Chapter III and Sunda and Lewis 1978), for _Daphnia_ _magna_, a freshwater cladoceran (data from Andrew _et_ _al_. 1977), and for _Salmo_ _gairdneri_, rainbow trout (from Waiwood and Beamish 1978).
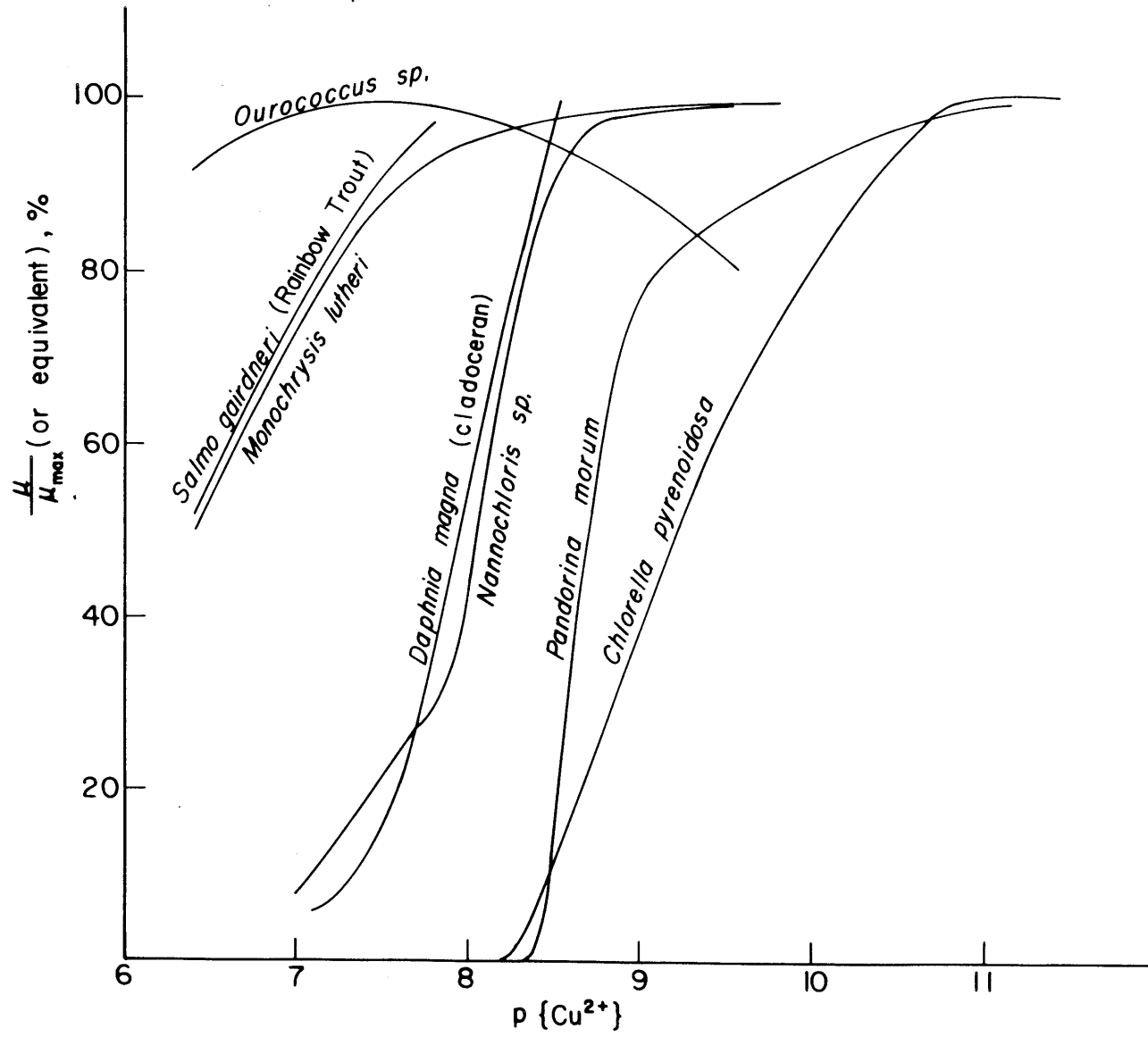
Chemistry of copper in freshwater. In the previous discussion the toxic response of both phytoplankton and zooplankton was shown to be primarily a function of the cupric ion activity. There is, however, no one chemical process which regulates the cupric ion activity after copper sulfate addition to different lakes and reservoirs. The relevant processes are: 1) inorganic complexation (e.g. $CuCO_3(aq)$, $Cu(CO_3)_2^{2-}(aq)$, $Cu(OH)_2^{2-}$, $CuOH^+$, etc.); 2) precipitation (amorphous $Cu(OH)_2$, $Cu_2(OH)_2CO_3$, CuO, and CuS); 3) complexation by organic compounds (amino acids, polypeptides, humic and fulvic acids, etc.); 4) adsorption by clays, metallic hydroxide precipitates and other particulate material; and 5) biological uptake (Stiff 1971).

All or none of the above processes may be important at some time after a copper sulfate treatment. The key parameters are pH, alkalinity, the relative concentrations of copper, dissolved organic complexing agents, and surface binding sites on particulates, and the potential for copper assimilation by the biota.

Inorganic complexation and precipitation. If only inorganic complexation and precipitation are considered, the major copper species and cupric ion activity can be computed from simple chemical equilibrium models. Figure 3 presents the major copper species as a function of pH and total copper concentration for two different concentrations of total carbonate: 3-A) $C_T = 10^{-3.4}$ as in Mill Pond (Chapter III) and B) $C_T = 10^{-2.15}$ as in lake 885 in Whitaker et al. (1978). The total copper concentrations and pH values were chosen to be relevant to the copper sulfate treatment of freshwaters. The free copper ion is the major species in the region below neutral pH. In the alkaline

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Figure 3 -A and B. -log(total copper) versus pH diagram showing
predicted precipitation of malachite and tenorite A- in Mill Pond
(C_T = $10^{-3.4}$) and B- in Lake 885 (C_T = $10^{-2.15}$).
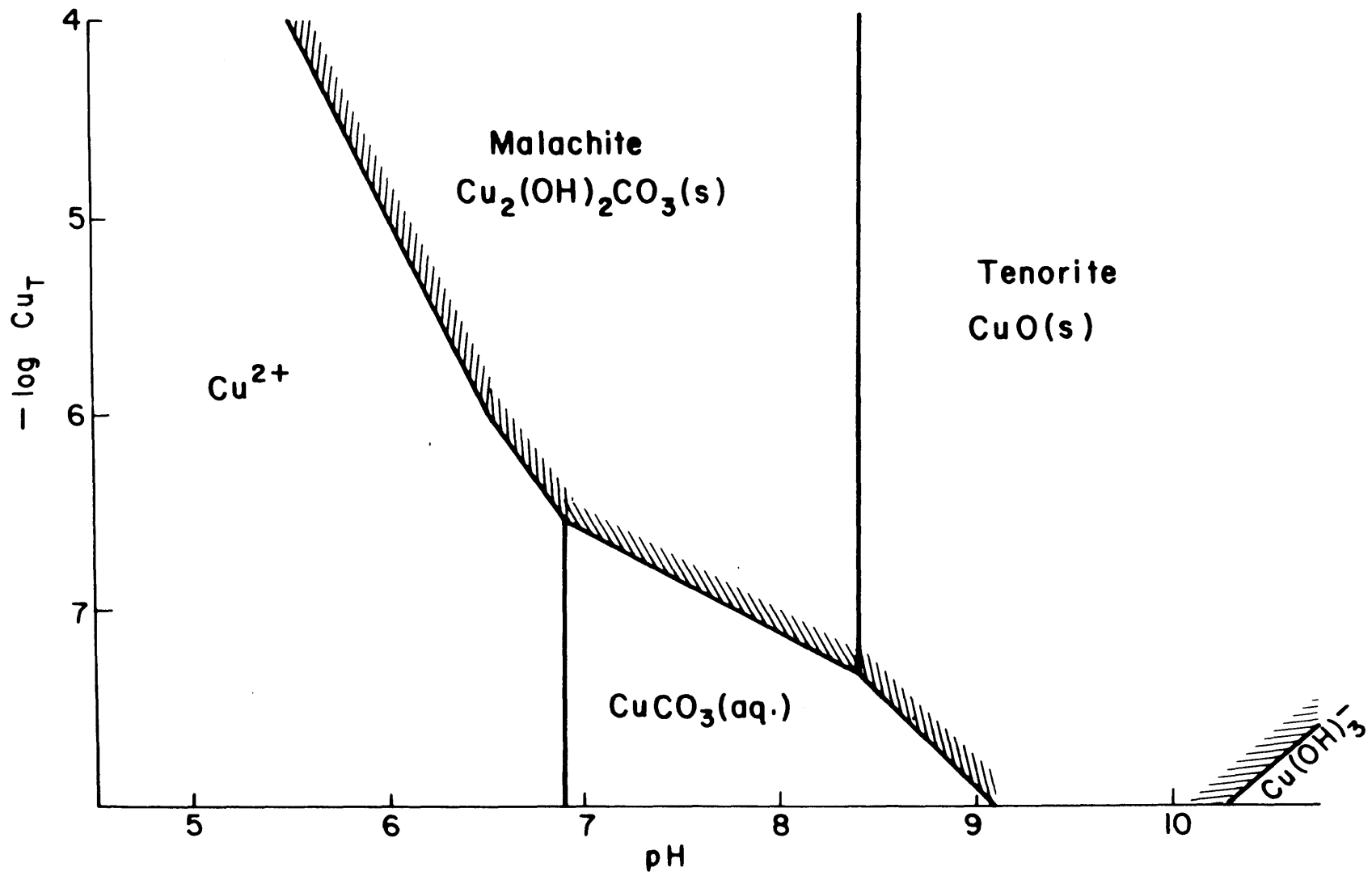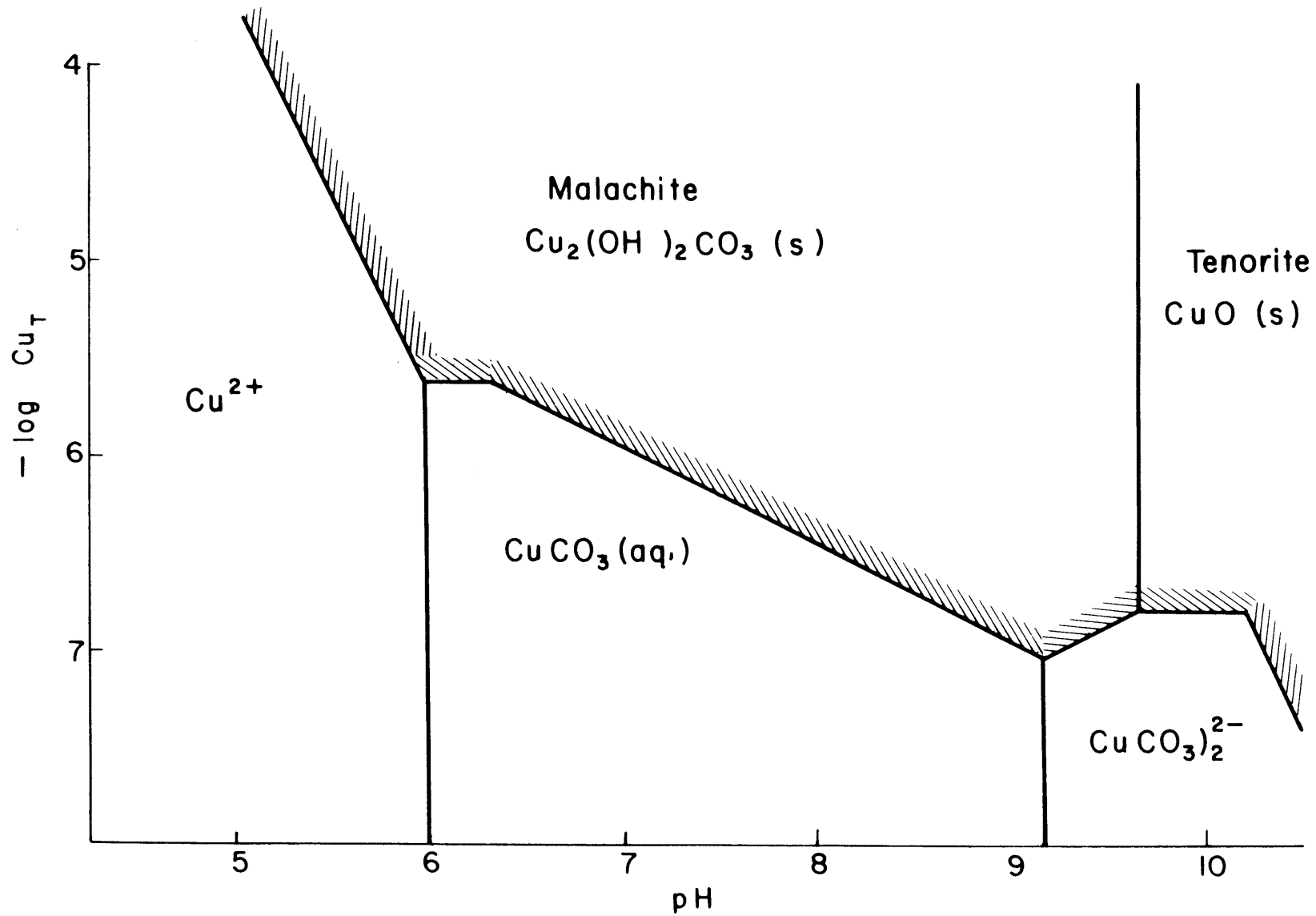
regions the major copper species are predicted to be carbonate

