EFFECTS OF COPPER SULFATE APPLICATION ON DIEL DISSOLVED OXYGEN AND METABOLISM IN THE FOX CHAIN OF LAKES

William J. Mitsch[1]
Systems Science Institute and Environmental Engeering
University of Louisville
Louisville, Kentucky 40292

Katie S. Kaltenborn
IBM Corporation
Lexington, Kentucky 40507

ABSTRACT

In-situ measurements of diel dissolved oxygen and metabolism were made of the euphotic zone of treatment and control bays in the Fox Chain of Lakes in northeastern Illinois during the application of the algacide, copper sulfate. Significant (>1 mg/1) diurnal changes in dissolved oxygen were seen in all fourteen diurnal measurements reported here. Both dawn and dusk dissolved oxygen were slightly lower in the bay being treated by the algacide. Respiration was significantly higher in the treated bay, probably due to decomposition of dead algae cells. No significant decrease was determined for gross primary productivity during the study period. The aquatic community apparently recovered rapidly from the copper sulfate stress. Overall primary productivity at the experimental and control bays compared well with some productivity studies made in other shallow aquatic systems although areal primary productivity was probably limited by the shallow depths and turbid waters in the bays studied.

INTRODUCTION

The Fox Chain of Lakes (Figure 1) are a series of nine natural lakes that have formed along the Fox River in Lake and McHenry counties in northeastern Illinois. The major inflows of water and nutrients are contributed from the Fox River as it flows from Wisconsin and the surface levels of the lakes are partially controlled by a down-stream dam at McHenry. The lakes are an important recreation area for northeastern Illinois although they have recently shown signs of excessive eutrophication. Fish kills have been documented by Muench (1964) while studies by the U.S. Public Health Service (1963) and the Illinois State Water Survey (1966) described the eutrophic conditions of several of the lakes.

A comprehensive limnological study of the Chain by Kothandaraman *et al.* (1977), summarized by Kothandaraman and Evans (1978a,b,c), determined water quality and nutrient budgets for the lakes and gave recommendations for control of the symptoms of eutrophication. The application of copper sulfate to control algal blooms was attempted in the summer of 1977 by the Illinois State Water Survey in Mineola Bay of Fox Lake (see Figure 1). Three applications were made at loading rates of 6.0 kg/ha each, the equivalent of 1 mg/1 copper sulfate for the top 2 feet of water. Descriptions of the chemical treatments are given in Kothandaraman *et. al.* (1978).

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[1]Field work done while at Pritzker Department of Environmental Engeering, Illinois Institute of Technology, Chicago, Illinois 60616.

