MOVEMENT AND ACCUMULATION OF APPLIED COPPER IN A HARDWATER SOUTHEASTERN MICHIGAN RESERVOIR

Thesis for the Degree of M. S.
MICHIGAN STATE UNIVERSITY
Kenneth Ray Roberts
1966

ABSTRACT

MOVEMENT AND ACCUMULATION OF APPLIED COPPER IN A HARDWATER SOUTHEASTERN MICHIGAN RESERVOIR

by Kenneth Ray Roberts

A study was made from January through May, 1965 on the dynamics of applied copper movement and accumulation in 85-acre Adrian Lake, a southeastern Michigan hard water water supply reservoir. The lake has accrued a copper accumulation during more than ten years of intensive algal control with copper sulfate.

During the study the lake's water dynamics were found to be constantly changing. Analysis of lake water copper profiles resulted in the conclusion that water movement is a very significant factor in the distribution of applied copper. Conditions apparently most important in the mechanism are volume of lake inflow, the rate of copper sulfate entering the system, and water volume going over the dam and/or through the sluices. Copper is transported out of Adrian Lake both by direct flow from the constant-flow source and from the sediments themselves. In each instance water current is the vehicle which determines the rate of removal.

Total copper values in the sediments were found to be high. A maximum downlake value of 1,932 ppm. was found two cm. deep at a point 1,145 feet from the point of copper sulfate introduction. Copper content progressively decreased with increasing sediment depth. This vertical trend apparently reflects the lake's rate of copper sulfate application. The data were considered insufficient to accept or reject the hypothesis of increasing sediment copper concentrations with increasing water depth in Adrian Lake. Nor did the data provide evidence of a strong relationship between sediment copper content and distance down lake from the constant-flow device. Wave action and intensified inflow, whenever they might occur, are attributed to result in continual full or partial downlake re-distribution of these compounds.

A literature review resulted in the conclusion that the high affinity of organic matter for copper ions has gone generally unrecognized in the field of lake copper ecology. A thorough understanding of reactions of copper ions in natural waters is precluded until such a time when a more ample background is established on the form of the copper ion lake water, the organic and inorganic materials present, their inter-relations, and relative copper affinities.

MOVEMENT AND ACCUMULATION OF APPLIED
COPPER IN A HARDWATER SOUTHEASTERN MICHIGAN RESERVOIR

By

Kenneth Ray Roberts

A THESIS

Submitted to
Michigan State University in partial
fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

Department of Fisheries and Wildlife

1966

ACKNOWLEDGEMENTS

I wish to acknowledge the patient guidance and advice supplied to this project by my advisor, Dr. Eugene Roelofs and the advice and assistance of Drs. Peter Tack, Andrew Timnick and Robert Ball. I am especially indebted to Messr's Carl Nelson and Garnet Campbell of the Adrian City Water Department for the great amount of time and assistance provided in collection of field data and provision of background information and to the Michigan State Agricultural Research Station for financial assistance provided. My thanks go also to the Michigan Water Resources Commission for the welcome use of its power ice auger and to Mr. Carlos Fetterolf for the insight he provided on Michigan lakes and streams. Use of the Ohlmacher-Gleason coring prototype was graciously made possible by Dr. Dale Gleason, presently of the Sault Ste. Marie Branch of Michigan Technological University. The Fish Section of the Michigan Department of Conservation made existing Adrian Lake survey data available. Fellow graduate students Willard Gross and Al Jensen provided both field and taxonomic assistance in the fishery survey of Adrian Lake. Finally, I wish to acknowledge the encouragement and assistance provided by my wife, Judith, without whom the project might never have been undertaken.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

Copper compounds, primarily copper sulfate ($CuSO_4 \cdot 5H_2O$), but including copper carbonate and copper oxide, have been widely applied to water areas for varying reasons. The most common use is for algal and bacterial control in water supplies. Other uses include the control of leeches, higher aquatic plants, fish diseases, and snails (for swimmers' itch). At least two state conservation agencies (Massachusetts and Ohio) apply copper sulfate to lakes routinely to stimulate fish movement, and thus increase the catch of fish in survey nets (Tompkins and Bridges, 1958; Brown, 1964).

Sustained annual programs of copper sulfate application carried out over long periods are not uncommon. Lakes Menona, Waubesa, and Kegonsa of the Madison Lakes, Wisconsin have received large applications of copper sulfate annually for a period of at least nineteen years for algal control. As part of a swimmers' itch program, Houghton Lake in Michigan received 555,400 pounds of copper sulfate from 1944 to 1963. As part of the same program over the same interval, Michigan's Big and Little Glen Lakes received 104,900 pounds.[1]

Documentation of the more immediate toxicity of copper applications on aquatic fauna is fairly extensive. However, the question of potential long range negative effects of repeated copper applications on lake ecosystems is meagerly treated in the literature, despite the fact

---

[1] Fetterolf, Carlos. 1963. Comments on the use of copper sulfate and the effects on lake ecology. Michigan Water Resources Commission mimeographed report.

that widespread speculation on this matter does exist. Hasler (1949) expressed concern by writing, "The question is not how little can be used to avoid killing fish, but what will be the effect of accumulations of copper in lake muds...." Hasler cited Frey (1940) who maintained reduction of the aquatic vegetation and molluscan fauna of lakes Menona, Waubesa, and Kegonsa occurred with the addition of copper. Klein (1957) and Placak et al. (1950) report that as little as 0.01 ppm. copper has a marked depressing effect on the B.O.D. of sewage. Rudgal (1946) found that increasing copper concentration in sludge caused a decreasing rate of digestion. Although 2,500 ppm. had a negligible effect, 50,000 ppm. allowed only 5 percent of normal gas production.

Equally meager evidence exists which suggests that high copper concentrations accumulated in the sediments does not harm aquatic ecology. Mackenthun and Cooley (1952) produced laboratory evidence that the copper accumulation then present in Lake Menona sediments (as high as 480 ppm.) was not toxic to Pisidium sp. over a 60-day period. They also reported that extreme concentrations (9,600 ppm.) were needed to kill certain bottom dwelling organisms from Lake Mendota. Domogalla (1935) reported that, "rooted aquatics grew luxuriantly through all eleven years of copper sulfate treatment at Lake Menona." Tompkins and Bridges (1958) reported that Lake Quannopowitt, Massachusetts, despite a long history of copper application displayed above average net catches of fish for that state. Moyle (1949) pointed out that commercial fishing yields were higher for a group of four Minnesota lakes treated with copper sulfate over a twenty-four year period than for five adjacent untreated lakes.

Obviously, any substance as toxic as copper introduced in sufficient quantities will influence lake ecology. The question of whether changes caused by accumulations of this heavy metal are of kind and significance to warrant concern cannot be answered until many more data are available.

The general objective of the present study was to measure the dynamics of movement and accumulation of copper in a lake receiving annual applications. Specific objectives of the study were: (1) measurement of the distribution of accumulated copper in the sediments of a treated hardwater lake with respect to depth and distance from the point of copper sulfate introduction; and (2) periodic analyses of water profiles during the 1964-65 winter and 1965 spring to record vertical concentrations of copper, dissolved oxygen, and pH in a hardwater lake during these periods. The water profile data were supplemented with lake discharge estimates to enable a projection of the amount of applied copper (regenerated from the sediments or otherwise) that was carried out of the lake by spring discharge.

Adrian Lake at Adrian in southeastern Michigan was the site of data collection. It has accrued copper during more than ten years of algal control with copper sulfate by the City of Adrian. This hardwater, 85-acre, gourd-shaped reservoir was an excellent study site, because of its small size, relatively unpolluted state, and the mode of copper sulfate application. Most of the chemical is introduced by a constant-flow device located at the lake's stream inlet, although additional treatments are made by boat. The stationary source of introduction provided a unique opportunity to measure copper accumulation in the sediments of a hardwater lake with respect to (1) distance from the point of copper sulfate introduction and (2) water depth.

Literature Review

Little is known about mechanisms of copper ion reactions in natural waters. Copper ions react readily with many materials common at one time or another to lakewater. These substances include both organic matter (algae, higher aquatic plants, invertebrates, organic colloids, vertebrates, etc.) and inorganic matter (carbonates, chlorides, clays, hydroxides, oxygen, etc.).

It seems universally accepted that most applied copper finds its way to the bottom, although this may not necessarily be true. Several mechanisms for its course to the bottom have been advanced. As early as 1930, precipitation of copper salts after applications to hardwater western lakes was observed (Hale, 1954). Prytherch (1934) suggested that wastes of an alkaline character may cause precipitation of normal amounts of copper from river water. Prescott (1948) and Nichols et al. (1946) experimentally confirmed that precipitation of a bluish substance does occur from water with pH above neutral. Nichols et al. feel that, ". . . much of the copper added to lake waters of notable alkalinity is precipitated as a basic copper compound, of somewhat variable composition, depending upon prevailing conditions . . ." Hutchinson (1957) points out that two well-defined basic copper carbonates (malachite and azurite) are known in nature and the mechanism of basic copper carbonate formation is likely to be complicated.

Riley (1939) in work on softwater Connecticut lakes cited evidence which indicates binding with algae and colloidal organic matter is a prime means of copper deposition. Benoit (1956) reported that Riley later determined that copper added to Lindsley Pond inlet water was rapidly fixed and that the copper was not precipitated through formation of insoluble hydroxide, carbonate, phosphate, or sulphide.

It might be noted that the concept of alkaline water precipitating all applied copper is presently widely held, yet is based on very limited evidence. Hutchinson cites unpublished data collected by Stecker in 1938, which compares total copper concentrations of more alkaline to softwater Wisconsin lakes. Based on measurements from 136 lakes, the data actually indicate a slightly higher copper concentration in the more alkaline lakes (32 mg. m^{-3}) than in the softer lakes (29 mg. m^{-3}). Hutchinson attributed these results to a tendency for water with more total solids in solution to contain more copper and came to the conclusion that Stecker's data gave no indication of copper content of harder waters with natural concentrations being regulated by precipitation.

A possibly important facet of copper ecology heretofore little considered in the literature is the importance of dissolved organic materials such as amino acids, porphyrins, and carboxylic acids in tying up copper in lake water. Although limited information presently exists on the dissolved organic fraction of fresh waters, work by Shapiro (1959) shows the existence of a mixture of hydroxy carboxylic acids in softwater Connecticut lakes. Vallentyne (1957) indicated the occurrence of amino acids, polypeptides, and porphyrins in natural waters. Fogg and Westlake (1955) reported that an extracellular polypeptide produced by *Anabaena sp.* formed a soluble complex with various ions including copper. Saunders (1957) suggested that dissolved organic substances, acting as chelators, may influence concentration of trace elements in natural waters.

The high affinity of organic matter for copper ions is widely recognized and documented. Soil scientists have been particularly interested in copper exchange capacity of the soil organic fraction. Bremner, et al.

(1946), Coleman, et al. (1956), and Broadbent (1955) all report the existence of stable complexes between soil organic matter and copper. Broadbent and Oh (1957) reported that soil organic matter complexes were found capable of forming complexes with copper in very dilute solution, and the amount of complex formed was shown to be dependent on copper concentration, pH, and time of contact. Thompson (1950), working on browning reactions of foods, calls proteins avaricious copper-grabbers; he reports that a neutral solution of protein, such as casein or albumen, will saturate iteslf with copper while in contact with an insoluble copper compound, such as the oxide, in a relatively short time. Corwin (1950) reports that amino acids will break copper-ammonia complexes to take the copper and that the affinity of porphyrins for copper is so great that they will extract it from copper sulfide. Assuming the constant presence of dissolved (and particulate) organics in both hard and soft water, it seems that ionic and/or inorganically bound copper would eventually find its way into the "avaricious" organic matter.

Obviously, a thorough understanding of copper ion reactions in natural waters is precluded until an ample background is established on the form of copper ion in the water, the organic and inorganic materials present, their inter-relationships, and relative affinities for copper.

THE STUDY AREA: ADRIAN LAKE

Location

Adrian Lake (Figure 1) lies within Sections 26 and 35 of Township 6-S Range 3-E, Lenawee County, Michigan. It is located on the northwest side and within the corporation limits of the City of Adrian. This 35.5-acre reservoir lies on Wolf Creek.

Drainage Area

Wolf Creek is part of the Raisin River Drainage. It flows directly into the Raisin River, which in turn flows into Lake Erie. The land area draining into Adrian Lake itself is approximately 80 square miles.[2] The headwaters of Wolf Creek arise in a series of small lakes in Cambridge and Franklin townships of Lenawee County. The connecting ditches between the lakes are intermittent, draining into Wolf Creek only during periods of high water. Wolf Creek itself is not intermittent and receives water from several tributaries, including Hunt, Ryan, Pouty, Onsted, and Black Creeks.

Early settlers found Lenawee County to be covered with dense forests. Red, white, and black oaks, sugar maples, and beech were the principle species. Little or no virgin timber remains. Presently existing woodlots are small and largely pastured (Striker and Harmon, 1961).