complexes, malachite and tenorite. These diagrams partially explain

the general need for higher $CuSO_4$ dosages in reservoirs with high pH

and alkalinity. At the higher carbonate concentration, soluble

$CuCO_3(aq)$ is the major copper species for a greater range of total

copper and pH. The importance of copper carbonate complexes in

natural waters was shown by Stiff (1970) and used by Andrew et al.

(1977) to explain the observation that copper was less toxic in hard

waters.

At both values of total carbonate, malachite is predicted to

precipitate in neutral or alkaline waters at total copper concentrations

that are commonly encountered in copper sulfate treatment of reservoirs.

The solubility constant for malachite used here (Smith and Martell

1976) is different from the one used in Stumm and Morgan (1970)

which accounts for the discrepancy between Figure 3-A and B and Figure

6-10 in Stumm and Morgan. This discrepancy is not significant compared

to the uncertainty associated with the time course of malachite

precipitation, which may take several days or longer (Stiff 1971). As

will be seen in Table II., malachite precipitation would result in

cupric ion activities several orders of magnitude less than the con-

centration of added copper.

The uncertainty about copper precipitates makes it difficult to

compare field data from copper sulfate treatment episodes with chemical

equilibrium calculations. Button et al. (1976) studied two $CuSO_4$

treatments of the Hoover reservoir in Ohio (pH 7.8 and alkalinity 96

mg/l). The added copper concentrations in the surface waters (1×10^{-5}

and 5×10^{-6}M) exceeded the solubility of malachite and the soluble

copper rapidly decreased to about 10^{-7}M over 24 hours. The particulate copper increased initially, and after 24 hours decreased to pretreatment levels at the surface and increased at 18 meters. Although this field data is consistent with the removal of copper from the surface by malachite precipitation, other explanations exist, for example uptake of copper by the dying populations of Melosira and Asterionella.

In another study the field data seem to be inconsistent with the control of the cupric ion activity by malachite precipitation. In Table II calculated cupric ion activities are compared with those measured with a cupric ion selective electrode following copper sulfate treatment of an alkaline farm pond in Manitoba (Whitaker et al. 1978). Here we see that even after two months the measured cupric ion activities were 4 to 5 orders of magnitude higher than those predicted by malachite precipitation. However the fact that the measured cupric ion activities are also greater than those predicted by $CuCO_3$(aq) formation, which is rapid, suggests that there may have been some interference in the measurements with the cupric ion electrode. In the other two field studies of $CuSO_4$ treatment episodes the solubility of malachite was not exceeded and the particulate copper either increased over a month (Elder and Horne 1978) or was much less than the soluble copper (Chapter III). Although far from complete, the data from the field studies are inconclusive regarding regulation of copper speciation by precipitation of malachite or tenorite during $CuSO_4$ treatments.

In reservoirs where the hypolimnion has become anoxic, precipitation of CuS (covelite) and Cu_2S (chalcocite) may become important (Sanchez and Lee 1978). Although precipitation of CuS(s) is unlikely

Table II

| Lake 885	measured total copper, $p(Cu_T)$	measured $p(Cu^{2+})$	calculated $p(Cu^{2+})$ with $Cu_2(OH)_2CO_3(s)$	calculated $p(Cu^{2+})$ with only $CuCO_3(aq)$
June 25 (initial)				
high (3000 μg/1)	4.2	4.9	10.1	7.5
medium (500 μg/1)	5.1	5.5	10.1	8.4
low (100 μg/1)	5.8	6.0	10.1	9.1
July 15				
high	5.0	5.4	10.1	8.3
medium	5.8	6.2	10.1	9.1
low	6.0	6.3	10.1	9.3

to be important in surface waters with abundant algal growth, it could determine the eventual fate of the added copper. Sulfide precipitation has been shown to control the low copper concentrations in Black Sea deep water (Spencer and Brewer 1971) and in hypolimnetic water from a copper mine tailing pond (Jackson 1978). Precipitation of CuS in the metalimnion may also be a mechanism for transport of soluble copper in the epilimnion to the sediments (Chapter III).

Organic complexation. The complexation of copper by dissolved organic compounds is even more difficult to predict since the nature of the organic compounds in lakewater and their copper-complexing properties are unknown. There are three categories of organic material in lakewater which may act as complexing agents: 1) low molecular weight compounds such as amino acids; 2) polymeric compounds such as polypeptides, polysaccharides and humic and fulvic acids; and 3) colloidal organic compounds and organic compounds which are bound to inorganic colloids (Stiff 1971; Stumm and Baccini 1978). It is not feasible to quantify the copper complexing properties of the individual organic compounds present in lakewater. The approach has generally been to determine the total complexing capacity by bioassay experiments (Gillespie and Vaccaro 1978; Gachter et al. 1978), by voltametric methods (Chau et al. 1974; Smith 1976) and potentiometric methods (Sunda and Hanson 1978; Chapter III). The advantage of potentiometric methods is that not only can the complexing capacity be determined but also the cupric ion activity as a function of total copper added. As was seen in the discussion of copper toxicity, the cupric ion activity is the critical parameter.

For organic complexation to be the dominant chemical process controlling the cupric ion activity during a $CuSO_4$ treatment, the added copper concentration must be less than or equal to the equivalent concentration of organic ligands. Gächter et al. (1973) estimated that $CuSO_4$ dosages of 1 mg/l (1×10^{-5}M) were needed in algal control in order to titrate the copper binding sites associated with the dissolved organic material in freshwater. Subsequent experimental results supports their hypothesis in some cases but not for reservoirs in general. Copper complexing capacities of freshwaters have been reported from 10^{-8} to 10^{-5}M. When these values are compared with the usual dosages of $CuSO_4$ (from 5×10^{-7} to 10^{-5}M), organic complexation would appear to be important only in lakewaters with high organic content. The rapid decrease in soluble copper in the Hoover Reservoir study (Button et al. 1976) implies that organic complexation was not significant compared to either precipitation or biological uptake. In the study of $CuSO_4$ treatment of farm ponds, the maintenance of soluble copper concentrations of the range of 10^{-6}M for several months could result from either carbonate or organic complexation. Similarly the high soluble copper concentrations 4 days after $CuSO_4$ treatment of Lake Perris (Elder and Horne) can be explained by formation of $CuCO_3$(aq) or copper-organic complexes.

