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THE GEOCHEMICAL AND BIOSTRATIGRAPHIC RECORD OF NATURAL
AND POLLUTIONAL EUTROPHICATION OF MINNESOTA LAKES

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The work upon which this publication is based was supported in part by funds provided by the United States Department of the Interior as authorized under the Water Resources Research Act of 1964, Public Law 88-379

August 1975

Minneapolis, Minnesota

Water Resources Research Center

University of Minnesota

Graduate School

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B-081-MINN (1)

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FOREWORD

This document serves as the Research Project Technical Completion Report for the following project:

OWRT Project No.: B-081-Minn

Matching Grant Agreement No.: 14-31-0001-4095

Project Title: The Geochemical and Biostratigraphic Record of Natural and Pollutational Eutrophication of Minnesota Lakes

Principal Investigators: Eville Gorham, Department of Botany, University of Minnesota and Herbert E. Wright, Jr., Limnological Research Center, University of Minnesota

Project Began: July 1, 1973

Project Completed: June 30, 1975

FCST-COWRR Research Category: 05-C

Publication Abstract:

Pigment analysis of profundal surface sediments in Minnesota lakes has demonstrated that sedimentary organic matter derives mainly from detritus produced within the lakes. Only in the most oligotrophic and unproductive lakes are terrestrial inputs to sedimentary organic matter likely to be considerable. It has been shown that rising concentrations of fossil pigments in sedimentary organic matter, which are easily and quickly measured, offer a clear stratigraphic indication of the onset of cultural eutrophication. The time of onset can then be determined by other techniques such as pollen analysis, radio-isotope dating, etc. A record has been obtained of the degree of leaching and of erosion in postglacial times at Kirchner Marsh, the site of intensive paleoecological studies by several investigators. Periods of low erosion are indicated by low concentrations of Na, K, and Mg in the lake sediments and correlate generally with periods of high lake productivity. Carbonates disappeared from the sediments about 5,000 years ago.

Stratigraphic analyses of short cores of lake sediments show a distinct change in diatom flora, which can be correlated with known historic disturbances in the watershed or the lake, such as waste disposal, agricultural land clearance, and logging. When the nature and the magnitude of the changes can be identified by this technique, it will be possible to plan lake-restoration projects.

Publication Descriptors: *Paleoecology/ *Pigments/ *Diatoms/ *Cladocera/
Carotenoids/ Chlorophyll/Erosion/ Eutrophication/
Geochemistry/ History/ Lakes/ Minnesota/ Sediments/
Weathering/ Pollution/ Limnology

PROJECT OBJECTIVES AND THEIR ACHIEVEMENT

- (1) Objective--to survey standing crops of chlorophylls and carotenoids in representative Minnesota lakes, as indices of phytoplankton biomass for correlation with the abundance of fossil pigments in recent sediments.

Achievement--depth profiles of chlorophyll and carotenoids were measured in seven diverse lakes on 3-5 occasions during the growing season of 1973, so that standing crops of pigments may be correlated with the fossil pigments in profundal sediments. The averages for whole depth profiles will be correlated with the surface concentrations only, to see whether the concentration of pigments at the lake surface is a reasonably good index to total algal standing crop. If so, then the standing crop survey can be greatly extended, and the data obtained from a much wider range of lakes for correlation with fossil pigment concentrations in sedimentary organic matter.

- (2) Objective--to analyze fossil chlorophyll derivatives and carotenoids, including those characteristic of blue-green algae, in sediment cores from diverse lakes. The aim is to obtain evidence of changes in past productivity, the time of onset of eutrophication, and the time at which blue-green algae become prominent in certain lakes.

Achievement--a 1.5 meter sediment core from Shagawa Lake in Northeastern Minnesota, subject to severe cultural eutrophication by sewage

over the past century, has been analyzed. Our data show a sharp rise in sedimentary pigments, including the pigment myxo xanthin which is characteristic of blue-green algae, subsequent to human settlement. The pigment data complement and extend the earlier analyses of diatoms and cladocerans which first documented stratigraphically the onset of eutrophication in this lake. They also indicate that Shagawa Lake was not highly oligotrophic prior to settlement, but was somewhat more productive than the average for lakes in Northeastern Minnesota. A paper on this work will be given at the June 1975 meeting of the American Society for Limnology and Oceanography, and has been submitted for publication. Another paper is in preparation.