Wolf Creek's watershed consists primarily of farmland. It does include the very small rural towns of Onsted and Springville. The 1954 census showed the average Lenawee County farm to be 123 acres with major

---

[2] Michigan Department of Conservation Map of Lenawee County

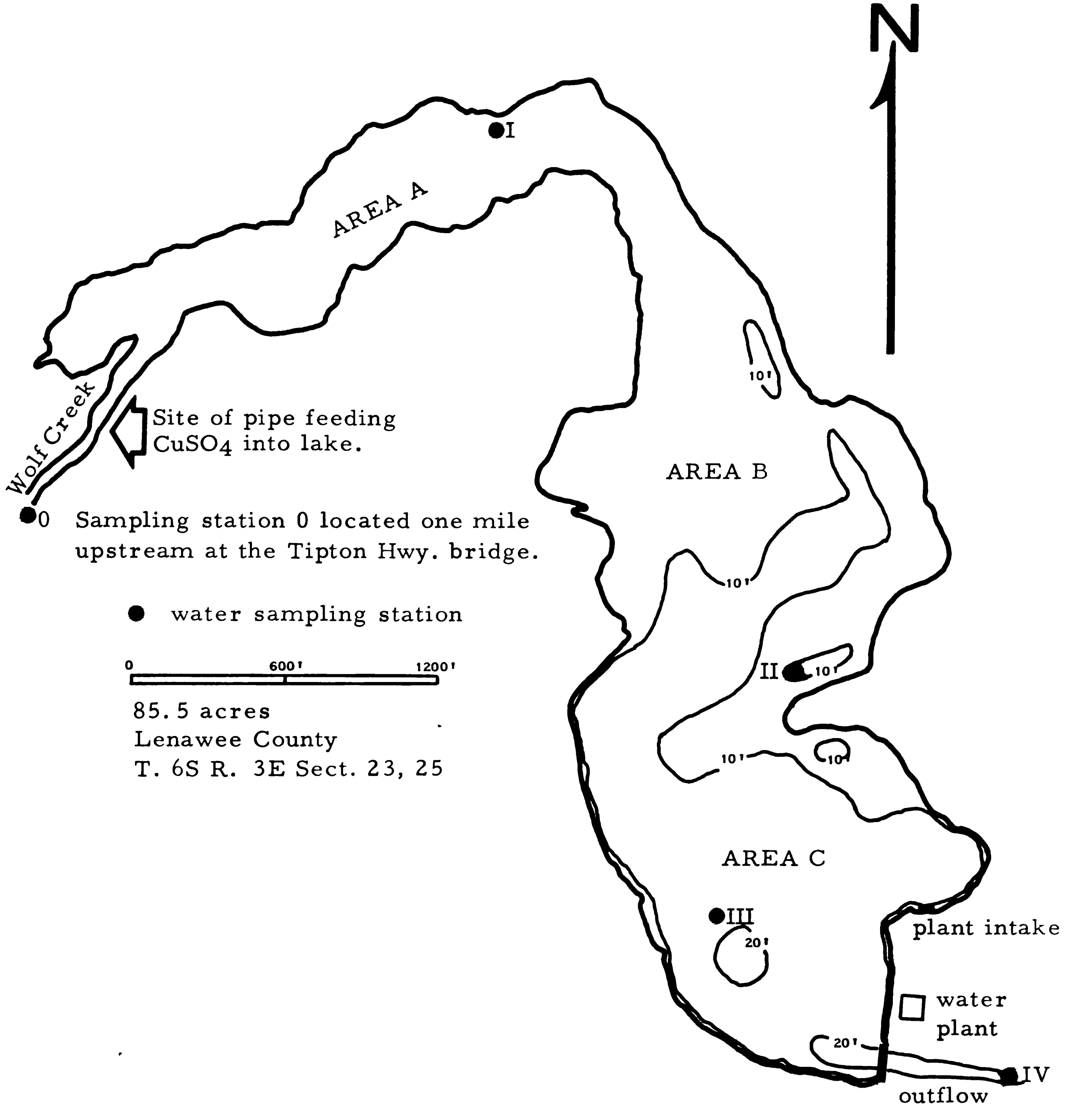


Figure 1. A map of the study site, Adrian Lake, showing water sampling stations and the study areas A, B, and C.

sources of income listed as field crops, dairy, livestock, poultry and fruit, in that order. Primary field crops include corn, oats, wheat, soybeans, hay and sugar beets (Striker et al.).

Geology and Soil Types

Bedrock formations underlying Lenawee County are flat-lying sedimentary rocks. Glacial action ground up the bedrock and left deposits of drift. Thus, the surface features of the watershed are a reflection of the glacial action.

Wolf Creek's drainage area is comprized of three general soil associations (Striker et al.). The northern-most portion in the headwaters consist of rolling to hilly, well-drained loamy sands. The central part is nearly level, consisting of imperfectly and poorly drained soils developed from clay loams, silty clay loams and clays. The lower portion displays undulating and rolling soils developed from limy clay loans, silty clay loams and clays.

More specifically, a large portion of Wolf Creek bottomlands, including the site of Adrian Lake, are of the Genessee and Griffin loam series. Gennessee soils are well drained and consist of an alluvium made up of loam, sandy loam and silt loam. Griffin soils are found in swales and old stream channels, are subject to overflow, and receive fresh deposits when flooded. Most Griffin areas are narrow and less than three acres in size. In Lenawee County, they are found in such intricate mixtures with the Genessee Series that the two are mapped together. These soils are fairly fertile and easy to till (Striker et al.).

Erosion

During periods of higher water, Wolf Creek and Adrian Lake become visably muddy. Striker et al. report that both of the upper watershed's soil associations require special land management practices to control erosion.

An outstanding example of watershed erosion was observed by the writer during the study. On February 10, 1965 Adrian City water personnel made an entry in the water plant diary which reads, "high water and mud," following a runoff from thawing snow. During late February and early March, sediment cores were collected through the ice. Examination of these cores showed a contrasting brown layer of fresh sediment one-eighth to three-eighths inch thick on the surface phase of each black core. This sediment was apparently deposited in the lake during and after the runoff.

Water Quality

The Adrian Lake drainage discharges a moderately hard enriched water. Bicarbonate alkalinity ranges from 150-350 ppm. The enrichment is sufficient to cause problem algal blooms in the lake with great frequency. As early as 1946, the Adrian Water Board chemist treated the lake with copper sulfate to control these blooms.[3]

Adrian Lake Proper

Adrian Lake displays characteristics common to most stream impoundments, including a shallow upstream end, and gradual deepening to the deepest point of 21 feet near the dam. Soundings show that much of the impounded stream channel is still intact. The lake is gourd-shaped, and the shoreline is far from regular.

---

[3] 1946 Adrian Lake Survey, Institute for Fishery Research, Michigan Department of Conservation. August 20, 1946.

The dam. The dam was constructed in 1941, and filling occurred in 1942. Approximately 600 feet wide and 30 feet tall, it is comprised of earthen fill, which is protected from wave action by stone riprap on the water side. At the extreme south side a concrete spillway, complete with two 42 X 42-inch sluices, was constructed. Lake outflow occurs at this point. The concrete dam is 25 feet high, and the spillway is 66 feet wide. The center 9-foot 4-inch spillway section is two and one-eighth inches lower than the remaining, forming a low flow weir. The entire spillway is adapted to receive 12-inch high oak planks, which are installed when additional water storage is desired.

The water plant draws raw water for municipal use from an intake located on the north end of the dam. The intake is approximately 5 feet underwater.

Water level fluctuation. In addition to seasonal fluctuations, Adrian Lake is subject to certain drawdowns, which are considered conducive to water plant operations and municipal water consumption.

Installation of 12-inch planks at the spillway occurs each spring. In 1965, installation of the planks with the sluice gates closed brought the water level up one foot in five days.

The sluice gates are an important cause of fluctuation. The 42 X 42-inch gates are capable of draining 576 million gallons per day when wide open. In practice they are seldom open more than six inches, and then only for short periods. Even this partial opening has a significant effect on lake level at times.

Dry conditions over the past few years have resulted in low lake levels. In 1963 and 1964, spring rains were sufficient to fill the lake, but permitted little or no overflow. During this period, the sluice gates were never opened.

The lake bottom. The lake bottom is essentially a reflection of the original stream valley. Bottom slope is varied, being generally low at the upper end and increasing as the dam is approached. The stream channel still exists, and there is evidence which shows it is still functional when the sluice gates are open.

Bottom materials consist primarily of rubble, gravel, sand, silt, clay and organic detritus. The dam riprap contains numerous boulders. The gravel and sand beds are found almost exclusively on wave-washed areas, particularly at the areas exposed to north-wind wave action. The deeper and less exposed bottom areas consist of silt-clay deposits. The deepest area, which is near the dam, exhibits a black-organic clay bottom. Organic matter is not present in abundance, because air-drying of this black clay material yields the characteristic color of grey clay.

Numerous stumps from trees cut prior to inundation are present, especially in Area A.

Adrian Lake inadvertently serves as a stilling basin for Wolf Creek. The result is that remaining original Genessee and Griffin soil series of the lake bed are being covered by erosion materials from the watershed. These foreign materials include gravel, sand, silt, clay and organic detritus.

In addition, organic matter is contributed by meager beds of *Potamogeton natans*, *P. pectinatus*, and *Najas sp.*, which are found in limited patches.

Lake margin characteristics. The shoreline slope is a reflection of the original impounded area. The slope is moderately low at the upper end. The lower half of the lake has very little shallow water due to the dam and high banks, which drop rapidly to the old valley bottom.

Erosion is conspicuous in many places. The higher banks in all places have been gradually undercut because of their steep slope. Wave erosion, however, is not proceeding at a rapid rate.

Zones of submerged higher aquatic vegetation are historically few in the lake and are restricted to sheltered areas. Carbine and Cooper[4] in August, 1946 reported, "silty water made good cover, vegetation scant." C. M. Taube[5] in June and September, 1953 reported, ". . . virtually no vegetation; _Najas sp._, _Potamogeton sp._ observed at the Girl Scout Camp and south." At the time of the current work, only _P. natans_, _P. pectinatus_, and _Najas sp._ were observed, and then only in scant, isolated beds.

Actually, shore holding capacity due to submerged higher aquatic vegetation is minimized by this lack of development.

During the early 1964-65 winter, the water level was about two feet below dam-top level, exposing a two to ten-foot-wide strip of lake bottom to the snow and air. The effect of such fluctuation on higher aquatic vegetation development can only be conjectured.

The Fish Population

Survey history. Since filling in 1942, Adrian Lake has received three fish surveys by biologists of the Michigan Institute For Fisheries Research. The first occurred in 1946 and was made by G. P. Cooper and W. F. Carbine. The second and third surveys were made in 1953 and 1957

---

[4] Ibid.

[5] 1953 Adrian Lake Survey, Institute For Fisheries Research, Michigan Department of Conservation.

by C. M. Taube and include net-survey data. To provide current information on Adrian Lake fishes, a seining and gill-net survey was made on June 14 and 30, 1965. Survey effort consisted of approximately fifteen pulls of a 100-foot seine at various places along the shoreline and four hours of fishing with an 80 foot 1 1/2-inch mesh gill net. The results of the 1965 survey are given in Table 1.

A comparison of species composition for all four surveys is given in Table 2. Information on fishes in the 1946 survey was limited to the personal knowledge of Messrs. Smith, Peters, and Munger of the Adrian City Water Board. The abundance designations assigned to the various species in the 1953 and 1957 surveys are those of Taube, and the criteria for assigning these designations are unknown. The 1965 data are expressed as numbers caught, except in the case of certain minnows, because survey effort was not geared to suggest estimates of abundance.

Stocking effort. Table 3 summarizes the official stocking history of Adrian Lake as obtained from the records of the Michigan Department of Conservation.

Population dynamics. The limited data of Table 2 seem to indicate that species composition is relatively stable and has been so since at least 1953. All but two of the species recorded in 1953 were found to be present in 1965. In addition the 1965 survey showed the presence of one heretofore unreported species, the mottled sculpin.

Insufficient information exists to conjecture on growth rates of the black basses and northern pike. However, the growth rate of sunfishes is apparently poor. In both 1953[6] and 1957[7], Taube reported the dominant

---

[6] Ibid.

[7] 1957 Adrian Lake Survey, Institute For Fisheries Research, Michigan Department of Conservation.

Table 1. Results of the Adrian Lake Seining-gill net survey conducted on June 14 and 30, 1965. Approximately fifteen seine pulls and four hours of gill net fishing are represented. The survey crew included W. Gross, A. Jensen, and K. Roberts.

Family and Common Name	Genus and Species	Number Caught	Number Measured	Length Range	Distribution Mode (inches)
CATOSTOMIDAE					
redhorse	*Moxostoma sp.*	41	34	3.7-11.3	4.9, 9.3*
white sucker	*Catostomus commersonii* Mitchell	1	-	-	-
CENTRARCHIDAE					
bluegill	*Lepomis macrochirus* Rafinesque	68	41	1.4- 5.3	2.2
green sunfish	*L. cyanellus* Rafinesque	124	30	1.8- 5.3	3.0
largemouth bass	*Micropterus salmoides* (Lacepede)	35	30	5.3-10.9	6.1
longear sunfish	*L. megalotis* Rafinesque	1	1	-	-
pumpkinseed	*L. gibbosus* (Linnaeus)	1,370	100	2,2- 6.1	3.7
rock bass	*Ambloplites rupestris* (Rafinesque)	2	2	1.9- 2.4	-
smallmouth bass	*M. dolomieui* Lacepede	4	4	4.1- 6.1	-
warmouth	*Chaenobryttus caronarius* (Bartram)	9	9	2.8- 7.3	-
COTTIDAE					
n. mottled sculpin	*Cottus bairdi* Girard	1	-	-	-
CYPRINDIDAE					
bluntnose minnow	*Pimphales notatus* (Rafinesque)	numerous			
carp	*Cyprinus carpio* Linneaus	4**	-	-	-
common shiner	*Notropis cornutus* (Mitchell)	56	19	3.5- 5.8	-
golden shiner	*Notemigonus crysoleucas* (Mitchell)	numerous			
rosy-faced shiner	*Notropis rubellus* (Agassiz)	numerous			
red fin shiner	*Notropis umbratilis* (Girard)	numerous			
swallow-tail shiner	*Notropis procne* (Cope)	numerous			
ESOCIDAE					
northern pike	*Esox lucius* Linnaeus	1	1	19.3	-
PERCIDAE					
blackside darter	*Percina maculata* (Girard)	1	-	-	-
johnny darter	*Etheostoma nigrum* Rafinesque	1	-	-	-
yellow perch	*Perca flavescens* (Mitchell)	6	5	4.3- 8.7	-

* Two clearly defined modes were present

** Approximately 18-inch fish which repeatedly escaped from the seine.

Table 2. Summarization of fish population information on Adrian Lake.

Family and Common Name	Institute For Fishery Research Surveys			Number
	1946*	1953	1957	in 1965
AMEIURIDAE				
bullhead	reported	reported	-	-
CATOSTOMIDAE				
redhorse	-	-	present	41
hog sucker	-	-	present	-
white sucker	-	present	present	1
CENTRARCHIDAE				
bluegill	reported	few	few	68
green sunfish	-	abundant	abundant	124
largemouth bass	reported	-	-	35
longear sunfish	-	abundant	common	1
pumpkinseed	-	common	common	1,370
rock bass	reported	rare	-	2
smallmouth bass	reported	reported	-	4
warmouth	reported	common	common	9
COTTIDAE				
n. mottled sculpin	-	-	-	1
CYPRINDIDAE				
bluntnose minnow	-	present	present	numerous
carp	reported	abundant	abundant	4
common shiner	-	present	-	56
creek chub	-	present	present	numerous
fathead minnow	-	present	-	-
golden shiner	-	present	present	numerous
mimic shiner	-	present	present	-
rosy-faced shiner	-	-	-	numerous
red fin shiner	-	present	-	numerous
swallow-tail shiner	-	-	-	numerous

Table 2. Continued

Family and Common Name	Institute For Fishery Research Surveys 1946*	1953	1957	Number in 1965
ESOCIDAE				
northern pike	-	-	reported	1
PERCIDAE				
yellow perch	reported	common	common	6
blackside darter	-	present	present	1
johnny darter	-	present	present	1

* Information on fishes in the 1946 survey was limited to the personal knowledge of Messrs. Smith, Peters, and Munger of the Adrian City Water Board.