Since the formation constants for $CuCO_3$(aq) and $Cu(CO_3)_2^{2-}$ are well known, measurement of the cupric ion activity will discriminate between inorganic and organic complexation. In the study of Mill Pond, potentiometric analysis showed that the cupric ion activity was definitely controlled by organic complexation. Both before and after treatment the soluble copper was recovered in the greater than

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Figure 4. Calculated cupric ion activity versus pH diagram for different concentrations of total copper and chelating agents in Mill Pond water: $(\cdots\cdots)$ $pCu_T=5$, $(----)$ $pCu_T=5$ and $pL_T=5.7$, $(\cdot-\cdot-)$ $pCu_T=6$, $(---)$ $pCu_T=7$, $(--\cdot---)$ $pCu_T=6$ and $pNTA=6$, $(——)$ $pCu_T=6$ and $pL_T=5.7$ and $(-\cdot\cdot-)$ $pCu_T=7$ and $pL_T=5.7$
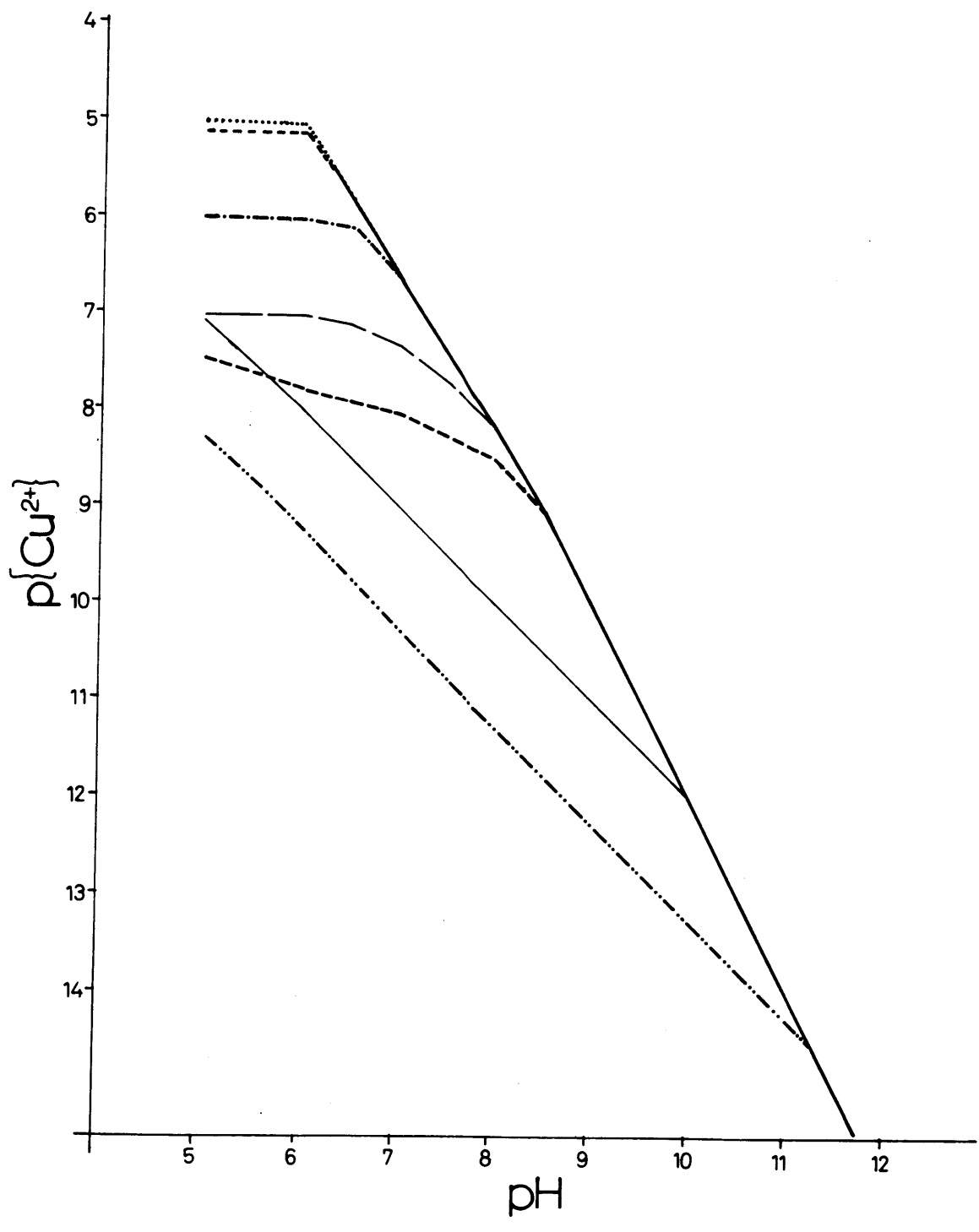
10,000 molecular weight size fraction. Organic compounds in this range correspond to large humic acids and colloidal material (categories 2 and 3). The source of these large molecular weight complexing agents was shown to be the Shawsheen River and these compounds are probably similar to complexing agents found in the Neuse and Newport Rivers by Sunda and Hansen (1979). Potentiometric methods were also used to analyse water samples from Spot Pond and Chestnut Hill reservoirs, both managed by the Metropolitan District Commission in Boston and treated with $CuSO_4$ on occasion. In both reservoirs the organic complexing capacity was below the detection limit (1 x 10^{-7}M) of the method and much less than the concentration of copper usually used in treatment. It follows that other processes, such as carbonate complexation, adsorption, or biological uptake, would regulate the cupric ion activity during treatment of these reservoirs.

Even in highly eutrophic reservoirs, the maximum equivalent ligand concentrations expected would be in the range of common $CuSO_4$ dosages. Therefore, unlike carbonate and hydroxide complexation, complexation by organic compounds can be saturated by addition of reasonable amounts of $CuSO_4$. In a reservoir with significant organic complexing capacity, a $CuSO_4$ dosage equal to or exceeding the complexing capacity is probably optimal. Titrating the organic ligand should give the maximum increase in the cupric ion activity for the minimum copper addition. Mill Pond is an example of this strategy; as a result of experience and coincidence, the added copper concentration was equal to the equivalence point of the copper titration of a water sample from the reservoir (Chapter III; Figure 4).

The presence of natural organic ligands may increase the effective-

ness of treatment by stabilizing the soluble copper and retarding

precipitation and adsorption. The stabilization of soluble copper,

"harnessing the elemental copper", has been the major advantage put

forth by proponents of synthetic copper chelates as algicides

(Annon 1976; Fair et al. 1971). Figure 4 presents the dependence of the

cupric ion activity on pH for different concentrations of copper and

synthetic or natural complexing agents with malachite precipitation

allowed. The same strategy of adding enough copper to titrate natural

ligands applies to synthetic ligands as well. Such synthetic

chelators as EDTA, NTA, and triethanolamine are likely to bind copper

more strongly than natural ligands such as humic and fulvic acids.

For the same concentrations of copper and ligand, the cupric ion

activity will be lower in the case of the synthetic chelating agents

(Figure 4). In fact, if the added copper is less than equimolar with

the added chelator, it is possible that the cupric ion activity will

be lower than before addition of the algicide.

Use of synthetic chelating agents has improved the control of

algal blooms primarily in hard water, alkaline reservoirs and lakes.

As can be seen in Figure VII, at complete equilibrium the addition of

chelating agents cannot yield cupric ion activities higher than those

allowed by malachite or tenorite precipitation. The advantage of

chelating the copper may lie in decreasing the degree of supersaturation

and therefore the rate at which equilibrium is approached in high pH

waters. Slower equilibration would result in maintenance of toxic

cupric ion activities and restricted algal growth for longer periods

after addition of the algicide. Because of the increased cost and

possible introduction of public health hazards, the actual changes in

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cupric ion activity caused by the use of synthetic copper chelates should be thoroughly assessed. Methods for determining the effects of chelators will be discussed in the following section.

Adsorption and biological uptake. Although there is a continuum from copper complexation by carbonate or simple amino acids to complexation by inorganic or organic surface groups, there are major differences in the transport rate of copper from surface water from one extreme to the other.

Adsorption has been shown to be an important process in the transport of metals to the sediments in aquatic environments (Collins 1973; Stumm and Baccini 1978). During a $CuSO_4$ treatment episode, the importance of adsorption will be determined primarily by the relative concentrations of copper and binding sites associated with the particulate matter. Organic detritus and hydrous oxides of silica, aluminum, iron and manganese have surface groups ($\equiv$ROH or $\equiv$MeOH) which can form surface complexes with copper (Stumm and Baccini 1978). Binding of copper by inorganic or organic surface groups is strongly pH dependent and becomes less significant at pH below $\approx$6 (Schindler et al. 1976). Adsorption is also dependent on the activity of the free copper ion in the surrounding medium; and will be less significant if the copper in solution is strongly complexed (Vuceta 1977).

Although adsorption and biological uptake are distinct processes they are discussed together for several reasons. Both processes are dependent on the pH and cupric ion activity in the external medium (e.g. Schindler et al. 1976; Sunda and Guillard 1976). It is not possible to make a priori generalizations about which process will be

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most important, especially when the plankton are a significant portion of the particulate matter. It is difficult, if not impossible, to analytically separate in a field sample copper that is adsorbed on clays, metallic hydroxides and dead plankton and copper assimilated by living plankton. Further confusion arises from the arbitrary definition of particulate copper as that retained on a .45 μm filter. From the perspective of controlling algal blooms, adsorption by clays, metal oxides and non-algal organic matter "detoxifies" copper, whereas uptake of copper by algae and adsorption on dead algal cells are processes associated with successful algal control.

The Hoover reservoir study is an example of the uncertainty surrounding particulate copper formation after $CuSO_4$ treatment. As mentioned earlier, the rapid (24 hrs.) formation and removal of particulate copper can be explained by malachite precipitation. However, the subsequent disappearance of particulate copper from the surface waters and accumulation at depth matched the distribution of diatoms and frustules, suggesting biological uptake as the dominant process. If so, the copper could have been assimilated by live diatoms which then died from excessive intracellular copper levels, or the diatoms could have died immediately and the added copper has been adsorbed on the silica frustules of the dead cells. A third alternative is adsorption of copper by clays, hydrous metal oxides, or other organic matter such as bacteria, fecal matter, and zooplankton exoskeletons. The point here is that none of these processes can be ruled out by theoretical arguments or by simple analysis of the particulate copper. The same statement holds for the field studies of Perris Lake (Elder and Horne 1978) and farm ponds in Manitoba (Whitaker et al. 1978).