Analyses of sedimentary pigments have also been completed on Cedar Bog Lake in central Minnesota, where a good deal of paleo-ecological work has been done in the past. Interpretation of these data has not yet begun. Analyses have also begun on Iron Lake in Northeastern Minnesota, which exhibits blooms of blue-green algae extremely anomalous for the area and not (as far as we know) ascribable to human influence. Work on Cedar Bog Lake and Iron Lake will continue after termination of Project B-081-Minn.

As part of the work on fossil pigments, data were gathered from three meromictic lakes in late-Wisconsinan moraine of the Itasca Park region of northwestern Minnesota. The intent was to extend our studies of permanently stratified lakes to establish the degree of preservation of plant pigments in sedimentary organic matter under conditions of continuous anoxia. In their highly organic

muds were found concentrations of chlorophylls and chlorophyll derivatives nearly three times, and carotenoids more than four times, those of typical eutrophic, holomictic lakes in Minnesota. These sites showed the highest concentrations of carotenoids ever recorded in this laboratory for lake sediments. After analysis of a few more such lakes, a paper will be prepared on the data.

- (3) Objective--to undertake stratigraphic studies of the proportions of organic matter, carbonate, and clastic material in lake sediments, together with an analysis of the mineralogy of the sand, silt and clay fractions, and an elemental analysis of the total sediment. The purpose of such studies is to obtain information on postglacial variations in erosion, weathering, and leaching of the soils surrounding various lakes.

Achievement--analysis has been completed on a sediment core from Kirchner Marsh in central Minnesota, where studies of pollen, plant macrofossils, and sedimentary pigments have already been published. A paper on this work will be presented at the June 1975 meeting of the American Society for Limnology and Oceanography, and is also being prepared for publication.

- (4) Objective--to analyze on a seasonal basis sedimentary pigments, organic matter, and carbonates in detritus caught in sediment traps. The aim is to determine whether sedimentary pigments integrate the

total phytoplankton deposition or mainly the fallout of major phytoplankton blooms, and to find out whether carbonate deposition (in hard water lakes) is correlated with organic sedimentation and hence largely biogenic and related to primary productivity.

Achievement--this work has not yet begun, owing to late changes in plans of the two successive students who were to undertake it for thesis work. One of these students is now at Minnesota after a year's delay, and may begin the work if funding can be found. In the meantime, a related objective not listed in the original proposal was substituted--to examine data already gathered on fossil pigments in surface sediments of diverse Minnesota lakes in order to assess the balance between terrestrial and aquatic inputs to sedimentary organic matter in lakes. These inputs were shown to be largely aquatic, with terrestrial inputs of importance only in strongly oligotrophic lakes. A paper on this work was presented to the International Limnological Congress in Winnipeg, 1974, and is now in press. As part of this study of fossil pigment sources, pigment diversity has been investigated by thin-layer chromatography in a range of plants characteristic of the evolutionary series from algae to angiosperms. It is clear that pigment diversity declined as the plants evolved, the number of TLC spots being as follows: algae 10-19, lichens 11-19, gymnosperms 9-12, and angiosperms 7-12. A paper on this work will be prepared during the coming year.

RESEARCH PROCEDURES

- (1) Sampling--at the deepest part of each lake, using a Livingstone piston-corer and a Jenkin surface-sediment sampler.
- (2) Fossil pigments--solvent extraction and partition (J.E. Sanger and E. Gorham, 1972, *Limnol. & Oceanogr.* 17:840-854), and thinlayer chromatography (modified after J.E. Sanger and E. Gorham, 1970, *Limnol. Oceanogr.* 15:59-69).
- (3) Sand/silt/clay fractionation--standard sieve and centrifuge techniques.
- (4) Clastic mineralogy--x-ray diffraction
- (5) Elemental analysis--atomic adsorption, supplemented by a standard wet chemical procedure (phospho-molybdate) for phosphorus.
- (6) Diatoms and Cladocera--analyzed microscopically after chemical preparation of sediment samples, with use of reference literature.
- (7) Sedimentation rate for short cores of sediment--determined by detection of level of increase in ragweed pollen, the prime indicator of agricultural development. Events of subsequent years are then correlated with the diatom and other stratigraphic profiles. Long cores can be dated by identification of pollen-zone boundaries that have been dated at other sites by the radio-carbon method.