Table 3. Stocking record for Adrian Lake as obtained from the Michigan Department of Conservation

Year Stocked	Species	Size Stocked	Number Stocked
1946	smallmouth bass	3.9" ave. length	7,018
1954	northern pike	3.0" ave. length	1,540
1961	northern pike	fingerlings	1,000

size for warmouth, green sunfish, pumpkinseed, and longear sunfish to be "small". He reported the growth rate of pumpkinseed sunfish in 1953 and 1957, based on scale readings from seven and twenty-two fish respectively to be "below average". Although no age-growth work has been done on the 1965 fish collection, the length-frequency of Table 1 supports the premise of poor growth.

At least one apparent exception is the growth rate of yellow perch. Taube described the growth rate as "above average" in both 1953 and 1957 based on aging of twenty-two and thirty-three perch respectively.

Survey information is also inadequate to evaluate the impact of the bass and pike stocking on the lake's angling. Taube cited angling reports of smallmouth bass catches in both the 1953 and 1957 surveys. He also wrote of a "few" northern pike catch reports between 1954 and 1957. The 1965 survey showed the presence of both northern pike and smallmouth bass.

METHODS

I. COLLECTION AND PROCESSING OF WATER SAMPLES

Initial water sampling efforts were directed at studying the stratification of copper in Adrian Lake. Two stations (II and III) were defined and samples were taken at one meter (and sometimes half meter) depth intervals with a Kemmerer Sampler. As sampling progressed, it became apparent that a knowledge of copper concentrations, as the water traversed the gourd-shaped reservoir was equally important. Thus Stations 0, I, and IV were eventually established. The stations are marked on Figure 1 and are located as follows:

Station 0. This station is the Wolf Creek bridge on the Tipton Highway. It lies approximately one mile above the inlet to the lake. Samples taken here represent copper concentration of water entering the lake. Samples were taken from midstream with the Kemmerer Sampler.

Station I. This station is in Area A, where the reservoir widens from the inflowing stream. It is approximately 730 yards downstream from the point of copper sulfate introduction, and lies in the stream channel. The lake at full pool is approximately two meters deep at this point, and all samples (save one) were taken at a one-meter depth.

Stations II and III. These stations represent midlake and downlake areas. Both lie in the old stream channel. Station II is 4.5 meters deep at full pool and 1,440 yards from the copper source, while Station III is 6 meters deep and 1,730 yards from the copper source. Samples were taken at one meter (and sometimes half meter) depth intervals.

Station IV. The outlet flow is represented by Station IV, which is midstream at the Bent Oak Highway bridge on Wolf Creek 400 yards downstream from the Adrian Lake dam.

Sampling schedule. Water sampling occurred at approximate two-week intervals during the period January 16 through May 27, 1965, except during February, when a great deal of time was devoted to sediment core collection. Dates of sampling were: January 16 and 30; February 6; March 15; April 6, 14, and 29; and May 12 and 27.

Lakewater Fractions.

Riley (1939) in his more comprehensive study of lake copper ecology defined four lakewater fractions in which copper is found. His definitions included: (1) sestonic; (2) organic-colloidal; (3) soluble (ionic); and (4) total fractions. The sestonic fraction was defined as that fraction held back by a 0.6 micron filter and included plankton and organic and inorganic detritus of sufficient size. The organic-colloidal fraction was defined as that matter small enough to pass through the 0.6 micron filter and included bacteria and inorganic and organic matter. Riley does not specifically mention copper complexed with dissolved materials. The soluble or ionic fraction was defined as that copper in a free ionic state. In lakewater, this apparently would be copper in some form of equilibrium with copper compounds in the water. Total copper was defined as the sum of the three above-mentioned fractions.

For the purpose of this study, the fractions as defined by Riley will be used, with some modification of definition and nomenclature. The sestonic fraction is defined as that lakewater matter, which will not pass through a 0.45 micron filter. Since Riley's organic-colloidal term is considered to be a misnomer, the term filtrate fraction will be used for want of a better term and is defined as small bacteria, viruses, organic and inorganic particulate matter smaller than 0.45_u in diameter, dissolved organic and inorganic compounds, and ionic copper. The ionic fraction will have the same definition as Riley's. However, the ionic fraction was not successfully measured and is not pursued further. Since Adrian Lake water is relatively hard, it is doubtful if any significant amount of ionic copper ever exists in solution, except after a copper sulfate application.

Processing of Total Copper Fraction

Glassware for all copper analysis was washed, rinsed with concentrated hydrochloric acid, and then finally rinsed with de-ionized distilled water. One hundred ml. samples of lakewater were placed in 250 ml. beakers and evaporated to near dryness. Ten ml. of concentrated nitric acid and 2 ml. of 72% perchloric acid were added to each beaker, and the samples were again evaporated until dense perchloric acid fumes were evolved. At this stage the minute amounts of organic material were digested. The digested samples were washed into separatory funnels and the bathocuproine determinations made.

Processing of Sestonic Copper Fraction

One hundred ml. samples of lakewater were passed through 0.45 micron millipore filters at approximately 30 pounds per square inch pressure. The filters, containing the sestonic fraction, were placed in clean glass bottles until digestion and copper measurements were possible.

The filters and their residues were individually placed in 250 ml. beakers and digested with 10 ml. of nitric and 2 ml. of perchloric acids. Bathocuproine determinations were made immediately after the digestion step.

Processing of Filtrate Copper Fraction

The filtrates from 100 ml. samples passed through the 0.45 micron filters were transferred to 250 ml. beakers. These were processed in a manner identical to that for measuring total copper.

Measurement of Ionic Copper

It was felt that no satisfactory way of measuring ionic copper in lake water has been advanced. Some preliminary work was done with extraction of ionic copper with a Dow copper-specific ion-exchange resin. However, the results were not considered sufficiently precise, and the effort is disregarded herein.

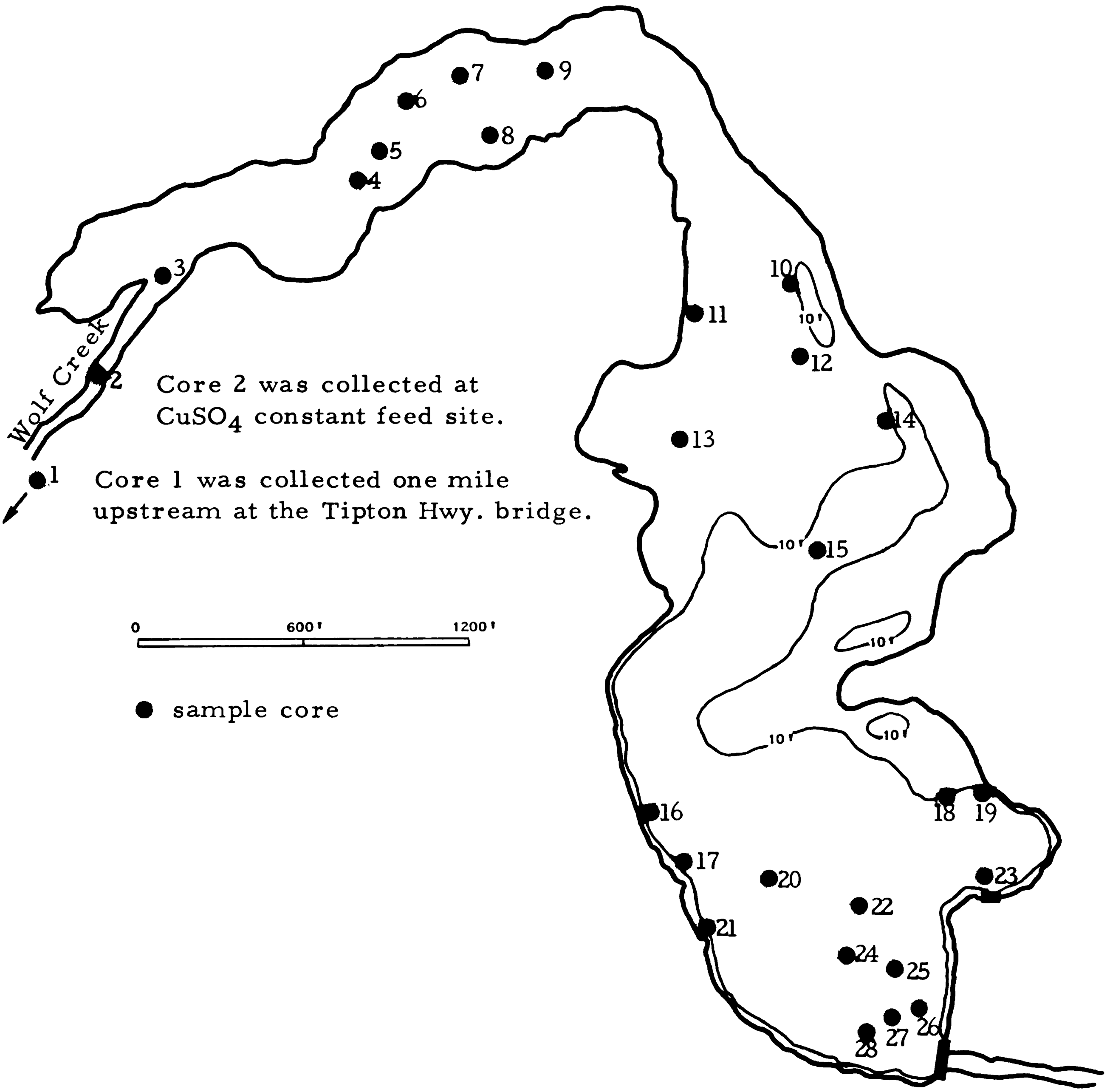
II. SAMPLING SEDIMENT FOR COPPER

Selection of Sampling Stations

Twenty-five widely distributed sediment cores were collected from February 24 through March 5, 1965 at varying depths ranging from 0.4 to 5.8 meters. The breakdown was: Area A - 6 cores; Area B - 6 cores; Area C - 13 cores. Locations of the respective cores are shown in Figure 2.

Core collection stations were selected from a master plan of 300 sample stations laid out prior to collection. The master plan was prepared by superposing a scaled grid with transects (1 unit = 50 feet) over a 24 X 30-inch lake map and selecting 300 grid intersections as sample points by use of random number tables. These intersections comprised sample stations and were assigned numbers.

Collection was made through the ice. Sample stations were located by: (1) laying out a primary transect for each area; and (2) measuring perpendicularly to these transects with a graduated cord to find individual stations. Sampling through the ice at temperatures below freezing proved to be a very laborious process with the instrument used. When



Core 2 was collected at $CuSO_4$ constant feed site.

Core 1 was collected one mile upstream at the Tipton Hwy. bridge.

Figure 2. A map of the study site, Adrian Lake, showing the sampling distribution of the twenty-eight sample cores.

it became apparent that relatively few cores could be collected, the sample size was reduced to approximately thirty, and sampling stations in Areas A, B, and the upper half of C were selected from the master plan with a table of random numbers. Thus, a random sample was literally taken from another random sample, ensuring randomness for most of the sample.

Ohlmacher-Gleason Frozen Coring Device

Cores were collected with a prototype corer, which freezes the core before the device is lifted from the lake bottom. This type of device was developed by F. J. Ohlmacher, while a graduate student under the direction of Dr. D. R. Gleason at Central Michigan University. A patent for the device was received by Central Michigan University during the course of this study.

The purpose of the device is to obtain undisturbed samples of profundal sediments, particularly at the mud-water interface (Ohlmacher, 1964). Once the corer is seated in the sediment, freezing is accomplished by rapid injection of an eight-ounce acetone charge into a chamber packed with crushed dry ice. The dry ice chamber surrounds the core tube, which contains the sediment to be frozen. Ohlmacher states that dry ice reportedly generates a solution temperature of - 80° C and that he confirmed temperatures in excess of - 29° C.

Operation of the device is illustrated by the three steps shown in Figure 3, which have been reproduced from Ohlmacher's thesis. Prior to dropping the device to the lake bottom, the removable copper core tube must be inserted and fastened by pinning, the ice chamber packed with crushed dry ice, and the acetone chamber charged with acetone. The corer is then lowered into the water and dropped. Gravity imbeds it in the sediment (it was found to be less successful on gravel and sand bottoms). A

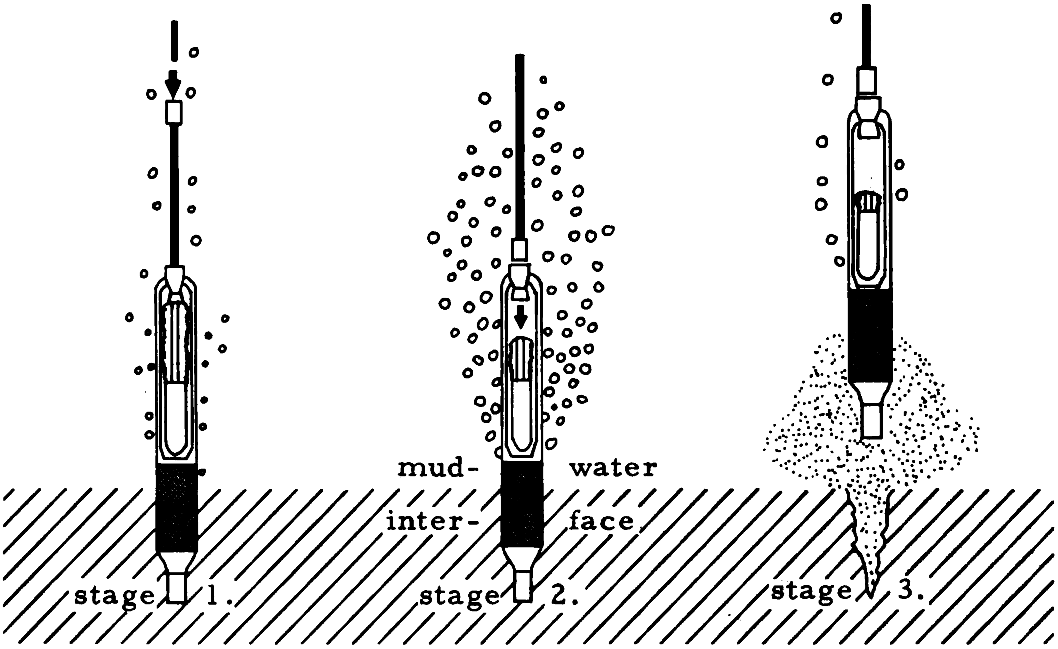


Figure 3. Position and action in sediment of the Ohlmacher-Gleason frozen corer, as reproduced from Figure 4 of Ohlmacher's thesis.

brass messenger is then dropped (Stage 1), which trips the spring, driving the acetone into the dry ice chamber (Stage 2). For the Adrian Lake work, a five minute freezing period was allowed before pulling the device from the bottom (Stage 3). At the surface the copper core tube is removed from the device and warmed (by immersion back into the hole in the ice), until the core can be extruded easily from the core tube with a wooden dowel. Adrian Lake core samples were rolled in aluminum foil, along with a card recording the sample number and depth in meters from which it was collected. The cores were placed in an ice chest with dry ice, until storage in the Department of Fisheries and Wildlife freezer was possible. The sediment portions of the cores were 1 1/2-inches in diameter and averaged about 10 cm. in length.