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The Mill Pond $CuSO_4$ treatment (Chapter III) is an example in which complexation by large molecular weight humic acids was more important than adsorption. The particulate copper was always an order of magnitude lower than the soluble copper; and the increase in particulate copper ten days after treatment appeared to correspond to uptake by copper tolerant green algae.

Accumulation of copper in the sediments. Many of the chemical and biological processes important in $CuSO_4$ treatments will transport copper from the surface waters to the sediments. These processes include precipitation, adsorption, and biological uptake. The limited data on the toxicity of copper to benthic organisms has already been discussed. There are also limited quantitative data on the enrichment of copper in sediments from $CuSO_4$ treatment. Frost (1965) mentions that in measurements of copper in New Hampshire lake sediments the concentration of copper was not correlated with a history of $CuSO_4$ treatment. Paleolimnological techniques were used by Brugam (1978) to study the sediments of Linsley Pond in Connecticut, which had been treated once with $CuSO_4$ in 1938. There was no evidence of increased copper deposition in 1938. In fact, the deposition of copper was highest in terms of mg/g mineral matter from 1900 to 1920, when Bordeaux mixture (lime and $CuSO_4$) was used as a pesticide on apples. In a study of the environmental chemistry of copper added to Lake Monona (1.5×10^6 lbs over a 30 yr period), Sanchez and Lee (1979) found the sediments to act as a sink for the added copper. Peak copper concentrations (600 mg/kg dry matter) were found at 60 cm depth. Since $CuSO_4$ treatment has been discontinued, new sediments have

covered the copper enriched sediments. In both Lake Monona and

Linsley Pond copper concentrations in recent sediments (250 and 180

mg/kg dry matter) are higher than in sediments from the turn of the

century (50 mg/kg) even though $CuSO_4$ is not currently being used in

either lake. Clearly, the accumulation of copper in reservoir sediments

should be the subject of further research.

Future of copper sulfate as an algicide. Recently Illinois has lowered

the drinking water standard for copper from 1 mg/l to .02 mg/l.

The new standard appears to be based on the laboratory data for toxicity

of copper to fish and not on any epidemilogical studies of the possible

toxicity of copper to humans, which by this time should be possible.

The new standard is below the current effective treatment dosages for

$CuSO_4$, and yet the control of algae is necessary in Illinois water

supplies. Also, the Department of Environmental Protection in the

State of Maine has recently recommended the discontinuance of the use

of copper sulfate in Maine. Their reasons are summarized: "1) copper

compounds are extremely toxic, non-selective, and non-biodegradable...

2) extensive use of copper sulfate has resulted in no long term control

of nuisance algae. Improper applications have resulted in problems...

3)...copper presents a potential hazard...as a result of copper

accumulated in sediments and aquatic organisms..4)...the possible harm...

outweighs any short term cosmetic benefits" (Anon 1976).

These statewide policies ignore several of the advantages of

$CuSO_4$ over other potential algicides. Copper is an ecological "known",

treatment increases its concentration 2-3 orders of magnitude above

background for short periods (days-months). Further, the chemical and

biological processes which regulate the effect and fate of copper in aquatic environments are well understood and can be followed in the field. There is no need to make statewide decisions based on incomplete laboratory experiments, which may not be relevant to a given reservoir because of differences in copper chemistry and copper sensitivity. With appropriate field data (pH, alkalinity, soluble and particulate copper and phytoplankton speciation) a sound decision can be made on whether to discontinue treatment or reduce dosages.

The recommendations against $CuSO_4$ treatment also seem to be based on the erroneous assumption that potable, and palatable drinking water is an unnecessary luxury. The prompt complaints by the public about unusual tastes and odors in tapwater contradicts this assumption. Algal blooms are most likely to develop during the summer, when community water demands are high and water reserves are low. A non-treatment policy risks shut-down of water treatment plants during the critical summer months.

The use of organic algicides and their associated public health hazards are discussed in Appendix I. Beyond the public health issue there is no evidence that new organic algicides will be less harmful to non-target aquatic organisms than copper sulfate. In contrast to copper, most "hard organics" are ecological "unknowns" and previous experience (i.e. DDT) suggests that their impact may be cumulative. Further, it is much more difficult to analyze water samples for trace organic compounds and their degradation products than for copper. It is not feasible to conduct field studies of treatments with Silvex (2[2,3,5-trichlorophenoxy] propionic acid), which could be compared with the field studies of $CuSO_4$ treatments discussed previously.

Potential for improvements in copper sulfate treatment practices. Just
because detailed field studies are feasible does not mean that they would
be worthwhile. Application of low $CuSO_4$ dosages (>100 ppb) when algal
counts and weather conditions indicate an incipient nuisance algal bloom
is currently the treatment strategy followed by water supply managers in
the Boston metropolitan area and in many other localities (Faucher 1978).
From the previous discussion it is concluded that this strategy is
optimal, providing algal control with minimal impact on other aquatic
organisms and without risking inadequate water supply to the public.
The success of this strategy depends on the ability of water supply
managers to anticipate nuisance algal blooms. The best guide here is past
experiences at the specific reservoir and frequent and detailed algal
counts. At reservoirs where the optimal strategy is effective, it is
unlikely that more complete understanding of the copper chemistry would
lead to major changes in how or when copper sulfate is applied.

It may be possible to successfully control algal blooms with
copper concentrations as low as 10 ppb. Such low dosages are most
likely to work in acidic, soft water reservoirs. However the advantage
of the carefully timed "surprise attack" may be lost by treating with too
low a dosage. Much higher concentrations may have to be used later on to
break up a fully developed algal bloom.

Detailed study of the chemistry and biology of copper may help
improve treatment practices in reservoirs where the optimal "single shot"
strategy is not practiced or does not provide adequate algal control.
There are several reasons why infrequent application of low quantities
of $CuSO_4$ could be inadequate. One is failure to predict algal blooms
from patterns of algae growth in the reservoir. The ecology of blue-green

algae--the most common nuisance algae--is very complex (Whitton 1973) and no one parameter can reliably predict a bloom.   In some cases predictions may be improved by measurements of major nutrients such as nitrate, ammonia, phosphate and silicate.

The two other reasons why low $CuSO_4$ dosages ($\geq$ 100 ppb or 10^{-6}M) may be ineffective are that: 1) the dominant nuisance algal species in the reservoir can tolerate cupric ion activities of the order of 10^{-6}M and 2) "detoxifying" chemical processes (precipitation, complexation, adsorption) control the chemistry of low copper additions such that cupric ion activities are low ($<10^{-10}$M).   Experimental methods based on potentiometric measurements of cupric ion activity can be used to determine the copper tolerance of the nuisance algal species and to identify the important chemical processes controlling copper speciation (as in Chapter III).   In large reservoirs with serious algal problems, these advanced methods and detailed field studies may be beneficial. If the problem is rapid adsorption of copper and loss to the sediment, use of synthetic chelating agents may be worthwhile.   However, if the problem is copper tolerant algae, synthetic chelating agents are unlikely to improve algal control, and more precise timing of $CuSO_4$ treatment, destratification, or reduction of nutrient inputs to the reservoir, may be necessary.

Proposed experimental procedures.   In the following section experimental procedures are outlined which could be carried out in a laboratory with standard equipment and access to an atomic absorption spectrophotometer for copper analyses.   As greater demands are placed on marginal water supplies where copper sulfate treatment is ineffective or requires high

dosages, the data from such experiments may be necessary to upgrade

algal control practices. These experiments will not provide quick,

precise answers as to how much copper sulfate to use but will help

identify the important processes regulating the effectiveness of copper

sulfate treatment in a reservoir. The optimal strategy will still

include carefully following the growth of algal populations and treating

with copper sulfate just when rapid growth of a nuisance algal species

is observed. Because time spent doing experiments at that critical time

would jeopardize the success of the treatment, these experiments are seen

as being carried out one summer and used to improve treatment practices

the next summer.

Copper sensitivity of nuisance algal species. The suggested experiments

presented here are scaled down from the ones presented in the study of

Mill Pond (Chapter III). The design presumes knowledge of the important

nuisance algal species in the reservoir from previous experience. The

first step is to obtain unialgal cultures of these species when they are

first observed in the plankton. Although sterilization of medium is

advisable, there is no need for axenic cultures. A small degree of

contamination with another algal species can also be tolerated if the

experiments are done promptly. Techniques for isolating algae are

described by Guillard (1973; Hoshaw and Rosowsik 1973; Allen 1973).

The best medium for isolating nuisance algal species is filtered (.4 µm)

reservoir-water enriched with nitrate, phosphate, silicate (for diatoms)

and trace metals without EDTA or NTA (see Guillard 1975 for suggested

concentrations of nutrients). Cultures can be grown on a sunny laboratory

bench; temperature regulation is only necessary for species isolated in

the early spring. Some species are more easily cultured than others.
If a viable culture can not be obtained, the experiments may have to be
redesigned to use concentrated phytoplankton samples from the reservoir.

The second step is to determine the cupric ion activity as a function
of total copper added to reservoir water and filtered, nutrient enriched
reservoir water. This determination requires a cupric ion selective
electrode, a reference electrode, pH electrode and a pH meter. All are
standard equipment except the cupric ion electrode which can be purchased
for less than $500. The detection limits of cupric ion electrodes
(10^{-7}M total copper) are equal to the lowest practical copper sulfate
dosages (1×10^{-7}M). The electrode should be standardized in copper
standards at pH 4 (see Chapter I for details). A suggested series of
total copper additions is 1×10^{-7}, 5×10^{-7}, 1×10^{-6}, 2×10^{-6},
5×10^{-6}, 1×10^{-5} and 2×10^{-5}. The pH should be maintained at the pH
of the reservoir for all copper treatments. The signal from the cupric
ion electrode can be converted to cupric ion activities using the Nernst
equation:

$$E_h = E_o - \alpha \log (Cu^{2+})$$

where $\alpha = \dfrac{RT}{ZF} = 29.5$ mv for copper. The measurements in the standard
copper solutions should fall within $27 < \alpha < 31$ mv/decade. It is important
to wait unitl the signal has become stable (Δmv < 2 mv/hr) before record-
ing the measurements. Failure for the signal to stabilize may indicate
slow precipitation and measurement of particulate copper would be informa-
tive. A log-log plot is made of cupric ion activity ($\{Cu^{2+}\}$) versus
total copper added (Cu_T) for both filtered and unfiltered water. The line
$\{Cu^{2+}\} = Cu_T$ is included for reference. Significant differences between

filtered and unfiltered samples indicate that either adsorption or biological processes are important. The electrode techniques are not simple but are at least straight forward and are preferable to calculating the cupric ion activity from chemical equilibrium models.