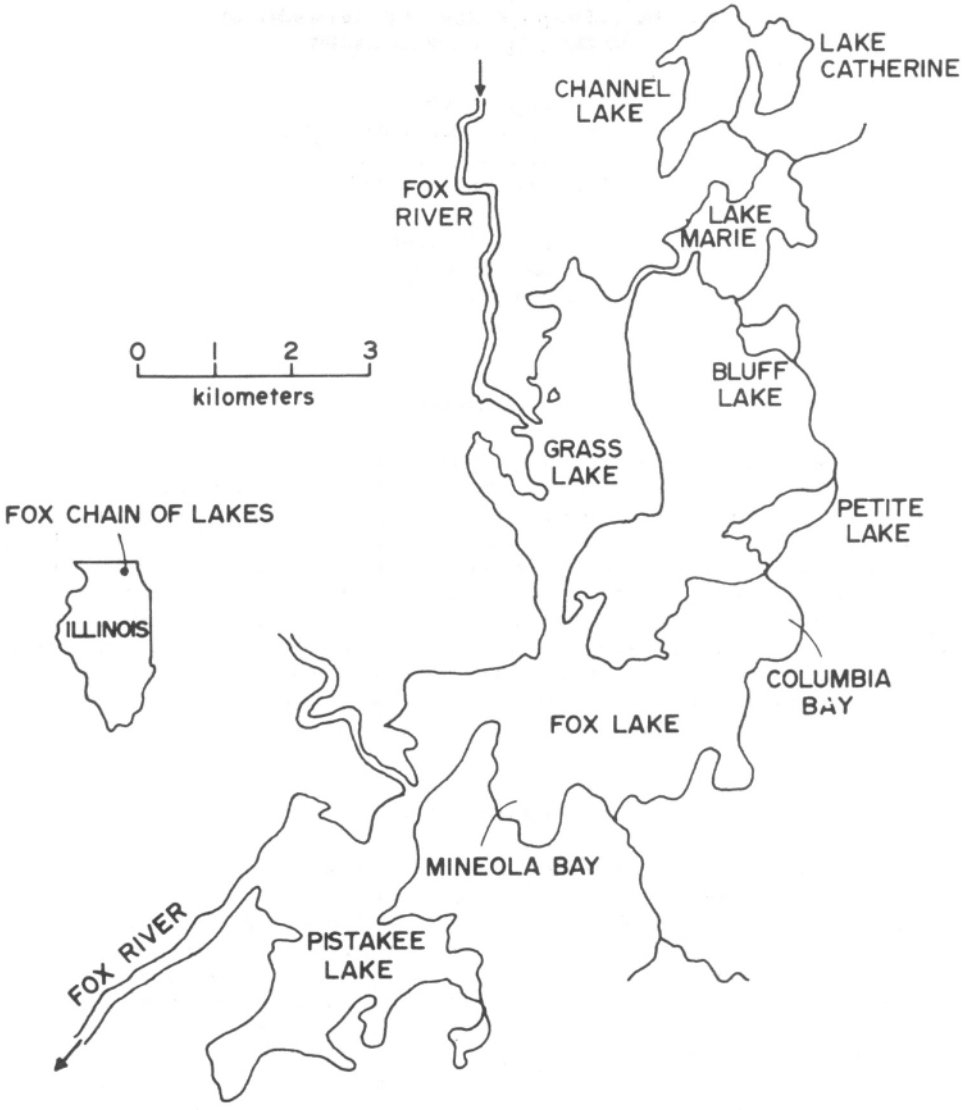

Figure 1. Fox Chain of Lakes Study Area in northeastern Illinois.

This study presents the results of free-water diel dissolved oxygen measurements in Fox Lake to determine the effects of the copper sulfate treatments on overall euphotic zone metabolism. Diel or diurnal dissolved oxygen methods in free water have frequently been used to measure aquatic ecosystem metabolism in streams (Odum, 1956, 1957; Duffer and Dorris, 1966; Owens, 1969), estuaries (Odum and Hoskin, 1958; Nixon *et al.*, 1976; McKellar, 1977) and lakes and reservoirs (Welch, 1968; Manny and Hall, 1969; Eley, 1970). The use of free water measurements rather than incubation samples overcomes several problems of isolating samples in bottles. Reduction of turbulence in bottles may inhibit metabolism, glass surfaces may serve as a good substrate for bacteria and algae, and some light may be absorbed by using incubation samples. The major limitations of the open water method include its lack of sensitivity in oligotrophic waters, not a problem in the Fox Chain of Lakes, and the uncertainty of the necessary oxygen diffusion corrections. Hall and Moll (1975) summarize many of these advantages and disadvantages.

MATERIALS AND METHODS

Sampling stations were located in Mineola Bay (treatment site) and in Columbia Bay (control site) on Fox Lake (Figure 1). We chose Columbia Bay, about 3km from Mineola Bay, as the control site in our study despite the use of Fox Lake itself as a control by Kothandaraman *et al.* (1978). We felt that their control site was not properly chosen because 1) it was too close to the treatment (about 300 m in some cases), 2) it was not in waters with similar "bay-like" shoreline protection from waves and other turbulence, and 3) flow-through characteristics were probably dissimilar for their experimented and control sites.

Dissolved oxygen was measured by the Azide modification of the Winker titration (A.P.H.A.,1975). Replicate 125 ml samples were obtained just below the surface and at one meter depth at the treatment and control sites (8 samples per run) with a Kemmerer sampler. Solar radiation was measured by a recording pyroheliograph. Secchi disk measurements were taken to estimate euphotic zone depth according to the relationship (Cole, 1975):

$$d_{ez} = 2.4\ d_{sd}$$

where,

d_{ez} = euphotic zone depth, m
d_{sd} = Secchi disk reading, m

Chlorophyll *a* was determined by the spectrophotometric method described by Strickland and Parson (1968) and was uncorrected for pheophytin pigments.