Miscellaneous Core Collection

Three additional cores were obtained in a much different manner during July, 1965. The cores were respectively taken: (1) 150 feet below the point of copper introduction in midstream; (2) directly from the pile of flocculent material surrounding the plastic pipe from which the copper sulfate is introduced; and (3) from a silt bed in Wolf Creek one mile upstream from the constant-flow outlet. These cores were collected by pushing 4-feet lengths of 1 1/2-inch copper pipe into the sediment, corking the tops, pulling out the cores, and corking the bottoms securely. They were kept in a vertical position until placed in a walk-in freezer at the University. They were allowed to freeze overnight, and were then removed from the pipes for copper analysis by warming the exteriors of the pipes with tap water. These cores were much longer than the others, ranging from 40 to 85 cm.

III. COPPER ANALYSIS

The literature was reviewed for procedures in the quantitative determination of copper in lake water and in sediments. Selection of a method for the oxidation of organic matter in the samples was also necessary. The procedures finally selected represent a mixture of reviewed techniques.

An important initial step was the selection of copper specific reagents for use in spectrophotometric analysis. Such reagents are numerous and Borchardt and Butler (1957) present a comprehensive review and critique of most of them. Two reagents were selected: 2,9-dimethyl-4, 7-diphenyl-1, 10-phenanthroline (hereafter called bathocuproine) and 2,9-dimethyl-1,10-phenanthroline (hereafter called neocuproine). These reagents have numerous advantages including (1) formation of copper complexes with relatively high molar absorbtivity, (2) freedom from interference by common cations and anions, (3) simplicity of use, and (4) stability. The use of bathocuproine is reviewed by Borchardt et al. Neocuproine is reviewed in the 1960 Edition of Standard Methods.

Structurally, bathocuproine and neocuproine differ only by the presence of two symmetrically arranged phenyl groups on the bathocuproine molecule. The net result of this difference is that bathocuproine's molar absorbtivity (14,160) is roughly twice that of neocuproine (7,950). Bathocuproine has the highest molar absorptivity reported in the literature, making this reagent more desirable from the standpoint of measuring trace amounts of copper found in lake water. On the other hand, such high absorbtivity is not advantageous when measuring large concentrations of copper in sediment. For these reasons, bathocuproine was used for water analysis and neocuproine for sediment analysis.

Before spectrophotometric measurement of copper in lake water and sediment is possible, there is a necessity to free bound copper from organic compounds in the sample. An organic oxidation process is therefore necessary. Wet-ashing was selected over dry-ashing, because of erratic results by the dry-ashing technique as reported by Borchardt et al.

Several methods for the wet-ashing of organic matter were reviewed. These included various mixtures of sulfuric acid, nitric acid, hydrochloric acid, and perchloric acid. Concentrated perchloric acid digestion is undoubtedly the most efficient from the standpoint of destroying highly refractory organic matter (Standard Methods, 1960). However, a mixture of perchloric and nitric acids was chosen for digestion because this combination will effectively digest small amounts of highly refractory organic matter and yet minimize the explosive hazzard of perchlorate accumulations (Smith, 1954).

Procedure for determination of copper in lake water. All digested water samples, regardless of the respective copper fraction, were treated identically. All glassware was washed, rinsed with concentrated hydrochloric acid, and then rinsed repeatedly with copper-free distilled water to remove adhering copper ions. Digested solutions were diluted to approximately 50 ml. with copper-free water and then transferred to separatory funnels.

Each digested sample then received respectively 2 ml. of .001 M bathocuproine (dissolved in 1:1 water-hydrochloric acid), 2 ml. 10 percent hydroxylamine hydrochloride, and enough 40 percent sodium acetate solution to raise the pH to just above 5 (congo red indicator paper was used). At this stage the complexed copper exhibited the red-brown color.

Removal and concentration of the complex from the aqueous solution was achieved by extraction with re-distilled n-hexyl alcohol. Initial work involved use of 1.0 cm. cells in the spectrophotometer, and 10 ml. of hexyl alcohol was used for each sample. However, low copper concentrations prompted the procurement of 10 cm. cells (to increase the light path length, and thus increase absorption and sensitivity) and 32 ml. volumes of extractant were then used. Extraction was executed by pipetting the n-hexyl alcohol into the separatory funnels containing the complexed samples and shaking for two to three minutes. One extraction was found to be sufficient to remove the colored complex from the aqueous layer. After five minutes of standing, the colorless bottom aqueous layers were drawn off and the samples were transferred to clean dry 50 ml. bottles or left in the funnels. The samples were kept overnight before spectrophotometric analysis.

A Beckman DK-2A ratio-recording spectrophotometer was used for measuring absorbance. One cm., and later 10 cm., matched silica absorption cells were used. The maximum absorption wave length for the bathocuproine complex, as measured with the DK-2A, occurred at 473 millimicrons, and all readings were made at this wave length.

Before a series of samples were run, the instrument was calibrated using reagent blanks prepared by running 100 ml. of copper free water through the procedure. A constant check was kept on reagent blank absorbance. Immediately after calibration, the reference cell (reagent blank) absorbance was marked with the servo pen of the DK-2A on the chart paper using air as reference. The mark was circled with pencil, and periodically during the sample series, the reference cell was replaced into the sample cell compartment and the absorbance was checked against air. The quality of the instrument and the stability of the reagent blanks permitted little deviation from the initial pen mark after periods as long as several days.

Procedure for determination of copper in sediment. Sediment cores were unwrapped from their foil covers. While still frozen, small (0.5-1.0 g.) horizontal chips were sawed from their sides. The chips were individually dried in acid-washed glass vials in an oven at 100° C. overnight and then cooled in a desiccator for at least thirty minutes before weighings. Weighings were made to the nearest mg. on a Mettler single pan balance. The samples were then placed in acid-washed 250 ml. beakers.

Digestion was done by wet-ashing under a hood at a temperature near boiling with 10 ml. concentrated nitric acid and 3 ml. of 72 percent perchloric acid. Fuming was continued until dense white perchloric acid fumes evolved. If a yellow or brown color persisted, a watch glass was placed over the beaker and digestion was permitted to continue until the color disappeared. The samples were then removed from the hotplate and diluted with water to approximately 30 ml.

The samples were suction-filtered through gooch crucibles with asbestos linings into a clean suction flask. The crystal clear filtrates were transferred to separatory funnels.

Ten ml. of .001 M. neocuproine, 5 ml. 10 percent hydroxulamine hydrochloride, 10 ml. 40 percent sodium citrate, and enough ammonium hydroxide to neutralize the solution to red with congo red paper (pH change in 4-6 range) were respectively added. Extraction of the red-brown copper complex was made with 32 ml. of redistilled n-hexyl alcohol, as with the water samples.

The absorption maximum of the neocuproine complex in visible light was found to occur at 452.5 millimicrons. However, since maximum absorption, when working with the expected high copper concentrations, was less desirable, readings were made on the shoulder of the single peak at 473 millimicrons.

IV. SUPPLEMENTARY DATA

Copper Sulfate Application Data

All data on copper sulfate applications were drawn from two primary sources, both of which were available at the Adrian Water Plant.

Monthly water plant chemical records. These records provided data on total pounds of copper sulfate introduced into Adrian Lake from 1951 to present. They do not differentiate between copper sulfate applied by boat and that introduced by the constant-flow device.

Water plant diaries. The 1952-64 diaries contained entries on pounds of copper sulfate applied by boat each month. These amounts were tallied and subtracted from the monthly totals obtained from the water plant chemical records, thus supplying data on boat versus constant-feed applied copper sulfate.

Lake Discharge and Water Plant Consumption Data

These data were used to project estimates of copper transported out of Adrian Lake.

Discharge over the dam. One objective of the study is to estimate pounds of copper transported out of the lake during the 1965 spring overturn. To estimate the volume of water discharged over the dam required the construction and installation of a water level measuring device. The device installed was both simple in design and efficient.

Description of water level measuring device. A 2-inch free-rolling pulley was nailed to the 4-inch side of a twelve foot 2 X 4-inch board approximately six inches from the end. An eight-foot length of downspout was strapped and metal-screwed to the end opposite the pulley, so that the board and downspout overlapped about five feet.

The 2 X 4 was bolted vertically to the rail of the Adrian Lake concrete dam in such a way that all but two feet of the downspout was submerged, and the pulley was about three feet above eye level of a person standing on the dam. A yardstick was nailed vertically along the side of the 2 X 4 at eye level. A fine diameter copper wire, to which a weighted plastic float was tied at one end and a lead counter-weight to the other, was placed over the pulley. The float and counter-weight were lowered down the downspout into the water. The desired effect was a raising and lowering of the float with lake level fluctuation without interference from wave action.

The copper wire was taut and lay flat along side the vertical yardstick. A tiny white marker was affixed to the wire. The marker traveled vertically with any lake level fluctuation, permitting accurate daily recordings of lake level.

Period and frequency of lake level observations. Daily readings of lake level were taken each noon to the nearest quarter inch by water plant personnel over the interval April 14 through June 17, 1965. Records were kept on forms prepared for that purpose.

Over the dam discharge projections. The engineering firm, which designed the spillway, provided the water plant with a weir discharge chart. Estimates in total gallons per day were taken from this table, using the daily noon water level readings as assumed daily averages. These values were graphically plotted on a daily basis to illustrate water level trends during the measured period. They were also summed to provide monthly estimates of surface discharge.

Discharge Through Sluice Gates

No plausible means were available for measuring discharge through the sluice gates.

Water Plant Consumption

Daily records of raw lake water intake by the water plant were available. These data were summed to provide annual water consumption statistics for the period 1960-64.

Daily estimates for April, May, and June, 1965, were obtained in order to project total pounds of copper removed in raw water consumption during this period.

General Water Chemistry Measurements

In addition to water samples for the copper profiles, dissolved oxygen and pH profiles were obtained on each sampling trip. Water samples were collected at one-meter intervals with a Kemmerer sampler. Dissolved oxygen was measured with the azide modification of the Winkler method. H-ion concentration was measured in the field with a Hach A-36-P wide-range pH kit.

Alkalinity values were determined at Station III from levels of two and five meters on five sampling trips. Two hundred ml. water samples were treated respectively with phenothalein and brom-cresol green-methyl red indicators. Phenothalein never produced a color change, proving a general lack of carbonate alkalinity. Samples were titrated with 0.02 N sulfuric acid to the grey end point for brom-cresol green-methyl red to obtain bicarbonate alkalinity values.

Vertical profiles of water electrical resistance were measured on the March 15, 1965 water samples with a calibrated conductivity meter.

RESULTS AND DISCUSSION

I. ADRIAN LAKE DURING THE STUDY

During the five-month period of the study (January through May, 1965), Adrian Lake water dynamics can be described as constantly changing. Dissolved oxygen and pH values were used as indices of stratification and are summarized in Appendix 1.

H-ion Concentration

On all eight sampling days, pH was found to be constant from surface to bottom, except on February 6, when surface readings were influenced by snow-melt water running into the sample ice holes. There seemed to be little fluctuation in lake pH from week to week since the values never deviated from the range 7.0 to 8.0 among the sample days or between surface and bottom.

Dissolved Oxygen During Under-Ice Sampling

Under-ice sampling extended from January 15 through April 12. During January and early February, the lake water was very clear, and a January 15 profile showed dissolved oxygen to be relatively constant from surface to bottom. Profiles taken on January 30 and February 6 showed the lake was tending toward chemical stratification with values decreasing to a low of 8.0 ppm. at the bottom.

During the days February 7-9, rains and a thawing of snow brought a large silt-laden discharge, which served to mix the lake under the ice. A March 15 profile showed oxygen concentrations to be high and constant from surface to bottom. This situation remained constant until the ice went out on April 12.

Dissolved Oxygen During Open-Water Sampling

Open-water sampling extended from April 13 through May 27. An April 14 profile showed dissolved oxygen values to be homogeneous from surface to bottom. On April 29 the samples revealed a slight lowering of dissolved oxygen values in deeper water, and on May 12 a clearly defined decrease from 11.0 ppm. at the surface to 3.8 ppm. at the bottom was recorded. On May 27 there was less than 1.0 ppm. in waters four meters and deeper at Station III.

Alkalinity

Total alkalinity was measured on five sampling days at depths of two and five meters. It was found in all cases to consist entirely of bicarbonate. Values ranged from 102 to 194 ppm. at two meters and from 125 to 228 ppm. at five meters. Values were consistently higher at the lower level. These data are summarized in Appendix 2.

II. MOVEMENT OF APPLIED COPPER IN THE LAKE

The Constant-Flow Copper Sulfate Device and Its Operation

On October 23, 1956 installation of a permanent copper sulfate constant-flow device on a high bank over the Adrian Lake stream inlet was completed. This device was still in operation at the time of the present study. Copper sulfate is automatically dissolved in water, and the solution is pumped into a buried polyethylene pipe, which leads downhill and out into the center of the inlet stream. The operation is normally continued 24-hours a day for most of the year.

The basic premise of the constant-flow operation is that constantly introduced copper sulfate serves to eliminate troublesome algae and/or bacteria from the lake. Barthelomew (1958) reported similar use of a constant-feed copper sulfate device with success in the Los Angeles aqueduct.

The monthly rate of copper sulfate application to Adrian Lake with the device has been variable, with amounts ranging from nothing to as high as 3,400 pounds per month. During January through May, 1965, 3,400 pounds of copper sulfate were applied.

During the first six months of 1965, the device was shut down from February 12 through March 15 and March 30 through May 4. The two shut-downs occurred during periods of high water, when copper sulfate treatment was not considered to be worthwhile.

Reliability of Lake Water Copper Analyses

The accuracy and precision of the copper measurements are considered to be acceptable. The more important sources of error encountered were considered to be loss of copper ions through adherence to beaker surfaces and the very low copper concentrations, which often necessitated working in the 0-0.1 absorbance range on the DK-2A. The first error source was minimized through acid washing and rinsing of glassware prior to and during use. The second error source, although never eliminated, was minimized by replacing the 1 cm. absorption cells with 10 cm. cells, thus intensifying absorbance ten times.