The next step is to measure the growth of the nuisance algal species in filtered reservoir medium with four or five evenly spaced cupric ion activities, from 0 to 1×10^{-6}M added copper. Clean glassware should be used; but at these copper concentrations there is no need for exacting trace metal clean techniques. Replicate cultures at each copper addition are made and inoculated with the nuisance algal species. Growth is monitored daily for 5-10 days by either cell counts, optical density, chlorophyll a, dry weight or other convenient biomass measurement. At the end of the experiment a final {Cu^{2+}} measurement is recommended. It may also be worthwhile to filter some of the cultures and measure the copper that has been assimilated by the cells (see Chapter III). The growth rate is then computed from the growth curves (Guillard 1973) and plotted as a function of the negative logarithm of the cupric ion activity (p{Cu^{2+}}; see Figure 18 in Chapter III).

From the results of these experiments sound decisions can be made about changes in $CuSO_4$ treatment practices at the reservoir. The cupric ion activity which will prevent a bloom of the nuisance algal species with minimum impact on non-target organisms will be about twice the cupric ion activity of the breakpoint of the growth rate (μ) versus {Cu^{2+}} plot. The corresponding copper addition can be taken from the plot of {Cu^{2+}} versus added copper in unfiltered reservoir water, and that value can be used to compute how much copper to add to the reservoir during treatment.

The relationship between growth rate and $\{Cu^{2+}\}$ is not expected

to change much from year-to-year for the same algal species. However,

the chemistry of the water in the reservoir may change during a spring/

summer season and from year-to-year. The determination of $\{Cu^{2+}\}$ for

different copper additions in unfiltered samples is not a lengthy

procedure and it should be repeated a week or so before an anticipated

$CuSO_4$ treatment if time permits.

There are several possible combinations of copper tolerance of

nuisance algal species and copper speciation in reservoir water and

these are represented schematically in Figures 5, 6 and 7.

Copper-tolerant algae. The graph of μ/μ_{max} versus $p\{Cu^{2+}\}$ in Figure 5

is meant to be representative of copper tolerant algae, similar to the

species of Nannochloris and Ourococcus which replaced Ceratium in Mill

Pond reservoir after $CuSO_4$ treatment (Chapter III). The algae isolated

from aquatic environments contaminated by copper from mining operations

(Stokes et al. 1973; Foster 1979) may have similar copper tolerance.

A - The plot of $p\{Cu^{2+}\}$ vs. pCu_T is representative of acidic,

soft waters (pH < 6.2; alkalinity < 5×10^{-4}M) where complexation and

adsorption of copper is minimal. The arrow on the plot points to 10^{-5}M

(< 1 ppm) the dosage of copper sulfate that is likely to control the

growth of this hypothetical copper-tolerant nuisance algal species. This

dosage is at the high end of those currently in use and may be toxic

to many non-target aquatic organisms. In general, however, a temporary

decrease in Daphnia populations is an acceptable cost for potable water.

However, the need to use high dosages dictates considerable caution on

the part of the water supply manager to avoid unnecessary $CuSO_4$ treatment.

Figure 5. Relationship between **copper** sensitivity of nuisance algal species and dosage of copper sulfate for three representative freshwaters: Copper tolerant algae.

Copper tolerant

DOSAGE
($CuSO_4$, M)

A. 10^{-5}

B. 10^{-5}

C. Not feasible
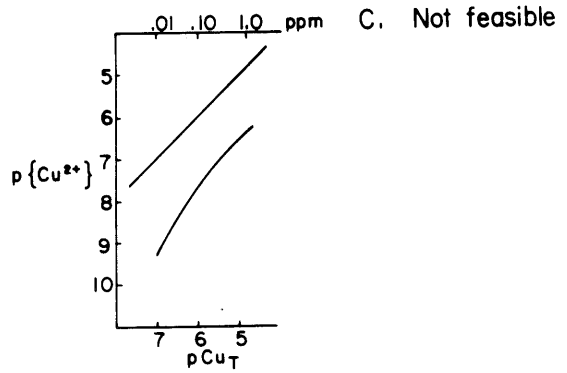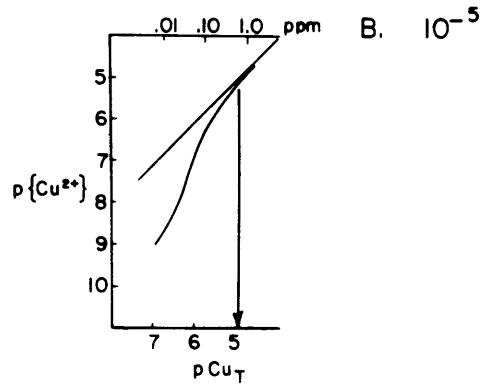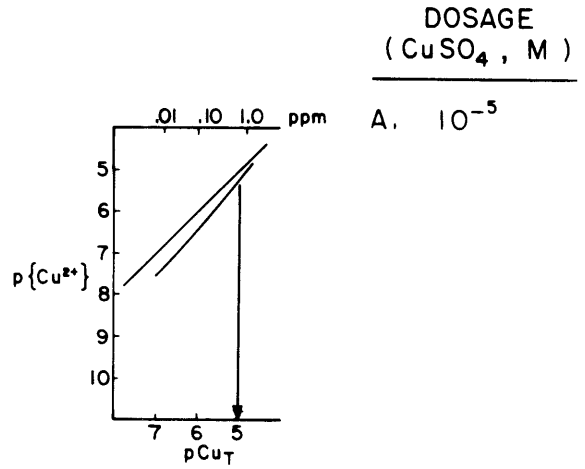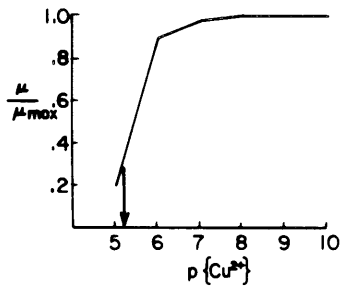
B - Here the plot of $p\{Cu^{2+}\}$ vs. pCu_T represents reservoirs similar

to Mill Pond, with micromolar copper complexation/adsorption capacity,

neutral pH and moderate alkalinity ($5 \times 10^{-4}M$). In the case of a copper

tolerant nuisance alga, the toxic cupric ion activity is beyond the

complexing capacity of the water. Therefore the amount of $CuSO_4$ needed

to control its growth is no different from that needed in an acidic

reservoir, and the same caution against unnecessary treatments applies.

C - Hard water, alkaline reservoirs (pH 8, alkalinity = $10^{-3}M$)

with moderate copper complexation/adsorption capacities are represented

by this plot of $p\{Cu^{2+}\}$ versus pCu_T. $CuCO_3$(aq) is assumed to be the

major copper species at the higher copper concentrations. If the dominant

nuisance alga species in such a reservoir is not inhibited by cupric ion

activities near $10^{-6}M$, it will not be feasible to control its growth

by $CuSO_4$ treatment. In fact it will not even be possible to observe copper

inhibition in a medium based on water from the reservoir. Clearly these

results would mandate another method for algal control besides treatment

with $CuSO_4$. Some alternatives are reduction of nutrient inputs to the

reservoir, use of inorganic algicides such as potassium permanganate,

destratification, or acidification (Shapiro et al. 1975).

Algae with intermediate copper-tolerances. Algae that are somewhat more

copper tolerant than Pandorina morum, Chlorella pyrenoidosa and Monochrysis

lutheri (Figure 1) are represented by a copper toxicity threshold of

$10^{-7.5}M$ (Figure 6). Since so few freshwater algae have been studied in

these terms, it is not known whether or not this graph is typical for

freshwater algae. This hypothetical nuisance alga is interesting because

the concentration of added copper needed to control its growth varies

Figure 6. Relationship between copper sensitivity of nuisance algal species and dosage of copper sulfate: Algal species with intermediate copper tolerances.
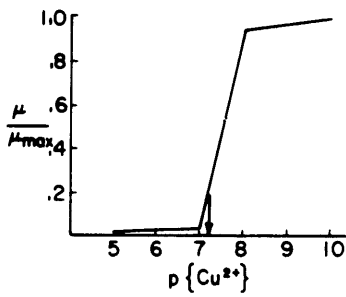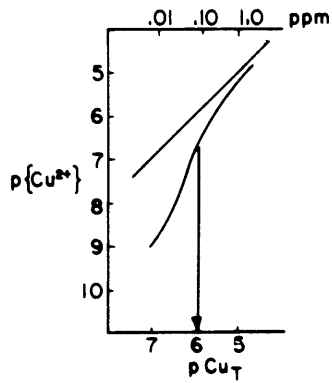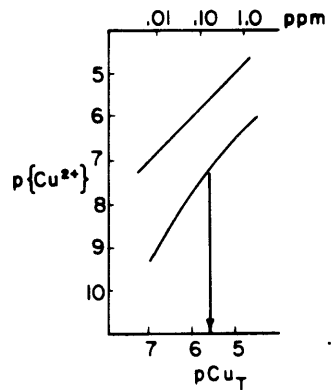
DOSAGE
(CuSO$_4$, M)

D. 3 x 10^{-7}

E. 1 x 10^{-6}

F. 3 x 10^{-6}
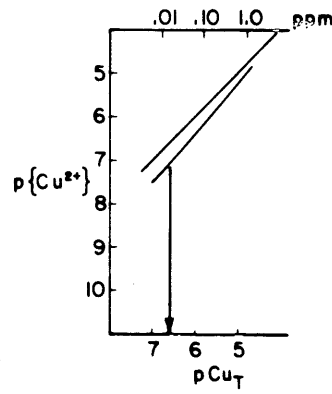
INTERMEDIATE COPPER

SENSITIVITY

significantly.