Primary productivity and respiration were measured by an abbreviation of the diel oxygen curve method of Odum and Hoskin (1958). The abbreviated method involves the use of dawn-dusk-dawn dissolved oxygen measurements rather than more frequent sampling. Simultaneous measurements by the abbreviated and full diel methods on six occasions during the study period in the Chain of Lakes showed no significant differences in productivity calculations ($P < 0.05$). This was also found to be the case by McKellar (1977).

The diel calculations were corrected for oxygen diffusion to or from the atmosphere by means of measurements of diffusion by a floating plastic dome (Copeland and Duffer, 1964). An average diffusion coefficient of 0.65 g O_2/m^2-hr @ 0% saturation from four measurements was used for correction. No differences were found in the conclusions mentioned below using the entire range of diffusion coefficients measured during the study.

An implicit assumption with the diel oxygen method for lakes is that the station being sampled is well mixed with surrounding waters which are also displaying similar oxygen patterns.

Figure 2 shows results from a typical diurnal patterns of dissolved oxygen in the control site; the surface oxygen increases by 5 to 6 mg/1 during daylight. This range suggests that the diel oxygen method is sensitive enough for productivity measurements in this body of water; measurement of dissolved oxygen by Winker titration can generally achieve repeatability of 0.1 mg/1.

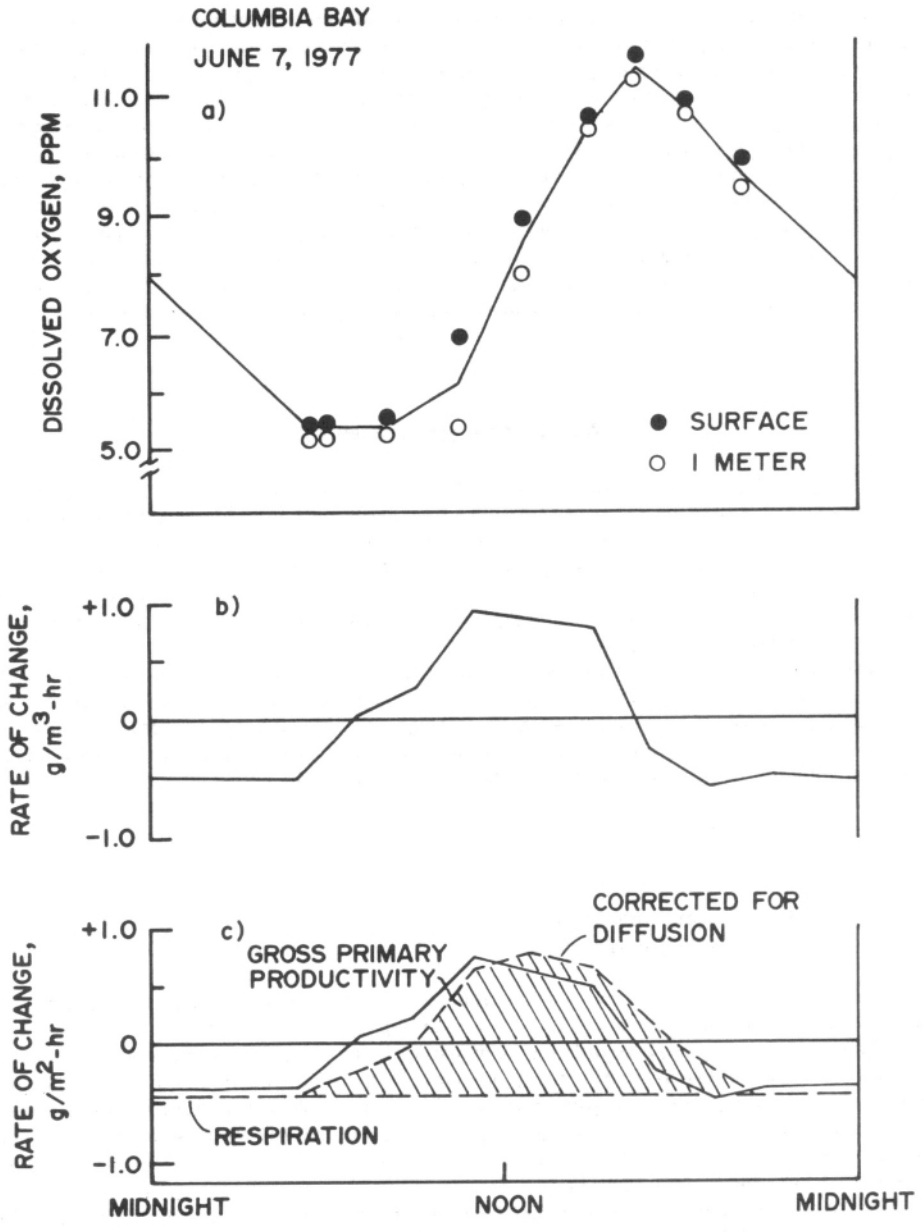

Figure 2. Example of calculation of euphotic zone metabolism on Columbia Bay showing a) diurnal change of dissolved oxygen, b) rate of change in oxygen per unit volume, and c) rate of change of oxygen per unit area of euphotic zone showing curves corrected and uncorrected for oxygen diffusion.

RESULTS AND DISCUSSION

Diel Oxygen Changes

The dawn-dusk-dawn dissolved oxygen measurements made in both Mineola bay ($CuSO_4$ treatment) and Columbia Bay (control) are given in Table 1. Diurnal differences of at least 1 mg/1 were seen in all cases and often differences were much higher. Significant productivity continued in Mineola Bay during the copper sulfate treatment even though some measurements were made within two days after application. Both dawn and dusk dissolved oxygen was lower in the treatment site than in the control site during the treatments with dawn readings averaging 0.5 mg/1 lower and dusk readings averaging 1.0 mg/1 lower. Dissolved oxygen at dusk continued to be 0.7 mg/1 lower in the treatment bay well after (2 months) the treatment suggesting that the effect might be prolonged.