Final standard curves were readily reproduced, with virtually no deviation from the straight-line relationships, which in turn indicates precision in results. This precision was enhanced by the great stability of the bathocuproine-copper complex and the reproducibility of the Beckman DK-2A.

An example of the precision obtained is shown in Figure 4. Duplicate series of 100 ml. samples were processed, and the results clearly show that either series could independently represent the profiles.

Water Movement and Its Effect on Lakewater Copper

All estimates of copper concentrations are listed in Appendix 3. An initial study objective was to relate vertical stratification of copper concentration to under-ice lake stratification. The static conditions of the 1964-65 winter, however, did not permit advanced under-ice stratification to occur. As a result a factor heretofore not considered as important was brought to focus. The data indicate that water movement through Adrian Lake was of prime import in controlling copper profiles during the entire period studied.

The March 15 data.

The March 15 data displayed a copper profile in which values were highest at the surface and bottom, and low at midwater. This trend was observable at both Stations II and III. Since water was being drawn through the sluice gates, there was still ice cover, a large volume of water was entering the lake, and no water was going over the dam, it was hypothesized that a density current of inflowing water was traversing the lake through the old Wolf Creek stream bed.

To test this hypothesis, profiles of resistence were obtained at all five stations. Examination of the resistence data graphed in Figure 5 shows that a density current did exist. Inflowing Wolf Creek water displayed a relatively low resistence and was obviously being pulled through the lake at depths below two meters and discharged through the sluice gates. The constant-flow copper sulfate device had been shut down for almost a month and the presence of dilute runoff water traversing the lake explained the lower copper concentrations at midwater. However, it did

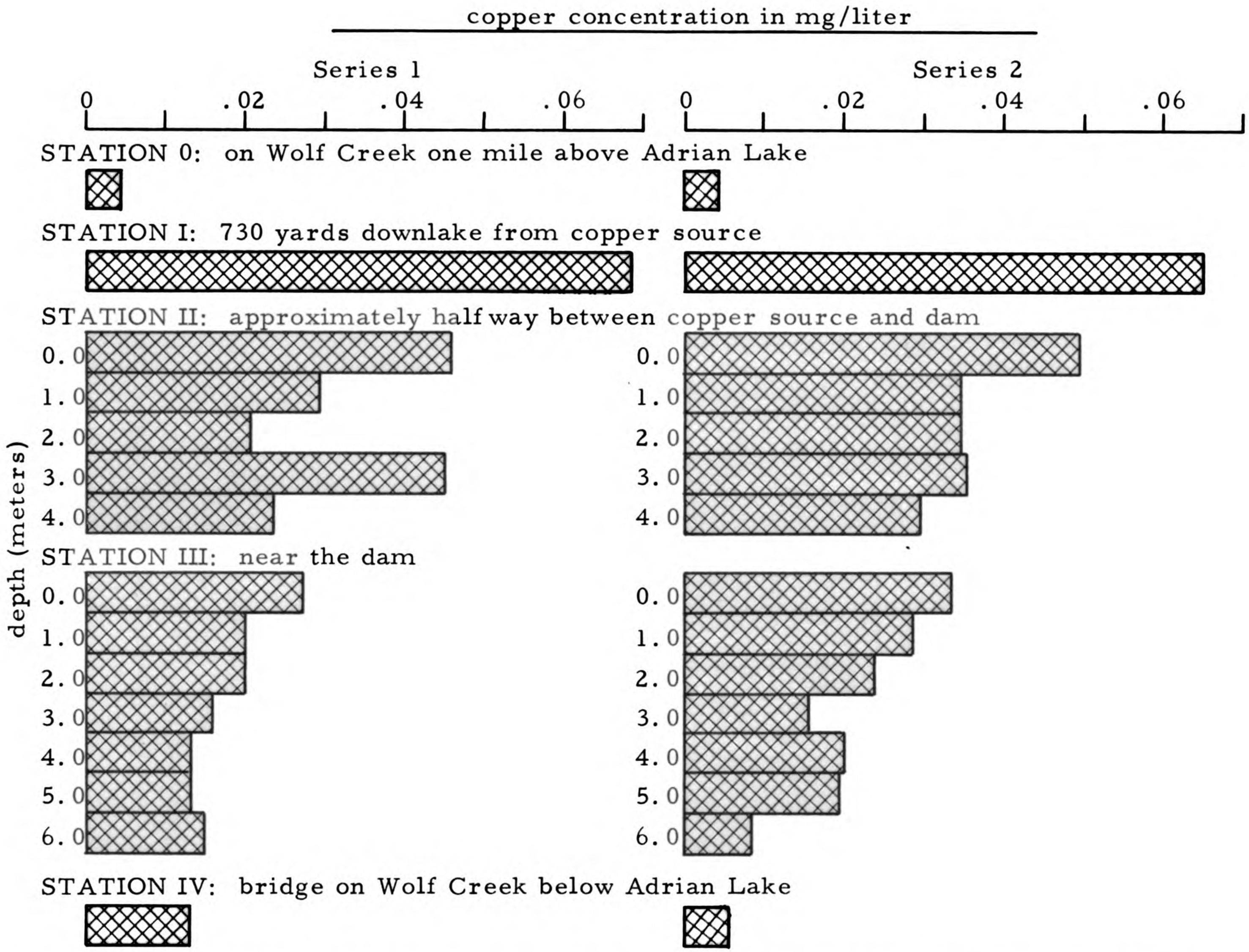


Figure 4. Analyses of two separate series of 100 ml. water samples from the April 14 collection for total copper, illustrating the precision of the bathocuproine method of copper analysis.

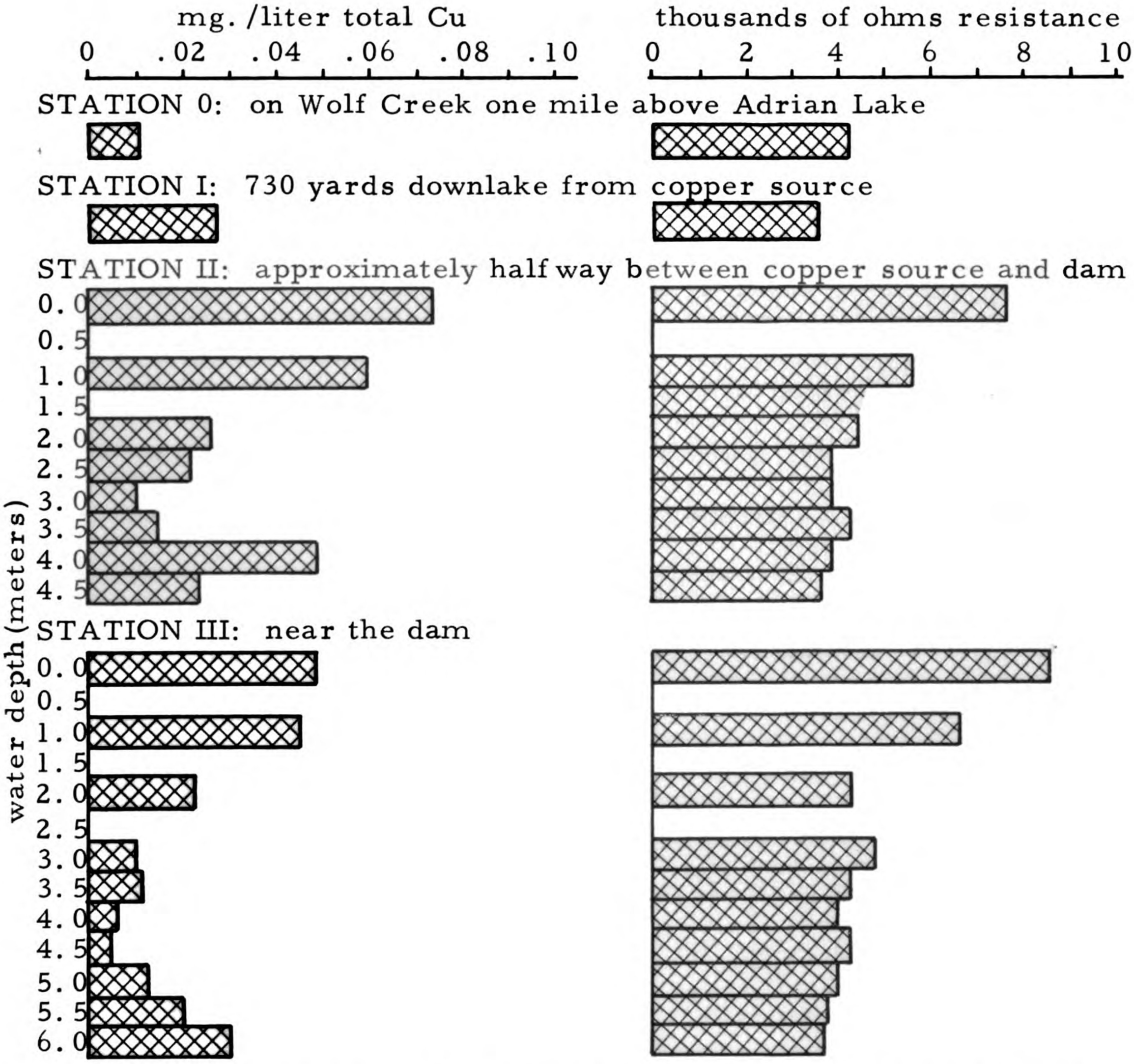


Figure 5. Comparison of total copper concentration and lake water resistance data for March 15, 1965, which illustrates the effect of a density current on copper concentration. The $CuSO_4$ feed device was shut down an entire month prior to this date.

not explain the higher copper concentrations below mid-water, since the density current extended to the bottom.

A secondary hypothesis was suggested; that the inflowing current was sweeping particulate matter bearing copper from the bottom and keeping it in adequate suspension to reach the dam area and perhaps be carried through the sluices. This hypothesis was tested and supported through examination of the sestonic and filtrate copper data (Appendix 3). Profiles at Stations II and III showed filtrate copper was higher at the surface, but low and constant below two meters, whereas the sestonic fraction increased progressively from three meters to the bottom. Indeed, wave action must provide essentially the same mechanism to eventually transport applied copper to deeper waters of lakes, as suggested by Nichols et al. (1946).

Application of the water movement hypothesis to other data. An evaluation of the data from all eight water sampling dates was made in light of the March 15 data, and it was found that the copper profile dynamics could be largely explained by the presence or lack of water movement. Factors apparently most important are: (1) volume of inflowing water; (2) amount of copper sulfate entering the lake; (3) amount of water going over the dam; and (4) sluice gate discharge. Figure 6 provides a running account of these factors at Station III. The January 30 profile was omitted from Figure 6 because it reflects essentially the same picture as the February 6 profile.

On January 30 the sluice gates were open and copper sulfate was flowing. A resulting bottom density current exhibited high copper values picked up at the inlet. Sluice gates were closed on February 2 and no water was flowing over the spillway. The February 6 profile indicates this closure stopped the density current and "froze" the

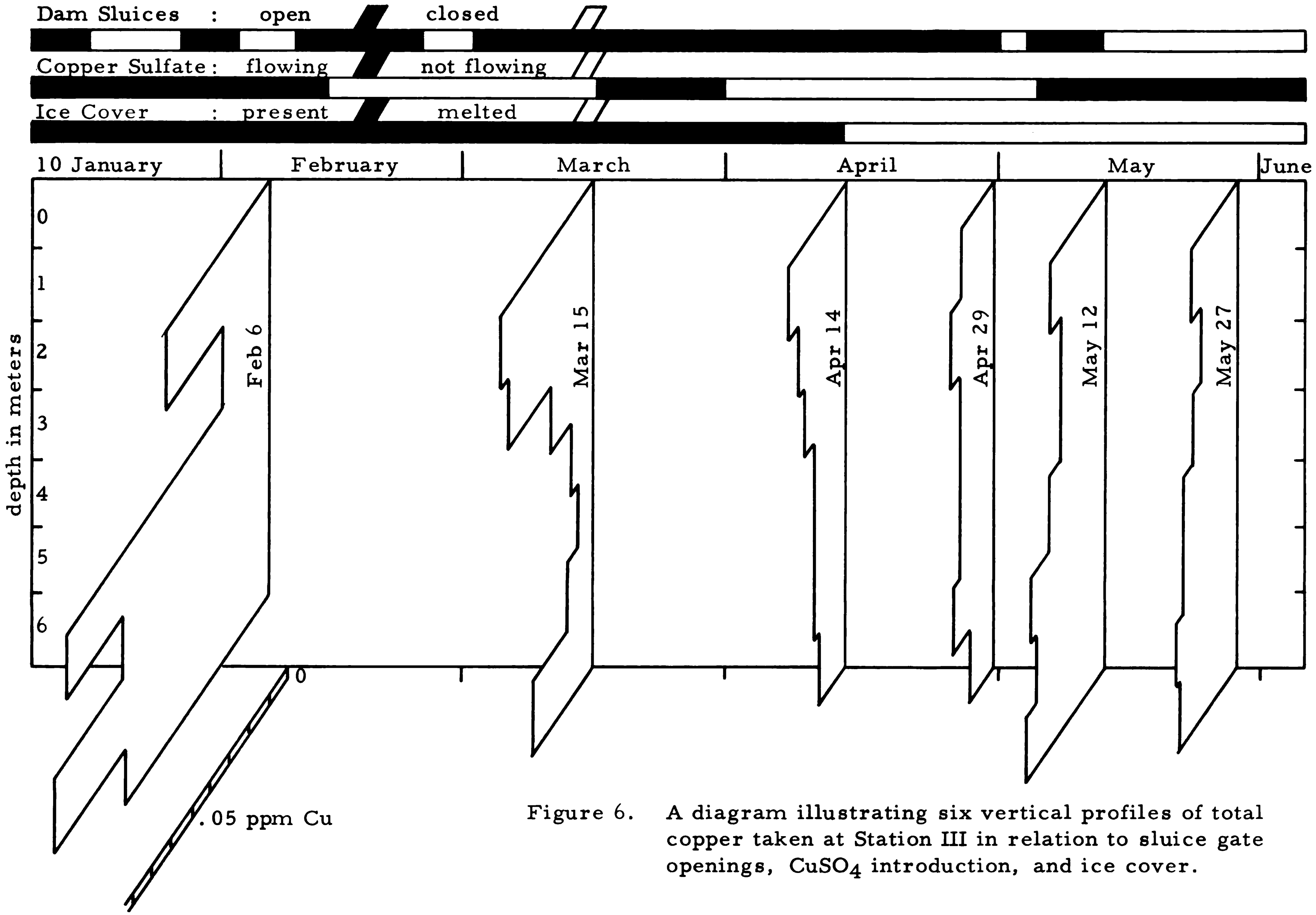


Figure 6. A diagram illustrating six vertical profiles of total copper taken at Station III in relation to sluice gate openings, $CuSO_4$ introduction, and ice cover.

lake's copper profile.