D - In a softwater, acidic reservoir an added copper concentration of $\underline{ca}$. 2 x 10^{-7}M (15 ppb) should prevent a bloom of this nuisance alga. If a much higher dosage is currently being used in the reservoir, it would be advisable to reduce the dosage incrementally (by about 50% each treatment). It is possible that studying copper toxicity in flasks on a lab bench has eliminated some phenomena, such as migration, which decrease the susceptibility of the algae to copper toxicity. Decreasing the $CuSO_4$ dosage from 1 x 10^{-5}M to 2 x 10^{-7}M all at once would risk inadequate control of the nuisance alga.

E - In reservoirs with micromolar complexing capacity, enough copper should be added to titrate the ligand. If prescribed copper concentration near the equivalence point are used, small losses of copper from solution will result in large decreases in cupric ion activity and correspondingly large increases in the growth rate of the nuisance alga. This is why the dosage recommended in case E is 1.3 x 10^{-6}M and not 8 x 10^{-7}M. Gambling on the lower dosage maybe worthwhile though since there would be less of an impact on non-target organisms.

F - For the hardwater, alkaline reservoir the prescribed $CuSO_4$ dosage is $10^{-5.6}$M. This copper concentration is on the boundary between $CuCO_3$(aq) and malachite precipitation. If malachite precipitation is slow the cupric ion activity should be maintained at toxic levels for at least several days, long enough to prevent the developing algal bloom. Again, incremental reductions in dosage are recommended if much higher dosages are currently being used.

If the $\underline{Aphanizomenon}$ species studied in Lake Perris (Elder and Horne 1978) had a copper tolerance similar to this hypothetical alga, we can
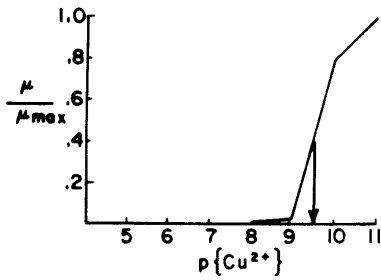
Figure 7. Relationship between copper sensitivity of nuisance algal species and copper sulfate dosage: Copper sensitive algae.
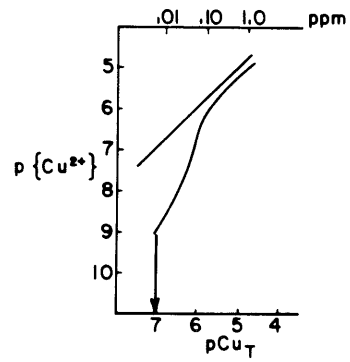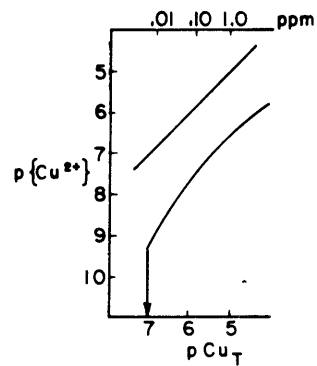
DOSAGE
(CuSO$_4$, M)

G. 1 x 10^{-7}
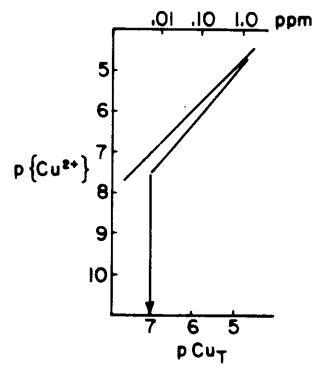
Copper Sensitive

H. 1 x 10^{-7}

I. 1 x 10^{-7}

see that if the copper speciation in Lake Perris was similar to either

case E or F, effective control would not be obtained with the 10^{-7}M copper

dosage that was used. In fact, an increase in the _Aphanizomenon_ population

in Lake Perris was observed four days after treatment.

Copper sensitive algae. Completing the discussion, nuisance algae that

tolerate only very low cupric ion activities (10^{-10}M) are considered

in Figure 7. These experiments will probably only be carried out in

reservoirs where effective algal control has not yet been achieved.

Relatively few extremely copper sensitive algal species are anticipated,

since the growth of these species is probably being adequately controlled

with current copper sulfate treatment practices.

The recommended $CuSO_4$ dosage (1×10^{-7}M) does not change with the

chemistry of the reservoir. It is assumed that 10^{-7}M is the lowest

concentration that can be applied uniformly to a reservoir. Where burlap

bags of $CuSO_4$ crystals are dragged in a motorboat this is certainly true.

In the acidic reservoir, a dosage of 10^{-7}M results in a cupric ion

activity over an order of magnitude greater than the toxicity threshold.

In the other two examples the resulting cupric ion activity is only

slightly higher than the threshold. No great ecological benefit would

be anticipated from applying even lower quantities of $CuSO_4$. Most

aquatic organisms should be able to tolerate cupric ion activities below

10^{-9}M, since these activities are probably typical of natural aquatic

environments.

Precipitation and adsorption. Ineffective treatment because of rapid

decreases in soluble copper caused by either precipitation or adsorption

was not considered in the above discussion. The analytical problems

associated with particulate copper have already been mentioned. If

precipitation or adsorption are important, significant particulate

copper should be detected if the samples are filtered after measurement

of cupric ion activity with the electrode. Use of chelated copper

compounds may improve the effectiveness of treatment, but only if the

nuisance algal species are moderately sensitive to copper (Figures 6 and

7).

Conclusions. Copper sulfate has been the algicide of choice since 1905.
Consideration of alternative algal control methods and the chemical
and biological processes acting in a $CuSO_4$ treatment episode does not
point to major changes in the engineering practice of copper sulfate
treatment of drinking water reservoirs. Experiments characterizing the
copper tolerance of nuisance algae and the copper chemistry of reservoirs
may result in reduction of copper sulfate dosages from $10^{-5}M$ to 10^{-6} or
$10^{-7}M$ in some reservoirs. Further improvement could come from better
prediction of algal blooms by water supply managers. The
most obvious change in copper sulfate treatment practices will probably
be increased application of the $CuSO_4$ from motorboats equipped with pumps,
mixers and sprayers which dispense the copper more rapidly than dragging
burlap bags filled with $CuSO_4$ crystals. Although special equipment may
seem less anachronistic than burlap bags, the benefits are mainly in
economy and convenience and not in effectiveness of treatment. In our
technological age, the assumption tends to be that there is a better way
to do everything. The control of algae blooms by treatment with copper
sulfate, a technology which has not changed much in fifty years, may be

one example where this assumption does not hold true.

Appendix I

Abstract

In a survey of forty state water control agencies, copper sulfate
was found to be used to control nuisance algal blooms, either on a routine
or occasional basis, by almost every state (Muchmore 1976). Only four
state agencies reported any harmful effects on aquatic environments.
In the following appendix the use of copper sulfate is reviewed. The
disadvantages, both real and hypothetical, of copper sulfate treatment
are discussed and compared with those of alternative algal control methods.
Based on its long history of successful use and absence of long term
toxic effects, it is concluded that copper sulfate remains the algicide
of choice for most nuisance algal blooms.

A. Need for algal control measures.

In order to manage successfully water supply reservoirs and multiple use water systems, it is necessary to prevent or control the growth of nuisance algae. Blooms of nuisance algae can interfere with the operation of a water supply in several ways. The most common problem is with tastes and odors that reduce the palatability of the water. There are three major classes of odors: 1) Aromatic, caused by diatoms (e.g. Asterionella, Synedra); 2) Grassy, caused by cyanophytes (e.g. Anabaena, Aphanizomenon); and 3) Fishy, caused by some diatoms, green algae, chrysophytes and dinoflagellates (e.g. Tabellaria, Pandorina, Volvox, Dinobyron, and Ceratium) (Hale 1954). Most species cause taste and odor problems at cell densities on the order of 10^3/ml; however, a few species, such as Synura, can cause problems at very low densities (<1 cell/ml). Chlorination of the water may liberate noticeable tastes and odors at lower cell densities. Abundant algae may make drinking water turbid and cause scums to form. Buoyant algae, such as bluegreens, can cause distressing surface films. Another problem caused by algal blooms is the clogging of filters in municipal and industrial water treatment operations. Presence of algae in the water may also interfere with manufacturing processes, such as those for paper, dye stuffs, photography and laundries.

In lakes and reservoirs where the major water uses are recreational or agricultural, copper sulfate treatment may be desirable. At the extreme, some algal blooms are toxic to fish, and others may be harmful to man, domestic animals or wildlife if ingested (Fitzgerald 1963; Shilo 1964; Bartch 1967). Extensive algal growths will decrease such recreational uses as swimming and boating. The decomposition of dense algal blooms may result in anaerobic conditions that deplete fish populations.

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The noxious odors that may be released during decomposition may drive away vacationers; for example, the release of hydrogen sulfide may be sufficient to discolor paint on lakeshore residences.

In many recreational lakes growth of aquatic macrophytes may be perceived as more of a nuisance than planktonic algal blooms, and there may be some tradeoffs between the two nuisances. Organic herbicides, such as Silvex, are used more frequently than copper sulfate to control aquatic macrophytes (Annon. 1976). However, copper sulfate is used in the midwest to control aquatic plants in water distribution and irrigation systems which may interfere with delivery of water and maintenance activities (Bartley 1976).