Kothandaraman and Evans (1978a) report epilimnitic dissolved oxygen in Fox Lake in the summer of 1975 to range from about 6.5 to 9.0 mg/1, within the range seen by us in 1977 in both bays. However their study does not indicate if the dissolved oxygen measurements were taken at the same time of the day. This represents a significant omission for a study on the lake that often has greater diurnal changes in dissolved oxygen than the seasonal range given by Kothandaraman and Evans (1978a).

Euphotic Zone Metabolism

Dissolved oxygen, gross primary productivity, respiration, P/R ratios, chlorophyll *a* and Secchi disc transparency are compared for Mineola Bay and Columbia Bay in Figure 3 and Table 2. Paired t-tests were used to evaluate the results. Data for the entire summer were used for these statistical analyses because it appears from Table 1 that the copper sulfate applications suppressed algal bloom for the entire growing season. The production and respiration results were evaluated on both an areal basis ($g\text{-}O_2/m^2\text{-day}$) and a volume basis ($g\text{-}O_2/m^3\text{-day}$).

Productivity values were not significantly different ($P < 0.05$) between Mineola (treatment) and Columbia (control) Bays on either basis. The only noticeable decrease in productivity due to copper sulfate was seen approximately one week following the third treatment when the control bay productivity was 3.2 $g\text{-}O_2/m^2$- day while the treatment bay value was 0.6 $g\text{-}O_2/m^2$- day. Full recovery of gross primary productivity in Mineola Bay (treatment) was seen in 10 to 14 days after this last treatment. We observed a green scum coating the water surface for several days following the third treatment.

Community respiration in the treated bay was significantly higher than in Columbia Bay during the study period on both an areal and volume basis (Table 2). This would be an expected effect of the copper sulfate treatment. When the algae die and microbial decomposition commences, the microbial oxygen demand of the community increases. Respiration values were similar only immediately following the first and third copper sulfate treatments. Apparently, the heterotrophic microbial community is stressed along with the algal community immediately following copper sulfate application. More detailed follow-up on the third treatment shows that the community respiration of the treated bay increases dramatically over the control as microbial decomposition is accelerated, probably due to the presence of the dead algal cells.