On April 14 a large density current was going over the dam (estimated 113 million gallons per day), and the copper sulfate had been shut off for eight days. In this instance the incoming stream picked up copper in Area A and transported it across the surface of the lake to pass over the dam. Here, however, the mechanism for picking up copper from the bottom is uncertain. If it were current action picking up fine copper-bearing material, we would expect to find high sestonic copper values in the top water density current. However, sestonic copper values were actually relatively low and constant from surface to bottom, refuting the idea of physical suspension of particulate copper-bearing matter. These data indicate the copper was picked up in some other fashion.

On April 29 the volume of water entering the lake was considerably less than on March 15 and April 14, although the dam sluices were open and an estimated three million gallons of water per day was flowing over the dam. The copper sulfate was shut off. Dissolved oxygen concentrations were constant from surface to bottom, and water transparency had increased significantly. Copper concentrations were nearly constant from surface to bottom. It appears that a prolonged gentle mixing of the lake was responsible for the homogenous concentrations.

The May 12 sampling provided a definite contrast. The sluice gates were open, the copper sulfate had been flowing for eight days, and no water was going over the dam. In this instance, copper concentrations were higher below 2.5 meters and increased progressively to the bottom, suggesting a density current.

May 27 found the sluice gates closed, no overflow, and the copper sulfate flowing. About three million gallons of water per day were being

used by the water plant. Lake copper concentrations were relatively constant, although a slight, yet steady, increase with water depth was recorded.

Effect of Copper Sulfate on Lake Water Copper

The introduction of copper sulfate to the lake via the constant-flow device had a definite effect on copper content at all parts of the lake, as long as a volume of water was passing through the lake.

January 16, 30, and February 6, which exhibited discharge through the sluice gates and copper sulfate flowing, exhibited strikingly higher total copper values, ranging up to 0.177 ppm. on January 30. Further examination of the data showed the filtrate fraction to be very high and the sestonic fraction to be relatively low, showing most of the total copper had gone from the copper sulfate pipe into substances such as soluble inorganic compounds or organic complexes. The applied copper was not primarily tied up with algae, detritus, or clay particles, or it would have shown up in the sestonic fraction.

A shut down of the copper sulfate flow caused a marked decrease in the total copper content and a marked increase in the proportion of sestonic copper. Under this condition, total copper was primarily sestonic in nature on March 15, April 14, and April 29. The inflowing filtrate fraction, losing the source of constantly-fed copper-ions by the shut down, simply remained minute. The form(s) the sestonic fraction took are unknown. However, the lake was relatively turbid on all three of the above dates.

The constant-flow copper sulfate operation was re-continued on May 4. However, the sluice gates were closed on May 12 and no water traveled over the dam. The only draw on the lake was caused by the approximate three million gallons per day consumed by the water plant. With no significant current to bring the applied copper down the lake, total copper concentrations increased slightly, but not nearly to the extent of the January 16 through February 6 period.

It is assumed that the introduced copper remained at the upper end of the lake during the May sampling period. The form of the copper at this time can only be conjectured. Several alternatives as to what happens as the copper ions leave the constant-feed pipe include: (1) an accumulation of copper ions in solution; (2) formation of a soluble copper compound(s); (3) deposition as an insoluble copper compound, and (4) precipitation through adsorption to clay particles and/or other colloidal material. Alternative (1) is very unlikely, because of the alkaline character of the inflowing water. The remaining three are all possible and probable.

A pile of flocculent material completely covers the constant-flow pipe in the inlet stream each summer. The accumulated material exhibits a bright greenish-blue color on the downstream side, the color of which is doubtless due to an inorganic copper compound, possibly the carbonate. Sediment Core 2 was taken from the center of this pile of floc. The frozen 35-cm. long core exhibited numerous layers of the greenish-blue precipitate, while interim sediment layers were brown silty-clay. At least some of the copper ions passing from the pipe through the floc pile are reacting with components of the lake water. It is also possible that erosional destruction of this pile during periods of high water contributes greatly to the sestonic copper fraction of the lake at these times.

Estimated Amount of Copper Carried Out of The Lake

A prime objective of the study was to estimate the amount of applied copper which was carried out of the lake during the spring runoff. This was done to determine if such loss is actually a substantial amount.

The period surveyed for copper loss was April 14 through June 4. Table 4 summarizes the computations and gives the various estimates of copper inflow and loss. An estimated 153 pounds of natural copper was carried into Adrian Lake by the Wolf Creek during the survey period. An estimated total of 253 pounds was carried out, theoretically including 105 pounds of previously applied copper.

This estimate is at best crude. However, it does give dimension to the fact that a significant amount of copper is transported from the system via high water conditions. Of special significance is the fact that the greatest amount was carried out over the dam during high water conditions at a time when the copper sulfate was not being, and had not been, fed into the lake. This was copper picked up from the sediment, as indicated by the March 15 data.

The total copper values measured on January 16, January 30, and February 6 at Station III were very high, ranging from 0.067 ppm. to 0.177 ppm. As mentioned before, these high values were due to the fact that the copper sulfate was flowing. It is apparent that any large volume of water would carry these copper-rich waters through and out of the system. Although no discharge data are available, if a conservative sustained sluice gate discharge of twenty-eight acre feet of water per day containing 0.10 ppm. of copper is assumed, an estimated 230 pounds of copper would be carried out in a month as long as the copper sulfate flow was maintained. Since there is roughly twenty-five pounds of copper in

Table 4. Summarization of estimates for pounds of applied copper discharged from Adrian Lake during the period April 14 through June 4, 1965.

	Apr. 14 to Apr. 22	Apr. 23 to May 6	May 7 to May 20	May 21 to June 4	Total copper (in lbs.)
DISCHARGE OVER DAM					
acre feet discharged	1,639.3	472.2	83.5	77.7	
Cu con. at dam (ppm.)	.030	.017	.031	.025	
lbs. Cu per acre feet	.081540	.046206	.084258	.067950	
est. lbs. Cu carried out	137.7	21.8	7.5	5.3	172.3
DISCHARGE THROUGH SLUICE GATES*					
days sluice gates operated	9	10	6	none	
est. acre feet discharged	250.7	273.6	167.2	0	
Cu Con. at sluices (ppm.)	.015	.021	.042	.031	
lbs. Cu per acre foot	.040770	.057078	.114156	-	
est. lbs. Cu carried out	10.2	15.9	19.8	-	45.2
WATER PLANT CONSUMPTION					
acre feet consumed	88.4	145.7	162.5	190.5	
Cu con. at intake (ppm.)	.030	.017	.031	.025	
lbs. Cu per acre foot	.081540	.046206	.084258	.067950	
est. lbs. carried out	7.2	6.7	13.7	12.9	40.6
			Total Cu carried out		258.1
INFLOWING WATER					
est. acre feet inflow**	2,028.4	896.4	413.1	268.2	
Cu con. at inflow (ppm.)	.004	.024	.052	.019	
lbs. Cu per acre foot	.010872	.065232	.141336	.051642	
lbs. Cu carried into lake	22.1	58.5	59.1	13.9	153.5

Total pounds of copper carried out of the lake	**258.1**
Total pounds of copper carried into the lake	153.5
Total pounds of applied copper removed	104.6

* An arbitrary estimate of 28 million gallons per day is advanced, figuring one-tenth full-flow capacity of the sluice gates.

** The inflow was assumed to roughly equal the sum of the out flow components (sluice gate and dam discharge plus municipal consumption).

one-hundred pounds of $CuSO_4 \cdot 5H_2O$, this is equivalent to approximately 900 pounds of copper sulfate.

It is apparent that copper is transported out of Adrian Lake both by direct flow from the constant-flow source and by carrying it from the sediments. In both instances a water current is seemingly the prime factor which determines the rate of removal.

III. DISTRIBUTION OF APPLIED COPPER IN THE SEDIMENTS

History and Mode of Copper Applications

Adrian Lake received copper sulfate applications as early as 1946. In that year Cooper and Carbine[8] reported the, ". . . Water Board Chemist treats the lake with copper sulfate for algae control." No record of poundage applied is available until 1951, when the water plant diaries were initiated. Records of copper sulfate application compiled from the diary and other water plant records are given in Table 5.

Table 5. Pounds of copper sulfate applied to Adrian Lake over the period 1951-64.

Year	Copper Sulfate Applied by Boat	Copper Sulfate Applied by Constant-flow Device	% Applied by Boat	Total Pounds
1951	6,200	-	100	6,200
1952	4,000	-	100	4,000
1953	10,300	-	100	10,300
1954	4,500	-	100	4,500
1955	5,300	-	100	5,300
1956	4,500	7,500	38	12,000
1957	4,700	18,793	20	23,493
1958	6,900	17,375	28	24,275
1959	700	11,100	6	11,800
1960	11,050	10,600	51	21,650
1961	9,500	16,100	37	25,600
1962	9,600	18,300	34	27,900
1963	4,700	19,500	19	24,200
1964	3,600	18,300	16	21,900
Total	55,250	137,568	-	192,818

---

[8] 1946 Adrian Lake Survey

Applications were primarily made by boat until 1956, although some were made by stretching burlap bags of copper sulfate on a cable, which was stretched across the inlet stream. In 1956 the constant-flow device was installed. Table 5 shows that since its installation, most of the copper sulfate has been applied through this device.

Despite operation of the constant-flow device, algal blooms still occur on the lower half of the lake, requiring occasional boat applications. Boat application is achieved with an outboard-powered wooden boat especially fitted with an open-topped hopper on each side. The hoppers are filled manually. With the boat moving, lake water passes freely through each hopper with dissolved copper sulfate being dispersed behind the boat and mixed by the churning of the motor.

Reliability of Sediment Copper Analyses

Results are considered to be adequately precise and accurate. Repeatedly run standard solutions closely fitted the standard curve.

Precision was tested by running three samples from a volume of Adrian Lake organic-clay sediment, which to achieve homogeniety was respectively air-dried, powdered with mortar and pestle, oven-dried, mixed by shaking for one hour, and then re-dried overnight. The samples respectively weighed 0.3746 g., 0.1383 g., and 0.2875 g. Results yielded respectively 1,236.25 ppm., 1,229.50 ppm., and 1,228.69 ppm. total copper. The average and standard deviation of these three samples were found to be 1,231.48 ppm. and 4.15 ppm., indicating that 95% of any additional determinations would fall within the range 1,231.48 ± 8.30 ppm. This is judged to be adequate precision considering the high values of copper found in the sediments of Adrian Lake.

Findings

All values of total copper from sediment analyses are summarized in Appendix 4. In the lake as a whole copper values were found to be high, but not nearly as high as had been anticipated. A maximum down lake value of 1,982 ppm. was found 2- cn, deep in Core 5, which was collected in Area A, 1,145 feet from the point of copper sulfate introduction.

One specific trend was readily observable in all but five of the twenty-five cores collected down lake from the copper sulfate source. This tendency is a gradually decreasing copper content with increasing sediment depth and is graphically shown in Figure 7. Cores 4 and 6 of the figure came from Area A, cores 10 and 14 came from Area B, and cores 16 and 17 came from Area C. This trend apparently reflects the lake's copper sulfate application rate. The available water plant records (Table 5) show that annual applications have generally and progressively increased since 1951. Thus, at Adrian Lake, it would seem that when more copper is applied, more is incorporated into the sediments.

One disadvantage of the prototype coring model was that the average length of core acceptable for analysis was only 10 cm. (or 3.9 inches). Thus, it was not generally possible to sample deep enough to reach native values of copper. An estimate of native copper concentration, however, was obtained from Core 1, which was collected with copper pipe from the Wolf Creek stream bed one mile upstream from the lake. This core displayed total copper values varying from 8. to 33 ppm. at 5. cm. intervals down to 30- cm. Thus, the rapid decrease of copper content with sediment depth in the lake indicates that the applied copper accumulation does not extend far below the sampled 10 cm. depth. This is corroberated by the fact that the lower parts of several longer cores exhibited values as low

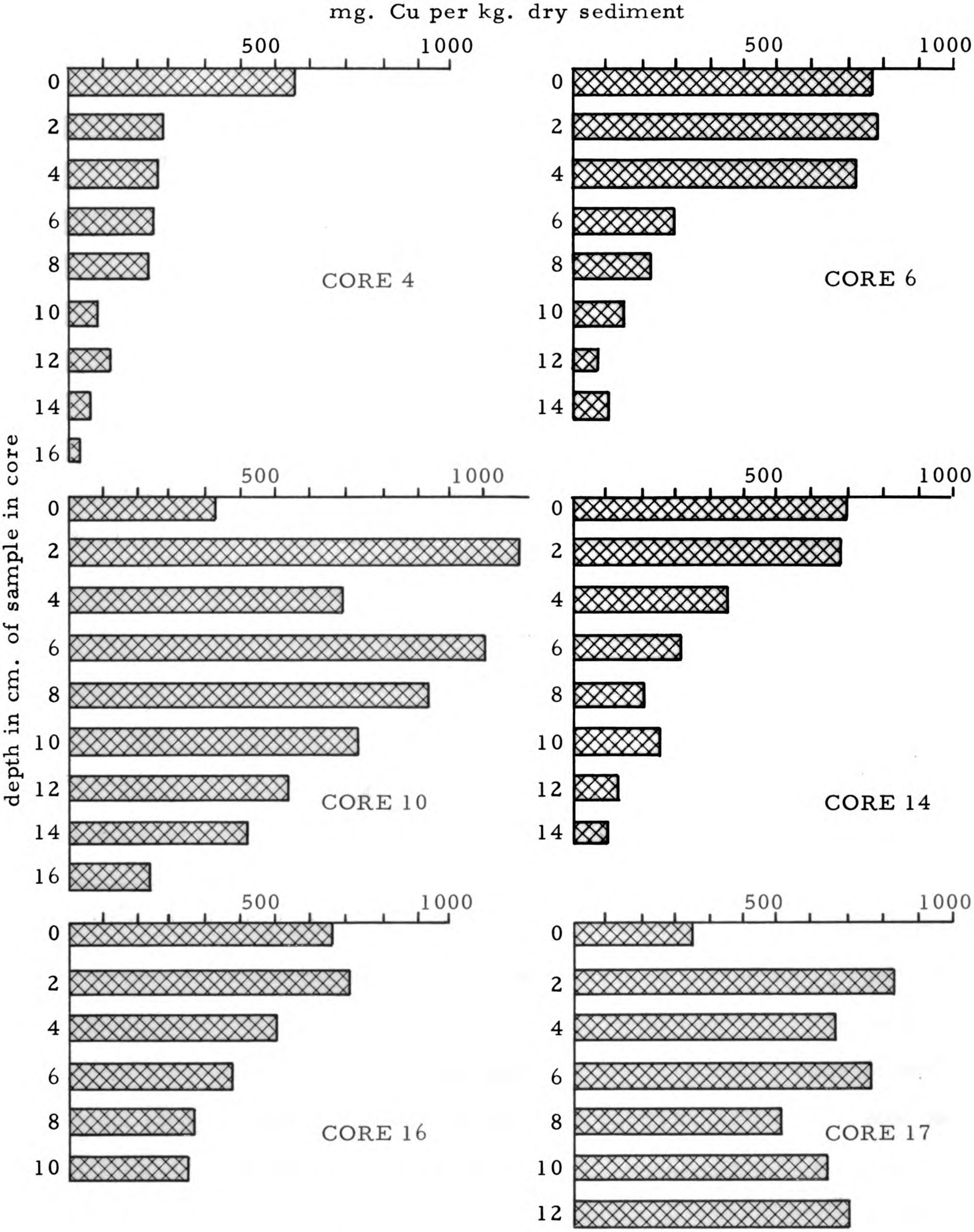


Figure 7. Vertical profiles of total copper in mg. per kg. dry sediment from six Adrian Lake cores.

as 23, 53, 67 and 77 ppm. Assuming each core's lower copper values represent applications of copper sulfate from the late 1940's and early 1950's, the 10 cm. depth probably represents the amount of sedimentation in Adrian Lake over this period.