Copper sulfate has been used successfully to control algal growth and to deal with the problems mentioned above. Copper sulfate is currently the only algicide registered with the Environmental Protection Agency for use in drinking water supplies (Jackson 1974) and the treatment of water reservoirs with copper sulfate is extensive. In a survey of forty states, eleven (mainly midwestern) states reported routine use of copper sulfate in most of their water supply reservoirs, and twenty-four reported occasional copper sulfate treatment (Muchmore 1976). Although copper sulfate is not the ideal algicide, it has been and still is the best available algicide for general use (MacKenthuen 1959; Hale 1954; Sledikova and Sladecek 1968; Gratteau 1970; Prows and McIlhenny 1973; Muchmore 1976; Otto 1977). The major advantages of copper sulfate are its effectiveness at concentrations below the federal drinking water standard of 1 mg/l (for most other potential algicides drinking water standards do not exist), its low cost and long history of successful use. Copper sulfate treatment of drinking water is not considered to be a threat to

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public health. The quantity of copper ingested with drinking water will not be greater than the 3-5 mg copper in the normal diet (Tuwiner 1976). For these reasons, copper sulfate is predicted to be the algicide of choice for the next 25 to 50 years (Otto 1977).

B. Copper sulfate treatment practice.

Although some reservoirs, especially in the Midwest, are treated with copper sulfate routinely (3-4 times) during the spring and summer, most reservoirs are treated only when algal counts or other observations indicate the development of a nuisance algal bloom. Algal blooms are most likely to cause problems during late spring and late summer. The optimum time for dosing with $CuSO_4$ is when populations of nuisance algal species, such as Anabaena or Aphanizomenon, are increasing but have not reached nuisance densities. If $CuSO_4$ is applied before rapid algal growth has begun, repeated applications may be necessary to prevent a bloom. Once nuisance algal blooms have developed, they may be eliminated by $CuSO_4$ treatment but undesirable odors and anoxic conditions may result from decomposition of the dead plant material. Much of the success of a copper sulfate treatment is determined by the water supply operator's ability to anticipate algal blooms. Besides monitoring the concentrations of nuisance algal species in the reservoir, the decision whether and when to apply $CuSO_4$ is based on previous experiences managing the reservoir, guidance from state officials and guesses about the weather and upcoming water needs of the community. The time between the decision to treat a reservoir and the actual application of $CuSO_4$ is generally on or two days.

Besides when to apply $CuSO_4$, the other critical decision is how much $CuSO_4$ to apply. In general, the dosage rate of copper sulfate required

to control algal growth depends upon the chemistry of the water and the

species of algae (Steeman Neilsen and Kamp Larsen, 1976). Alkalinity,

pH, temperature, dissolved organic matter and suspended particulates

can influence the solubility and the dosage rate of copper sulfate

used by water supply operators. The environmental chemistry of copper

in freshwater and implications for improved $CuSO_4$ treatment practices

has been discussed quantitatively in Chapter IV. Moore and

Kellerman (1905) initially attempted to prescribe definite dosage rates

in terms of ppm or lbs per million gallons for seventy algal genera.

Their recommendations have been reprinted extensively with modifications

(Hale, 1954). The dosages range from .05 ppm for Uroglena and 10 ppm for

Pandorina and Eudorina, with dosages between .5 and .1 ppm applicable to

most species (Hale, 1954). Because of variability in the chemical and

physical properties of the water to be treated, the application of such

tables has been found to be impractical in many cases. Doubling the

prescribed dosage for a given alga at alkalinities above 40 ppm (Fair et al.

1971) and in the winter (Hale, 1954) has been suggested. Increasing

the dosage by 5% for every 10 mg/1 of alkalinity (as $CaCO_3$), by 2% for

every 10 mg/1 of organic matter present, and using a temperature

correction based on a Q_{10} of 1.3 are recommended by Fair et al. (1971).

MacKenthuen (1959) reports that "rather arbitrary" dosages that

seemingly ignore different sensitivities of algal species to copper have

been used successfully in the midwestern states. The strategy is as

follows: lakes having an alkalinity greater than 40 ppm are treated at

a dosage of 1 ppm copper sulfate for the upper 2 ft of water regardless

of actual depth. Lakes having an alkalinity of less than 40 ppm are

treated with .3 ppm for the total volume of water. The apparent paradoxes

in this treatment strategy can be explained. In alkaline lakes, signifi-

cant concentrations of ionic copper will only occur in the upper layers,

where fortunately most of the phytoplankton are found. In more acidic

lakes the copper will reach a greater depth before precipitation, and

filamentous species, mainly blue-greens, that may lie near the bottom may

be the most important species to control.

The general treatment dosages used are between 2 ppm and .2 ppm

for certain depth of the lake or reservoir for certain periods of time

ranging from continuous to prior to or during blooms of a nuisance alga

(MacKenthuen 1959; Gratteau 1970; Hale 1954; Muchmore 1976). The

dosage rate and the corresponding total amount of $CuSO_4$ to be

applied to the water body is usually decided upon by local personnel with

the guidance of state officials, published recommendations as have been

cited here, and their own personal experience. The size of the crystals

used is another important parameter in the effectiveness of treatment,

and these decisions are also made locally (Otto 1977).

Treatment may either be marginal or complete, depending on the

physical properties of the lake, the magnitude of the algal problem, and

cost. Marginal treatment is designed for temporary relief in a restricted

area. Copper sulfate is applied to a 200 to 400 ft. wide strip along

the shore. Complete treatment involves application of copper sulfate

over the entire water body in a short time period. One to three complete

treatments in a spring-summer season may adequately control algal

growth (MacKenthuen 1959). A third strategy is continuous addition

of copper sulfate to the inflows to the lake or reservoir (Hale

1954). In irrigation and water distribution canals, continual inflow or plug flow additions successfully control aquatic pests (Bartley, 1976).

Several methods are used to apply copper sulfate. Dragging burlap bags of $CuSO_4$ crystals behind rowboats or powerboats is the common low cost treatment method for smaller lakes or reservoirs. Liquid spraying systems operated from powerboats are somewhat more expensive but are becoming the most commonly practiced methods. Dry feeding systems are also used, as well as liquid and dry application from crop dusting planes (MacKenthuen, 1959). One problem in the application of copper sulfate is its highly corrosive nature, and proper care of equipment must be taken. Several spatial strategies have been recommended for small and large reservoirs. Uniform and rapid distribution is the major design criterion for all application methods.

Nearly half the cost of treatment is commonly associated with the physical application of the copper sulfate. Treatment at too low a dosage rate to control the nuisance algae is therefore very costly, since the entire treatment process will then have to be repeated at a higher dosage rate. Furthermore, algal populations may increase to nuisance levels before another dose of $CuSO_4$ is applied. The economic benefits from using the minimum amount of copper sulfate necessary to control an algal nuisance are relatively low, while risks are high. Also, as can be seen from the previous discussion, a local operator has no available technique for precisely calculating the minimum dosage required with any certainty. This fact, combined with practical considerations, results in a probable application of greater copper sulfate dosages than are necessary to control algal growth in many instances.

Recently, several products which stabilize the copper ion and thus delay precipitation, have been recommended for use in conjunction with copper sulfate in high pH, high alkalinity lakes (Fair et al., _Applied Biochemists_, Inc., 1976). Examples of these compounds are cupric chloramine, Cutrine[R] (a copper-trithanolamine chelate), and a copolymer of ethyleneamine and polyfluoroalkine. Because of their higher costs relative to simple copper sulfate, the use of these compounds is infrequent but may be increasing (Faucher, 1978). The advantages of these copper chelates will be analyzed in terms of the environmental chemistry of copper in freshwater in subsequent sections.

C. Alternatives

Since the development of copper sulfate as an algicide (Moore and Kellerman, 1905) the major emphasis in algicide research has been on the development of new algicides or other treatment practices to replace copper sulfate. In order to evaluate the advantages and disadvantages of copper sulfate as an algicide it is necessary to consider the practicality and environmental impacts of alternative treatments.

Perhaps the most attractive alternative involves no direct treatment of the reservoir. It can be argued that nuisance algal blooms are in general caused by cultural eutrophication and that rather than treat the symptom, a better approach would be to eliminate the causes. Improved farming practices, soil erosion control and more complete treatment of municipal and industrial wastes will eventually alleviate cultural eutrophication. In fact, as current water quality and effluent standards are implemented, the input of such nutrients as phosphorus will probably

be reduced so that nuisance algal blooms no longer occur in some reservoirs (Muchmore, 1976). Nonetheless, with rising population and industrialization, the demand for algal control measures is more likely to increase than decrease in the near future.

The development of new algicides has been looked to hopefully, and extensive research has been carried out in search of an organic compound with properties approaching those of an ideal algicide (Palmer and Maloney, 1955; MacKenthuen, 1959; Prows and McIlhenney, 1973; Fitzgerald, 1974; Muchmore,1976; Anon, 1976). An ideal algicide would be 1) allowable in drinking waters, 2) kill only the nuisance algal species, 3) be nontoxic to zooplankton and fish at the acute or chronic concentrations resulting from treatment, 4) have a minimal impact on the aquatic ecosystem and 5) be of reasonable cost (MacKenthuen, 1959).

The approach of many researchers has been to test   numerous organic compounds for toxicity to nuisance blue-green algae at relatively low concentrations. Three hundred organic compounds were screened for toxicity to a bloom forming blue-green alga, Microcystis aeruginosa, and most were toxic in the range 10 to 1 ppm (Fitzgerald et al. 1952). The most promising compound, 2, 3-dichloronaphthoquinone, effectively controlled algal blooms in the field at concentrations of 30-50 ppb for several days with no observable toxicity to fish or zooplankton (Fitzgerald and Skoog, 1954). Seventy-six chemicals were screened for algicidal properties, and six compounds were found to be generally more effective than copper sulfate (Maloney and Palmer, 1956; Palmer and Maloney, 1955). A bioassay procedure for quantifying the algicidal and algistatic effects of possible chemicals on Chlorella pyrenoidosa were developed, and several copper

compounds, quaternary ammonium compounds and organic mercury compounds were studied (Fitzgerald and Faust, 1963). Although susceptibility to the different chemicals varied among the species tested, the generalization was made that the toxic dosage was dependent upon the algal biomass present and not on the volume of medium in which the algae were dispersed (Fitzgerald, 1964). Twelve algicides were applied to blooms of a filamentous green alga, Cladophora, in thirty-six shallow artificial ponds (Jordan et al., 1962) and only diuron was competitive with copper sulfate. Recently the Environmental Protection Agency has conducted a program to develop an algicide to control blue-green algal blooms (Prows and McIlhenney, 1973). Thirteen hundred compounds, selected from a computerized structure search of over 100,000 compounds, were screened for toxicity to Anabaena flos-aquae at concentrations at less than 1 ppm. Forty-one compounds were then tested more thoroughly and two final candidates were selected: 2,5-Dichloro-3.4-dinitrothiophene and p-chloro-phenyl-2-thienyliodonium-chloride. The former controlled growth of Microcystis aeruginosa at .2 ppm and the estimated reduction in cost relative to copper sulfate was fifty percent.