P/R (productivity/respiration) ratios were compared for the treated and control bays. P/R ratios were significantly lower in Mineola Bay, reflecting the greater degree of heterotrophy in the treated bay. The behavior of the P/R ratio following the third copper sulfate application is of interest. An algal bloom occurred in the control bay on July 29 with a dusk dissolved oxygen value of 12.4 mg/1, the highest seen in the study; a very high P/R ration of 2.6 was calculated for that date. The higher respiration seen at the treatment bay during this time coupled with a slightly lower productivity prevented the dissolved oxygen from going beyond 10 mg/1 at dusk. The P/R ratio for the treatment was accordingly much lower at 0.9.

Table 1. Dawn-Dusk-Dawn Dissolved Oxygen in Mineola Bay and Columbia Bay, Fox Lake During Study Period. Dates of Copper Sulfate Application to Mineola Bay Are Also Given.

Date	Solar Radiation, kcal/m²-day	Dissolved Oxygen, mg/l[1] Mineola Bay ($CuSO_4$)	Columbia Bay (Control)
June 2		COPPER SULFATE APPLICATION	
June 7-8	4982	6.5/10.0/6.2	6.4/10.0/6.2
June 27		COPPER SULFATE APPLICATION	
June 29-30	5706	5.0/7.8/4.7	5.6/9.8/6.2
July 19		COPPER SULFATE APPLICATION	
July 21-22	3363	4.7/7.2/5.4	6.1/6.9/5.1
July 26-27	4684	5.7/7.7/7.4	6.2/10.0/7.7
Average During Treatment	4684	5.5/8.2/5.9	6.1/9.2/6.3
		POST APPLICATION PERIOD	
Aug. 17-18	2938	5.6/7.0/5.8	5.4/7.4/5.6
Aug. 24-25	4386	6.2/9.0/6.3	6.5/9.8/7.0
Sept. 3-4	3662	5.7/7.1/6.1	6.3/7.9/6.7
Average After Treatment	3662	5.8/7.7/6.1	6.1/8.4/6.4

[1]Dissolved oxygen values are averages of two surface and two 1 m samples at Dawn/Dusk/Dawn.

Table 2. Comparison of Field Measurements Between Treatment and Control Bays for Copper Sulfate Treatment.

Parameter	Units	Mean Value Treatment	Control	Percent Difference
Less in treated bay*				
Productivity/respiration		0.5	1.0	−50
dissolved oxygen (dawn)	mg O_2/1	5.7	6.5	−12
dissolved oxygen (dusk)	mg O_2/1	7.8	9.4	−17
Greater in treated bay**				
respiration (areal)	g O_2/m^2-day	7.0	4.9	43
respiration (volumetric)	g O_2/m^3-day	11.1	7.7	44
No significant difference				
productivity (areal)	g O_2/m^2-day	3.8	4.2	−10
productivity (volumetric)	g $O_2/m_2{}^{-3}$-day	5.6	6.4	−12
Secchi disc	centimeters	25	25	0
chlorophyll *a*	mg chlorophyll/m^3	254	263	−3
assimilation ratio	g oxygen/g chlorophyll-hr	1.7	1.4	21

* significantly less in treated bay ($P<0.05$)
** signficiantly greater in treated bay ($P<0.05$)

Transparency and Chlorophyll

Secchi disc measurements are also given for treated and control bays in Figure 3. There was no significant difference between the bays. Secchi disc transparency decreased in both bays after late July, when peak algal blooms would be expected. After the third treatment, the transparency in Mineola Bay (treatment) decreased from 34 to 20 cm while the control bay readings decreased from only 30 to 25 cm. This difference was due to the dead algal scum observed after this treatment. Kothandraman and Evans (1978a) found a range of 15 to 53 cm for Mineola Bay in 1975 and Kothandraman *et al* (1978) found no differences in Secchi disk readings between the treatment site and their control.