Cores 17, 21, 23, and 27, all of which were collected in Area C, did not observably follow the trend exhibited by the majority of cores. Instead, these cores tended to exhibit constant values from surface to base, as exemplified by core 17 in Figure 7. It should be noted that cores 17 and 23 were respectively collected from 5.8 and 5.5 meters of water and are the deepest two samples taken. Cores 21 and 27 also rank among the deeper samples. It is reasonable to assume that the rate of sedimentation is greater in the deeper waters, and that the frozen corer simply did not obtain sufficient length cores to expose the decreasing copper profile shown by the remainder of the cores.

Copper concentration with respect to water depth. Nichols et al. (1946) report higher values of total copper in the profundal regions of treated Wisconsin lakes. Riley (1939) mentions this phenomena, though not providing data on Lindsley Pond.

The Adrian Lake data were examined to determine if higher concentrations of copper existed in the deeper waters of the lake. A linear regression analysis was run upon data from the eighteen cores collected in Areas B and C, using depth of the sample as the independent variable and total copper concentration as the dependent variable. The correlation coefficient was found to be 0.311 and a test of the hypothesis that the slope equals zero was found to lack significance at the 5 percent level (F = 1.719 with 1 and 17 d.f.). Thus, the data provide no evidence of increasing copper concentration with increasing water depth in Adrian Lake.

Nichols et al. felt the "natural grading process", wherein fine material is carried eventually to deeper water, is instrumental in achieving higher copper values in the deeper sediments of the treated Madison Lakes. Since Adrian Lake data does not support such a relationship, there is either (1) a significant difference between the Madison Lakes and Adrian Lake in the "natural grading process" or (2) the sample size collected at Adrian Lake is insufficient to portray copper concentration differences over the narrow depth range sampled. Although the sedimentation process will obviously be different between a small reservoir and large natural lakes, the latter explanation seems more plausible. Lake Menona has depths exceeding eighty feet, whereas Adrian Lake is not over twenty-five feet deep. The eighteen Adrian Lake cores compared were collected from 1.75 to 5.8 meter depths, which is a range of approximately twelve feet. In contrast, samples from Lake Menona were collected from a depth range over five times as great.

Copper concentration with respect to distance from the point of introduction. Since 71.3 percent of the 192,813 pounds of copper sulfate applied to Adrian Lake over the 1952-64 period were introduced by the constant-flow device, an excellent opportunity was afforded to analyze the importance of proximity to the point of introduction on copper accumulation in sediments. Theoretically, relatively fast precipitation of copper as insoluble inorganic salts and/or organic complexes, could result in very high copper concentrations in the upper end of the lake. The highest total copper values from all twenty-seven cores are shown plotted in Figure 8 arranged in order of distance from the constant-flow copper sulfate source. Although no regression analysis was done, it is evident

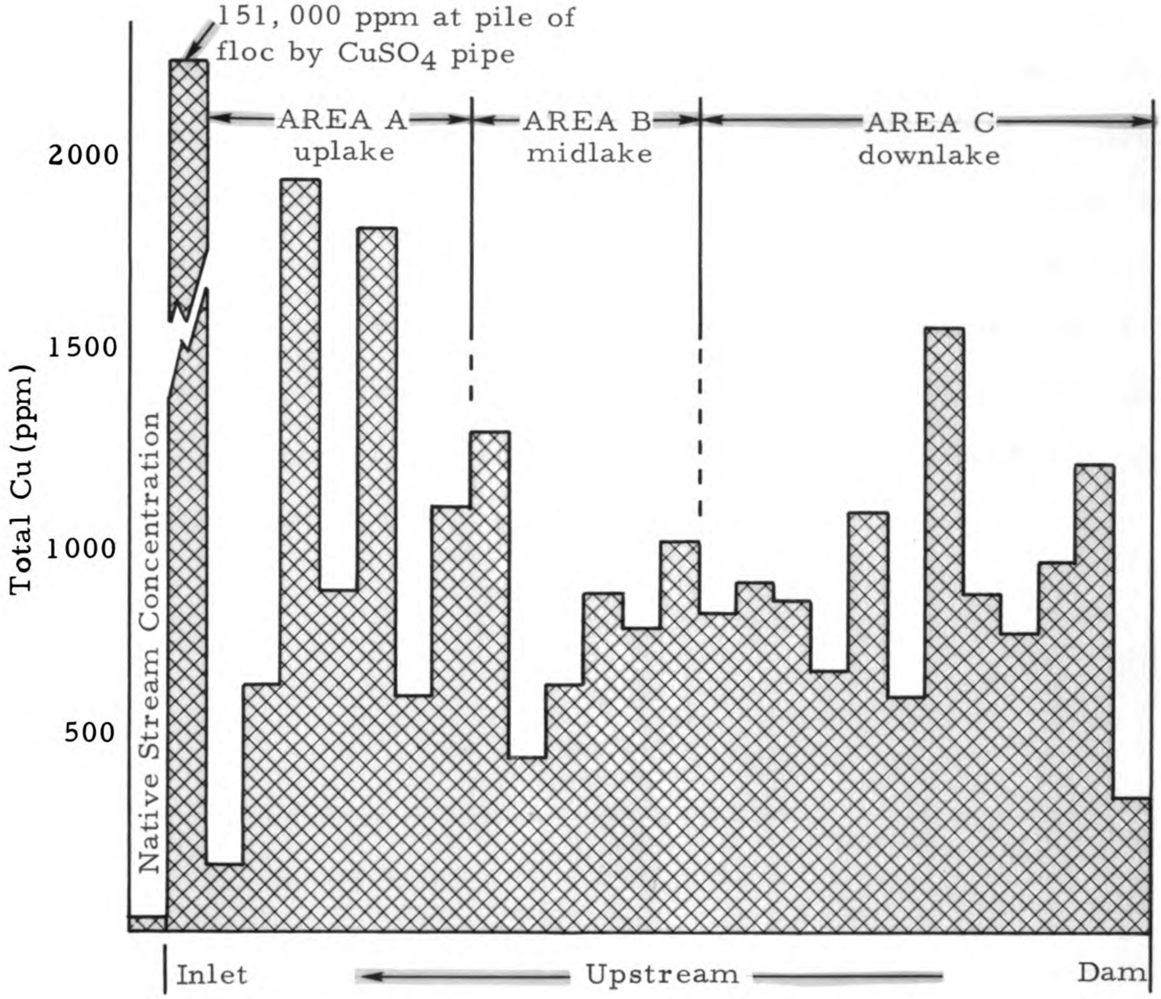


Figure 8. A graphic presentation of Adrian Lake sediment core copper concentration with respect to distance from the point of copper sulfate introduction.

that these data indicate no very strong relationship between copper concentration and distance from copper source.

Actually, little supporting evidence even exists, which might support such a <u>permanent</u> trend in Adrian Lake. Distribution of applied copper at the lake inlet and in Area A is obviously static. Despite the fact that becalmed and low-inflow conditions result in copper compound accumulations at the inlet, wave action and intensified inflow, whenever they might occur, result in full or partial re-distribution of these compounds. This re-distribution is of course ultimately down-lake. Supporting evidence of "re-distribution" by currents is provided by the March 15 water sampling data.

SUMMARY

1. A study was made of the dynamics of movement and accumulation of applied copper in Adrian Lake, an 85-acre southeastern Michigan hard-water water supply impoundment. The lake has accrued a copper accumulation during more than ten years of intensive algal control with copper sulfate by the City of Adrian. Applications occurred as early as 1946. Available records show that from 1951-64, 192,818 pounds of commercial grade copper sulfate were applied, and approximately 70 percent of the total entered through a continually operating constant-feed device located at the lake inlet.
2. The study extended over the period January through May, 1965. Specific objectives were: (a) to evaluate the accumulated copper distribution in the sediments with respect to water depth and distance from the point of constant-feed copper sulfate introduction; and (b) to evaluate vertical and horizontal copper profiles of lake water with respect to how they affect the movement and distribution of applied copper in Adrian Lake.
3. During the study Adrian Lake water dynamics were found to be constantly changing. Under-ice dissolved oxygen profiles showed a gentle progression towards stratification. A snow-melt and rainy period in early February resulted in a thorough under-ice lake mixture. Open-water sampling from April 13 through May 27 showed a gradual progressive development to stratification after the overturn. Dissolved oxygen values below 1.0 ppm. were found at the deeper levels during the latter half of May.

4. An evaluation of water copper profiles for the eight sampling dates resulted in the conclusion that water movement is a very significant factor in the movement of applied copper through and out of Adrian Lake. The measured copper profile dynamics can be largely explained by the degree of water movement. Factors apparently most important in the mechanism are: (a) volume of lake inflow; (b) presence, or lack, of copper sulfate entering the system; and (c) water volume going over the dam and/or through the sluices.

On March 15 a strong density current was traversing the submerged Wolf Creek stream channel to pass out through the dam sluices. Copper sulfate constant-feed was shut down and the residual or stagnant water layer above the density flow maintained relatively high copper values from some prior currentless period, when the copper sulfate was flowing. With no artificial source of copper the dilute density current exhibited low natural copper values with the exception of the bottom one and one-half meters. Examination of the sestonic copper profiles indicated that the density current was sweeping copper-bearing particulate matter into the seston from the bottom.

Introduction of copper sulfate via the constant-flow device had a definite effect on lake water copper content at all parts of the lake, as long as a volume of water was traversing the lake. With copper sulfate flowing and a sluice gate discharge, the proportion of filtrate copper soared and the sestonic fractions were low, indicating most applied copper had combined into soluble substances. With low inflow and no water going out the dam, and thus no current to bring the copper down lake, the data indicate that the introduced copper remained at the upper end of the lake. The forms are assumed to be deposited insoluble copper compounds and/or copper-colloidal material complexes.

During the period April 14 - June 4 an estimated 105 pounds of applied copper was transported out of Adrian Lake. A crude estimate at best, this statistic does give dimension to the fact that a significant amount of copper is carried from the system via high water conditions. Of special significance is the fact that the greatest amount of the estimate was transported out at a time when copper sulfate was not being, and had not been for some time, fed into the lake. Copper is transported out of Adrian Lake both by direct flow from the constant-flow source and by carrying it from the sediments. In each instance water currents are the vehicle which determines the rate of removal.

5. Total copper values in the sediments were found to be high, but not nearly as high as anticipated. A maximum down lake value of 1,982 ppm. was found two cm. deep in Core 5, 1,145 feet from the point of copper sulfate introduction.

A specific trend was found in the vertical distribution of copper in the cores. Copper content progressively decreased with increasing sediment depth. The available records show that annual copper sulfate applications have generally increased since 1951, and the vertical trend apparently reflects the lake's rate of copper sulfate application. It seems that when more copper is applied, more is incorporated into the sediments. Assuming each core's lower copper values represent applications of copper sulfate from the late 1940's and early 1950's, the 10 cm. depth probably represents the approximate depth of sedimentation in Adrian Lake over this period.

The data provide no evidence of increasing sediment copper concentration with increasing water depth in Adrian Lake. However, it was concluded that the sample size was insufficient to portray copper concentration differences over the narrow depth range sampled (12-feet).

Nor does data provide evidence of a strong relationship between sediment copper concentration and distance down lake from the constant-flow copper sulfate device. Little evidence even exists, which might support such a <u>permanent</u> trend at Adrian Lake, since the water sampling showed the distribution of applied copper at the lake inlet is static. Wave action and intensified inflow, whenever they might occur, are attributed to result in continual full or partial down lake re-distribution of these compounds.

6. The literature review resulted in the conclusion that the important high affinity of organic matter for copper ions has been generally unrecognized in the field of lake copper ecology. A thorough understanding of copper ion reactions in natural waters is precluded until such time as a more ample background is established on form of copper ions in the water, the organic and inorganic materials present, their inter-relationships, and relative copper affinities.
7. A review of the existing fish population records and a cursory seine-gill net survey was done. The limited data seem to indicate that species composition has remained relatively stable since at least 1953. All but two of the species recorded in 1953 were found to be present in 1965. In addition the 1965 survey showed the presence of one heretofore unreported clean-water species, the mottled sculpin. Sunfish growth has traditionally remained poor.

LITERATURE CITED

A. P. H. A., A. W. W. A. and W. P. C. F. 1960. Standard methods for the examination of water and wastewater. Eleventh edition.

Bartholomew, K. A. 1958. Control of earthy, musty odors in water by treatment with residual copper. A.W.W.A.J. 50:481-486.

Benoit, R. J. 1956. Studies on the biogeochemistry of cobalt and related elements. Ph.D. Dissertation, Yale University.

Borchardt, L. G. and J. P. Butler. 1957. Determination of trace amounts of copper. Anal. Chem. 29:414.

Bremmer, J. M., P. J. Mann, S. G. Heintze and H. Lees. 1946. Metallo-organic complexes in the soil. Nature 158:790-791.

Broadbent, F. E. 1955. Basic problems in organic matter transformations. Soil Sci. 79:107-114.

Broadbent, F. E. and J. B. Oh. 1957. Soil organic matter-metal complexes: I. Soil Sci. 83:419-427.

Brown, E. H. 1964. Fish activation with copper sulfate in relation to fyke-netting and angling. Pub. W-71. Ohio Division of Wildlife.