In the past decades economic constraints prevented the widespread use of these organic compounds to control algal growth in lakes and in reservoirs. Recently, public health constraints have also become important impediments. Since 1969 there has been considerable concern about the carcinogenic effects of halogenated hydrocarbons and other "hard organics" in drinking water (see Consumer Reports, 1974). The Safe Drinking Water Act (SDWA) was passed in 1974 and the regulations for organic compounds in systems that chlorinate and serve more than 75,000 people

a maximum contaminant level for total trihalomethanes of 100 ppb and

2) a treatment technique requiring the use of granular activated carbon

(Litten and Dall, 1978). Given these measures to reduce the public

exposure to carcinogens, it is unlikely that treatment with 200 ppb of an

organic algicide will replace treatment with copper sulfate in the

near future. Registration of **any new organic** algicide

with the Environmental Protection Agency for use in drinking water

supplies would be a lengthy and expensive process (Gratteau, 1970;

Prows and McIlhenney, 1973; Otto, 1977).

The algicidal potential of inorganic chemicals other than copper

sulfate has been successfully investigated. Hale (1954) reported on the

use of chlorination as an adjunct to copper sulfate in water treatment

processes and presented data on the toxicity of chlorine to many species

of algae. The algicidal properties of both silver and potassium

permanganate was studied (Fitzgerald, 1966, 1977). Potassium permanganate

was found to be effective against species with high tolerances to copper

sulfate (e.g. Dictyosperium). Along with potassium permanganate and

chlorine, lime is also used occasionally as an algicide.

Algal control procedures other than treatment with algicides have

been proposed: biological control of algae by viruses, zooplankton, or

fish, variable water intake location, destratification by air injection,

light exclusion by activated carbon addition, and ultrasonic radiation to

collapse gas vacuoles of blue-green algae (Muchmore, 1976). At the

present time, all of these alternatives are either more costly, more

ecologically hazardous, or both, than treatment with copper sulfate.

D. Problems with $CuSO_4$ treatment

As was stated before, copper sulfate is not an ideal algicide and it should be used with an awareness of its limitations and ecological impacts. However, the problems with copper sulfate have often been exaggerated and distorted, especially by those developing new organic algicides (e.g. Palmer and Maloney, 1955 and Prows and McIlhenney, 1973). As will be seen in the following summary, several of the more serious problems may be relieved by applying lower doses of copper sulfate, especially when treating potential algal blooms in lakes not used as drinking water supplies.

1. Toxicity to zooplankton and nekton.

A major concern has been the toxicity of copper to zooplankton and fish. The reported levels of toxicity range from 200 ppm to 2 ppb of total copper (Jackson, 1974). The environmental parameters which determine the solubility of copper and the effective dosage of copper sulfate, also influence the toxicity of copper to fish and zooplankton (Pagenkopf, 1974). The use of copper sulfate in fisheries and its toxicity to invertebrates, fish and mammals are reviewed by Jackson (1974). Fish kills or changes in fish populations have not generally been observed in association with copper sulfate treatment over its long history (Moyle, 1949; MacKenthuen and Cooley, 1952; Muchmore, 1976). Exceptions are some fish kills caused by anaerobic conditions upon decomposition of the algae (Muchmore, 1976). Treatment prior to development of massive blooms in fact can help to avoid oxygen depletion during the summer months. Fish also have ability to avoid areas of the lake receiving immediate treatment, and have been observed to do so (Lawrence et al., 1971).

Little field data exist on the effect of copper sulfate treatment on
zooplankton communities. Increased numbers of Cyclops, Diaptomus,
Daphnia, and Anuraea were observed by Tressler (1937) after copper sulfate
addition. In the field study presented in Chapter III, significant
mortalities of two species of rotifers, Keratella sp. and Tetramastix sp.,
and a cladoceran, Bosmina sp. were observed after copper sulfate treatment.

2. Toxicity to benthos

Another major ecological concern has been the detrimental
effects on the benthos of the accumulated copper precipitates in the
sediments (Hasler, 1947). In research on the absorption of copper by
different categories of bottom sediments, copper was found to be strongly
bound in all cases (Riemer and Toth, 1969). In lakes where the hypolimnion
becomes anoxic, copper may be present in the sediments as copper sulfides.
It is generally held that most of the copper added eventually accumulates
in the sediments, with greatest accumulations of copper occurring in the
profundal region (Nichols et al., 1946). In a survey of Wisconsin lakes,
including an alkaline lake that had received 2×10^6 lbs of $CuSO_4$ during
a 26 year period of continuous treatment, the concentrations of copper
in profundal sediments were found to be less than those toxic to benthic
organisms (9000 ppm on a dry basis) (MacKenthuen and Cooley, 1952). In
another study, benthic organisms were found to have been killed by acute
toxicity upon the addition of copper, but no chronic effects due to
accumulation were observed (Sohacki et al., 1969).

3. Inadequate control of blue-green algal blooms.

Another interesting problem has been the difficulty in controlling some blue-green algal blooms with copper sulfate (Prows and McIlhenney 1973; Otto 1977). This problem is peculiar since blue-green algae, especially bloom-forming species, have been found in several experimental studies to be more sensitive to copper than other algal classes (Tressler 1937; Horne and Goldman 1972; Gibson 1972; Elder and Horne 1977). Several possible explanations exist for instance when $CuSO_4$ has been ineffective against blue-green algal blooms. One explanation is the active or passive release of copper-detoxifying metabolites. Several blue-green algae have been shown to produce extracellular products that complex copper, reducing the concentration of the free cupric ion upon which the toxic response depends (Fogg and Westlake 1953; Lange 1969; Chapter I and II). Another is the difficulty in predicting blue-green algal blooms and in correctly timing $CuSO_4$ application. Noxious surface mats of blue-green algae may form quite abruptly under certain environmental conditions such as the cessation of heavy winds. The factors determining the success of copper sulfate treatments of blue-green algal blooms should be investigated thoroughly because blue-green algae blooms are the most problematical and the predominance of blue-greens in lakes has been rising with eutrophication.

4. Development of resistance to copper treatment.

A more long term problem may be decreases in the sensitivity to copper of phytoplankton assemblages. The most likely change would seem to be a shift in the phytoplankton species distribution towards species

that are more tolerant of high copper levels. Succession from an algal assemblage dominated by <u>Ceratium</u> <u>hirundella</u> and <u>Asterionella</u> sp. to one dominated by copper-tolerant species of green algae, <u>Nannochloris</u> and <u>Ourococcus</u>, was observed over a ten-day period following treatment of Mill Pond with copper sulfate (Chapter III). After copper sulfate treatments of <u>Aphanizomenon</u> <u>flos-aquae</u> blooms in prairie lakes, diatoms, chlorophytes, chrysophytes and <u>Microcystis</u> sp. dominated the algal assemblage (Whitaker et al., 1978).

The other possible change is the adaptation of the nuisance algal species to high copper concentrations. Populations of higher plants (<u>Agrostis</u> <u>tenius</u>) can adapt to increased copper levels both in the laboratory and in the field (Bradshaw <u>et</u> <u>al</u>. 1965). The boundary between copper-tolerant and non-tolerant populations was shown to be sharp, suggesting that copper-tolerant individuals were at a competitive disadvantage in normal environments. A similar trend for algal populations could control the adaptation to copper treatment since most treatment is intermittent rather than chronic.

Algal populations exist in contaminated lakes near mining operations. In these lakes the chronic copper concentrations are often close to those used in treatment. It is unknown whether these species were originally copper-tolerant or whether the tolerance was acquired. An isolate of <u>Chlorella</u> <u>fusca</u> from a contaminated lake with a copper concentration of .7 ppm and a pH of 4 was found to be less sensitive to copper than a laboratory strain of <u>Chlorella</u> <u>vulgaris</u> (Stokes et al., 1973). The uptake of copper by algal blooms in lakes of varying distance from mining operations was investigated but no general trend was found (Trollpe and

Evans 1976). Abundant algal growth is reported in Torch Lake, Michigan which has constant input of copper mine tailing deposits and chronically has concentrations of copper only an order of magnitude below dosages used in algal treatment (Lopez and Lee 1977). Many isolates of algae from streams draining mines in Cornwall, England were found to be relatively insensitive to copper, zinc and lead (Foster 1979).

Although copper sulfate has been applied to lakes and reservoirs since 1904, the only evidence for adaptation of an algal species to copper treatment is that of Moyle (1949). He reports a 2 to 5 fold increase in the amount of copper sulfate needed to prevent blooms of Aphanizomenon over a 26 year period. Changes in environmental parameters, such as organic matter and algal densities, may explain his observation, but adaptation has to be considered.

5. Need for repeated treatments.

One characteristic of copper sulfate as in algicide that has been listed as disadvantageous is its "biodegradability" (sic!) (Prows and McIlhenny 1973; Maine DEP 1976). Copper ions are removed from solutions in the water by precipitation, complexation, adsorption on suspended particulates, and uptake by microorganisms. These processes are different from the breakdown of large organic compounds by microorganisms, which is the usual connotation of biodegradation. Because of the gradual decrease in the concentration of copper ions in solution only short term seasonal control can be achieved with copper sulfate. This characteristic can be perceived as either an advantage or a disadvantage. Long term algicidal effectiveness and hazards to public health and environment would seem to go hand in hand.

6. Cost

A possible disadvantage of copper sulfate is the probable rise in the cost of copper on the world market in the future (Otto 1977). The effective use of lower dosages of copper sulfate would take some of the sting out of rising costs.

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