Samples were collected for chlorophyll *a* beginning July 21 (Figure 3 and Table 2). There were no significant differences in concentrations for treated and control bays. These results do not necessarily show that there was no reduction in viable algal cells after treatment because results were uncorrected for phaeopigments, chlorophyll degradation products, which may have been a significant percentage of the measured chlorophyll *a*. Chlorophyll *a* concentrations decreased in late August indicating that the algal bloom was decreasing from the summer maximum at this time. Kothandaraman *et al* (1978) found that algal counts dropped significantly after every chemical treatment but that the algal populations recovered within a few days. Our data and theirs, taken together, indicate that phytoplankton biomass was not significantly reduced over long periods by the copper sulfate treatment.

Aquatic Metabolism Comparison

The aquatic metabolism measurements made in this study are compared with other studies that have employed the diel oxygen method on lentic waters (Table 3). Our ranges compare well with those found by Nixon *et al.* (1976) in a shallow salt marsh embayment during summer measurements and with a study of an estuarine bay in Florida (McKellar, 1977). The annual averages found by Welch (1968) for a small Georgia pond could also easily represent the approximate annual values for the Fox Chain of Lakes. Eley (1970) measured very high metabolism values in a eutrophic reservoir in Oklahoma while Manny and Hall (1968) reported higher productivites in Lake Michigan. Both of these studies, however, are based on assumptions of euphotic zone depth that probably lead to overestimations.

Our assumption of determining euphotic zone by multiplying the Secchi disk reading by 2.4 may lead to slightly low metabolism values. Cole (1975) describes a multiplication factor of as high as 5.0 for highly turbid waters. It is possible for the calculated euphotic zone to actually exceed the depth of the bays which would lead to an overestimation of areal productivity. However, our assumptions appear to be valid for the shallow waters in the bays studied here. Our average calculated euphotic zone is 0.6 m while Kothandaraman *et al.* (1978) report an average depth of Mineola Bay of about 1.5m.

A comparison is also given with diel oxygen measurements made in two other lakes in the Fox Chain of Lakes in Table 3. Measurements in Bluff Lake, discussed by Kaltenborn (1978), gave consistently higher areal productivities than either of the bays in this study. This may also be due to assumptions about euphotic zone as Bluff Lake had higher water transparency. Solar efficiencies in the Fox Lake bays were reasonable, however, ranging from 0.05 to 0.7 percent of total insolation while a maximum of 2.2 efficiency was seen in Bluff Lake. Maximum solar efficiency in aquatic systems is accepted to be around 2% (Odum, 1971). More accurate measures of euphotic zone depth are obviously needed for future studies such as these.

Our studies here, as well as other measurements made in Illinois and elsewhere show the applicability of using the open water diel oxygen method to assess metabolism of certain aquatic systems. Widespread use of this method in Illinois would provide a useful method for comparing ecosystem function of a wide range of natural and managed bodies of water and could aid in classification and management schemes.