Coleman, N. T., A. C. McClung and D. P. Moore. 1956. Formation constants for Cu (II) - peat complexes. Sci. 123:330-331.

Corwin, A. H. 1950. The formation of copper complexes. In: A symposium on copper metabolism. Baltimore. The Johns Hopkins Press.

Domogalla, B. 1935. Eleven years of chemical treatment of the Madison lakes - its effects on fish and fish food. Trans. Am. Fish Soc. 65:115-120.

Fogg, G. E. and D. F. Westlake. 1955. The importance of extracellular products of algaes in fresh water. Verh. int. Ver. Limno. 12:219-232.

Frey, D. G. 1940. Growth and ecology of the carp, Cyprinus carpio Linnaeus, in four lakes of the Madison Region, Wisconsin. Ph.D. Dissertation. University of Wisconsin.

Hale, F. E. 1954. The use of copper sulfate in control of microscopic organisms. Phelps-Dodge Refining Corp. New York, N. Y. 44p.

Hasler, A. D. 1947. Antibiotic aspects of copper treatment of lakes. Wis. Acad. Sci. Arts & Letters. 39:97-103.

Hutchinson, G. E. 1957. A treatise on limnology. Vol. 1. Geography, physics, and chemistry. N. Y. Wiley and Sons, Inc. 1015 pp.

Klein, L. 1957. Aspects of river pollution. N. Y. Academic Press, Inc. Publishers.

Mackenthun, K. M. and H. L. Cooley. 1952. The biological effect of copper sulfate treatment on lake ecology. Trans. Wis. Acad. Sci. Arts & Letters. 41:177-187.

Moyle, J. B. 1949. The use of copper sulfate for algal control and its biological implications. In: Limnological aspects of water supply and waste disposal. Am. Asso. Adv. Sci., 87 pp.

Nichols, M. S., T. Henkel, and D. McNall. 1946. Copper in lake muds from lakes of the Madison area. Trans. Wis. Acad. Sci. Arts & Letters. 38:333-350.

Ohlmacher, F. J. 1964. A coring device for freezing samples of lake sediments. M. S. Thesis. Central Michigan University.

Placak, O. R., Ruchhoft, C. C., and Snapp, R. G. 1950. Copper and chromate ions in sewage dilutions. Industr. Engng. Chem. 41:2238-41.

Prescott, G. W. 1948. Objectionable algae with reference to the killing of fish and other animals. Hydrobiologia 1 (1): 1-13.

Prytherch, H. F. 1934. The role of copper in the settling, metamorphasis, and distribution of the American oyster, Ostrea virginica. Ecol. Monographs. 4(1):47-107.

Riley, G. A. 1939. Limnological studies in Connecticut. Ecol. Monographs 9:53-94.

Rudgal, H. T., 1946. Copper in sludge digestion: effect of copper on the operation of the Kenosha plant. Water and Sewage Works. 93:316.

Saunders, G. W. 1957. Interrelationships of dissolved organic matter and phytoplankton. Bot. Rev. 23:399.

Shapiro, J. 1957. Chemical and biological studies on the yellow organic acids of lakewater. Limno. and Oceanogr. 2:161-179.

Smith, G. F. 1954. The trace element determination of copper and mercury in pulp and paper. G. F. Smith Chem. Co., Columbus, Ohio.

Striker, M. M. and L. I. Harmon. 1961. Soil Survey of Lenawee County, Michigan. 1947 Series (10). U. S. Dept. of Ag. and Mich. Ag. Ex. Sta.

Thompson, J. B. 1950. A browning reaction involving copper-proteins. In: A symposium on copper metabolism. Baltimore. The Johns Hopkins Press.

Tompkins, W. A. and C. Bridges. 1958. The use of copper sulfate to increase fyke-net catches. Prog. Fish Cul. Jan. 1958:16-20.

Vallentyne, J. R. 1957. The molecular nature of organic matter in lakes and oceans, with lesser reference to sewage and terrestrial soils. J. Fish Res. Bd. Canada. 14:33-82.

Appendix 1. Dissolved oxygen and pH values recorded at Adrian Lake, 1965

	Jan.16		Jan. 30		Feb. 6		Mar. 15		Apr. 14		Apr. 29		May 12		May 27	
	D.O.	pH	D.O.	pH	D.O.	pH	D.O.	pH	D.O.	pH	D.O.	pH	D.O.	pH	D.O.	pH
Station II																
0 meters	-	-	-	-	13.3	6.5*	10.4	7.0	9.4	7.5	10.2	7.5	10.6	7.5	8.4	8.0
1	-	-	12.4	7.5	12.7	7.0*	10.6	7.0	9.4	7.5	10.3	7.5	10.6	7.5	8.2	8.0
2	-	-	12.2	7.5	12.2	7.5	11.2	7.0	9.4	7.5	10.2	7.5	10.3	7.5	8.5	8.0
3	-	-	12.4	7.5	10.4	7.5	11.4	7.0	9.6	7.5	10.2	7.5	9.8	7.5	7.4	8.0
4	-	-	9.2	7.5	9.4	7.5	11.4	7.0	9.4	7.5	10.0	7.5	8.4	7.5	5.0	8.0
Station III																
0 meters	-	8.0	-	7.5	12.4	7.5	10.8	7.0	9.2	7.5	10.3	7.5	11.0	7.5	9.1	8.0
1	-	8.0	12.2	7.5	12.0	7.5	11.4	7.0	9.2	7.5	10.3	7.5	10.9	7.5	9.1	8.0
2	16.8	8.0	12.4	7.5	11.2	7.5	10.8	7.0	9.2	7.5	10.3	7.5	10.6	7.5	8.8	8.0
3	12.9	8.0	12.2	7.5	10.8	7.5	11.3	7.0	9.3	7.5	10.2	7.5	9.6	7.5	8.4	8.0
4	12.5	8.0	10.2	7.5	10.4	7.5	11.1	7.0	9.3	7.5	10.0	7.5	7.4	7.5	0.5	8.0
5	12.6	8.0	8.0	7.5	9.4	7.5	11.0	7.0	9.2	7.5	9.1	7.5	5.4	7.5	0.3	8.0
6	12.6	8.0	8.0	7.5	8.5	7.5	11.1	7.0	8.8	7.5	8.9	7.5	3.8	7.5	0.2	8.0

* Samples taken from ice hole with snow melt running into it.

Appendix 2. Alkalinity values recorded from Adrian Lake, 1965

	Depth Sample Collected			
	2 meters		5 meters	
Date	Carbonates	Bicarbonates	Carbonates	Bicarbonates
January 30	0 ppm.	136 ppm.	0 ppm.	228 ppm.
February 6	0 ppm.	194 ppm.	0 ppm.	214 ppm.
March 15	0 ppm.	102 ppm.	0 ppm.	125 ppm.
April 29	0 ppm.	178 ppm.	0 ppm.	182 ppm.
May 27	0 ppm.	189 ppm.	0 ppm.	212 ppm.

Appendix 3. Lakewater copper values recorded at Adrian Lake, 1965 (Cu expressed as mg/liter of lakewater).

		January 16			January 30			February 6		
	Depth (m.)	Total	Sest.	0-C	Total	Sest.	0-C	Total	Sest.	0-C
STATION 0	1.0	-	-	-	-	-	-	.019	.021	.082
		-	-	-	-	-	-	.197	.052	.143
STATION I	1.0	-	-	-	-	-	-	.197	.052	.143
STATION II	0.0	-	-	-	-	-	-	.057	.011	.027
	1.0	-	-	-	lost	lost	lost	.032	.007	.047
	2.0	-	-	-	.060	.011	.032	.039	.013	.062
	2.5	-	-	-	-	-	-	.048	.006	.085
	3.0	-	-	-	.068	.001	.050	.090	.009	.144
	3.5	-	-	-	.070	.008	.067	.103	.023	.097
	4.0	-	-	-	.069	.004	.064	.035	.023	.086
	4.5	-	-	-	.049	.009	.057	-	-	-
STATION III	0.0	-	-	-	-	-	-	.058	.021	.054
	1.0	.160	-	-	.039	.005	.037	.027	.010	.049
	2.0	.177	-	-	.047	.003	.034	.107	.013	.076
	3.0	.085	-	-	.058	.007	.043	.077	.010	.063
	3.5	-	-	-	.049	.003	.037	.066	.008	lost
	4.0	.070	-	-	.043	.006	.043	.114	.011	lost
	4.5	.063	-	-	lost	lost	lost	.097	.012	.083
	5.0	.123	-	-	.045	.002	.054	.073	.011	.084
	5.5	.116	-	-	lost	lost	lost	.084	lost	.078
	6.0	.073	-	-	.067	.005	.067	-	-	-
STATION IV	0.0	-	-	-	-	-	-	-	-	-

Appendix 3. (Continued)

	Depth (m)	March 15			April 6			April 14		
		Total	Sest.	O-C	Total	Sest.	O-C	Total	Sest.	O-C
STATION 0	1.0	.011	.023	.016	.015	.005	.004	.004	.012	-
STATION I	1.0	.028	.040	.015	-	-	-	.067	.040	-
STATION II	0.0	.073	.056	.055	-	-	-	.043	.027	-
	1.0	.050	.064	.027	-	-	-	.032	.029	-
	2.0	.026	.052	lost	-	-	-	.028	.020	-
	2.5	.021	.045	.015	-	-	-	-	-	-
	3.0	.010	.042	.005	-	-	-	.040	.025	-
	3.5	.015	.044	.020	-	-	-	-	-	-
	4.0	.048	.046	.021	-	-	-	.026	.023	-
	4.5	.023	.047	.021	-	-	-	-	-	-
STATION III	0.0	.048	.049	.029	-	-	-	.030	.029	-
	1.0	.045	.032	.034	-	-	-	.024	.037	-
	2.0	.023	.023	.016	-	-	-	.022	.021	-
	3.0	.010	.011	.013	-	-	-	.016	.026	-
	3.5	.012	.024	.010	-	-	-	-	-	-
	4.0	.006	.032	.018	-	-	-	.017	.026	-
	4.5	.004	.028	.015	-	-	-	-	-	-
	5.0	.012	.043	.015	-	-	-	.016	.026	-
	5.5	.020	.038	.013	-	-	-	-	-	-
	6.0	.031	.029	.013	-	-	-	.015	.027	-
STATION IV	0.0	-	-	-	.025	.003	.017	.012	.023	-

Appendix 3. (Continued).

		April 29			May 12			May 28		
	Depth (m.)	Total	Sest.	O-C	Total	Sest.	O-C	Total	Sest.	O-C
STATION O	1.0	.027	.013	-	.052	.016	-	.019	.015	-
STATION I	1.0	.050	.039	-	.068	.030	-	.058	.060	-
STATION II	0.0	.027	.021	-	.058	.016	-	.025	.016	-
	1.0	.016	.015	-	.032	.010	-	.031	.025	-
	2.0	.015	.010	-	.033	.008	-	.024	.026	-
	2.5	-	-	-	-	-	-	-	-	-
	3.0	.025	.015	-	.061	.048	-	.029	.028	-
	3.5	-	-	-	-	-	-	-	-	-
	4.0	.025	.021	-	.050	.034	-	.037	.034	-
	4.5	-	-	-	-	-	-	-	-	-
STATION III	0.0	.017	.013	-	.031	.011	-	.025	.017	-
	1.0	.021	.012	-	.023	.008	-	.018	.020	-
	2.0	.020	.010	-	.024	.006	-	.022	.013	-
	3.0	.019	.009	-	.029	.002	-	.027	.014	-
	3.5	-	-	-	-	-	-	-	-	-
	4.0	.016	.012	-	.039	.023	-	.028	.021	-
	4.5	-	-	-	-	-	-	-	-	-
	5.0	.021	.016	-	.038	.019	-	.032	.036	-
	5.5	-	-	-	-	-	-	-	-	-
	6.0	.010	.020	-	.042	.023	-	.031	.027	-
STATION IV	0.0	.028	.015	-	.050	.026	0	.038	.015	-

Appendix 4. Sediment core copper values recorded at Adrian Lake, 1965 (Cu expressed as mg/kg dry sediment).

Core No.	1	2	3
Water depth (m.)	0.3	0.3	0.3
cm. down from mud-water interface		Total Cu in mg/kg dry sediment	
0	16	151,571	176
5	33	22,566	121
10	13	32,391	139
15	8	34,465	5
20	11	31,225	56
25	12	13,081	33
30	33	24,542	21
35	-	29,610	13
40	-	14,382	-
45	-	17,406	63
50	-	37,471	14
55	-	138,208	17
60	-	144,897	33
65	-	646	-
70	-	423	-
75	-	73	-
80	-	193	-
85	-	732	-

Appendix 4 (Continued).

Core No.	4	5	6	7	8	9	10	11	12	13	14	15
Lake depth (m.)	0.4	0.3	0.7	1.3	0.7	1.4	3.7	1.9	2.9	3.0	2.8	3.5
cm. down from mud-water interface	Total Cu in mg/kg dry sediment											
0	651	989	867	975	416	334	422	427	537	815	802	779
2	286	1,982	895	1,754	615	1,122	1,314	453	634	890	799	1,025
4	251	1,406	831	1,785	291	905	802	198	649	868	499	968
6	262	933	314	1,858	388	639	1,202	-	504	563	322	687
8	235	933	232	1,291	67	813	1,067	-	192	473	212	618
10	97	807	153	1,3218	-	337	864	-	-	-	252	732
12	128	-	85	-	-	-	657	-	-	-	142	303
14	74	-	110	-	-	-	543	-	-	-	112	153
16	53	-	-	-	-	-	258	-	-	-	-	240
18	117	-	-	-	-	-	439	-	-	-	-	-

Appendix 4 (Continued).

Core No.	16	17	18	19	20	21	22	23	24	25	26	27
Lake depth (m.)	4.5	5.8	3.2	3.2	4.5	4.3	4.3	5.5	4.5	3.8	3.8	3.8
cm. down from mud-water interface	Total Cu in mg/kg dry sediment											
0	783	348	667	680	338	527	920	508	534	974	1,238	203
1				687					794			
2	835	927	873	627	944	517	1,596	891	30	815	977	356
3				193					97			
4	621	794	830	74	1,105	626	1,055	892	20	787	650	317
5									64			
6	504	875	524	-	979	526	669	805	4	397	392	208
7									23			
8	387	613	-	-	503	562	-	869	250	467	-	336
10	386	766	-	-	453	316	-	349	-	77	-	-
12	-	820	-	-	552	-	-	-	-	-	-	-
14	-	-	-	-	-	-	-	-	-	-	-	-
16	-	-	-	-	-	-	-	-	-	-	-	-
18	-	-	-	-	-	-	-	-	-	-	-	-