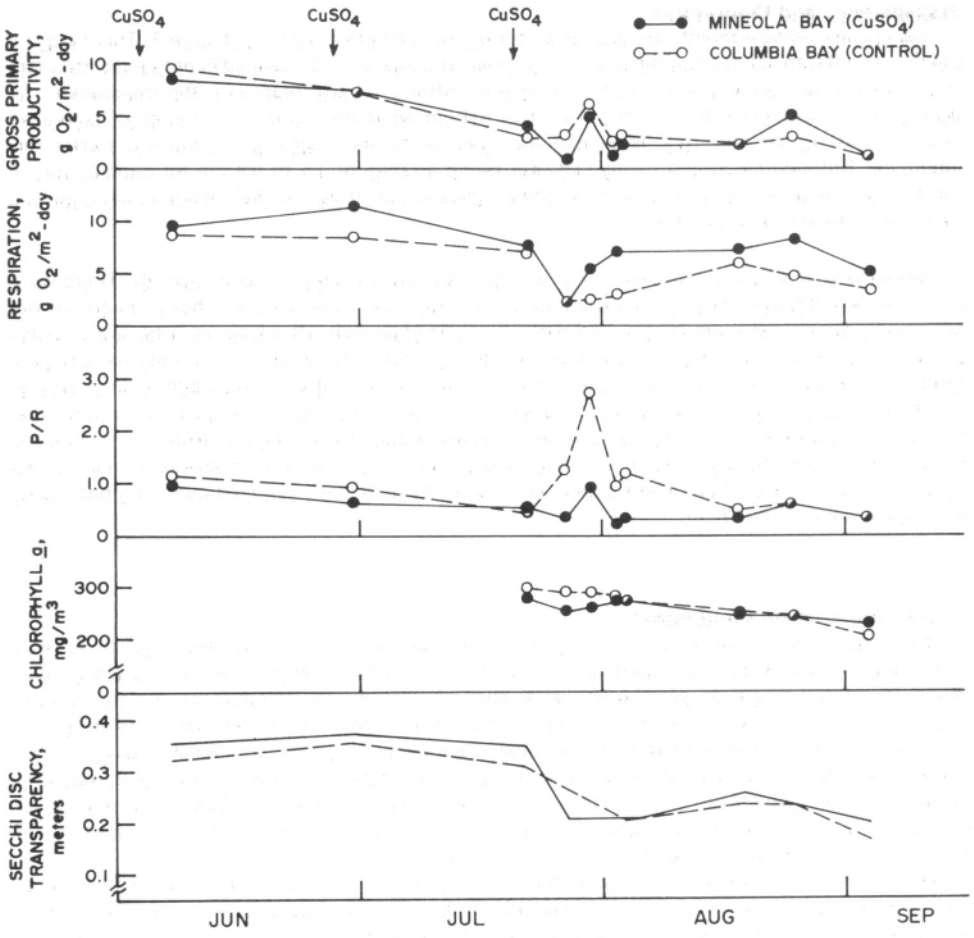

Figure 3. Results of metabolism, chlorophyll *a* and Secchi disk measurements for treated and control bays of Fox Lake during copper sulfate application.

Table 3. Comparison of Aquatic Metabolism of Lentic Systems Measured with Diel Oxygen Method

Reference	Study Site	g O_2/m^2-day	
		P	R
Welch (1968)	Lago Pond, Ga. (annual ave.)	5.3	7.6
Manny and Hall (1969)	Lake Michigan	23.7	26.4
Eley (1970)	Keystone Reservoir, Okla.	11.3-49.1	11.0-54.1
Nixon *et al.* (1976)	Narragansett Bay, R.I.(summer)	2.3-8.1	1.2-7.0
McKellar (1977)	Florida Estuary	5.3-5.6	2.6-2.9
Kaltenborn (1978)	Fox Chain of Lakes, Illinois		
	Bluff Lake (n = 7)	2.2-17.6	1.4-18.5
	Petite Lake (n = 7)	1.7.-11.1	1.9-11.8
This study	Fox Chain of Lakes, Illinois		
	Mineola Bay (n = 10)	0.6-8.6	2.3-11.5
	Columbia Bay (n = 10)	1.0-9.6	2.4-8.9

CONCLUSIONS

The following conclusions have been elucidated by this study on the Fox Chain of Lakes.

1. Copper sulfate, used as an algacide treatment in the Fox Chain of Lakes, has no apparent effect on aquatic primary productivity and no long term effect on phytoplankton biomass in the Fox Chain of Lakes.

2. Euphotic zone respiration was higher with copper sulfate treatment due to decomposition of dead algal cells. A noticeable scum of dead algae did appear after one of the treatments on the Fox Chain of Lakes, creating anesthetic problems as well.

3. Slight decreases in both dawn and dusk dissolved oxygen can be expected with the application of copper sulfate to the Fox Chain of Lakes. No dramatic dissolved oxygen depletions, however, can be expected due to the treatment.

4. Recovery of ecosystem function from the algacide stress in the Fox Chain of Lakes is rapid and almost complete within several weeks.

5. Overall aquatic primary productivity in the Fox Chain of Lakes, while extremely high on volumetric basis, is lower than some comparable ecosystems on an areal basis. It may be limited by shallow depths and highly turbid waters in the Fox Chain of Lakes.

6. Significant diurnal changes in dissolved oxygen occur during the summer and this should be considered when reporting dissolved oxygen for these lakes.

7. The Fox Chain of Lakes has bays and lakes with many different morphological and circulation characteristics and care should be taken in choosing the proper sites for experiments and controls.

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