CHEMICAL STRATIGRAPHY OF KIRCHNER MARSH MINNESOTA--

CORRELATION WITH PALEOBOTANICAL EVIDENCE

Variations in mineral and chemical composition of sediments in a core from Kirchner Marsh, Minnesota have been correlated with detailed postglacial paleolimnological interpretations based on pollen, plant macrofossils, diatoms, and fossil pigments. Periods of high rate of erosion and low rate of weathering are suggested by higher concentrations of the labile elements Na, K, and Mg in the clastic sediment fraction. Periods of low rate of erosion generally correlate with low Na, K, and Mg concentrations and high pigment concentrations in the sediments which suggest high lake productivity. Throughout most of the postglacial history of the lake, sedimentary organic matter appears to be the main factor controlling the Zn concentration in the sediments. Fe and Mn are redox controlled, and reach maxima during periods of possible meromixis suggested by pigment data. Carbonate content of the sediments is highest (maximum of 16% dry weight) in the immediate postglacial spruce/ash pollen zone and then decreases rapidly. Carbonate concentration fluctuates above this zone, reaching a maximum of 12% during the period of maximum postglacial dryness approximately 6,000 years ago. With a return to cooler, wetter conditions after the prairie period carbonate decreases rapidly, and is generally absent during the last 5,000 years of sedimentation.

Analysis has also been completed on a core of Elk Lake in Northwestern Minnesota, where again a good deal of paleoecological work has already been published. Interpretation of the data will be initiated after termin-

ation of Project B-081-Minn. A short core from another Elk Lake (in Grant County) is also being examined, because the lake water has an unusually high ratio of magnesium to calcium, and the mineralogy and diagenesis of carbonates looks uncommonly interesting. A longer core from this lake is planned for the future.

SIGNIFICANT RESULTS AND CONCLUSIONS

It has been shown that rising concentrations of fossil pigments in sedimentary organic matter, which are easily and quickly measured, offer a clear stratigraphic indication of the onset of cultural eutrophication. The time of onset can then be determined by other techniques such as pollen analysis, radioisotope dating, etc.

A record has been obtained of the degree of leaching and of erosion in postglacial times at Kirchner Marsh, the site of intensive paleoecological studies by several investigators. Periods of low erosion are indicated by low concentrations of Na, K, and Mg in the lake sediments and correlate generally with periods of high lake productivity. Carbonates disappeared from the sediments about 5,000 years ago.

Pigment analysis of profundal surface sediments in Minnesota lakes has demonstrated that sedimentary organic matter derives mainly from detritus produced within the lakes. Only in the most oligotrophic and unproductive lakes are terrestrial inputs to sedimentary organic matter likely to be considerable.

Diatom profiles prepared for short cores from lakes in different climatic and hydrologic environments in Minnesota show general stability of the diatom populations prior to the time of lake disturbance by human settlement or other activities in the watershed. The subsequent stratigraphic changes can be correlated with later events.

SUMMARY

Comparison of pigment concentrations in sedimentary organic matter with those in potential source materials indicates that major inputs to profundal sedimentary organic matter in Minnesota lakes are aquatic. It seems likely that terrestrial inputs are of considerable importance only in the relatively unproductive northeastern lakes with the lowest concentrations of sedimentary pigments.

The recent cultural eutrophication of Shagawa Lake is reflected in the content of fossilized pigments in organic matter from a core of profundal sediment. Concentrations of chlorophyll derivatives and carotenoids in the organic matter of recent sediments (1-10 cm depth) are three times as high as in the organic matter of sediments from the pre-settlement period (34-149 cm). Concentrations of the fossilized pigments prior to settlement also indicate that at that time Shagawa Lake was not among the more oligotrophic lakes on non-calcareous glacial drift in northeastern Minnesota. Owing to cultural eutrophication, it now appears to be the most eutrophic of the northeastern lakes, and is probably somewhat more eutrophic than the average lake in Minnesota, although the ratio of sedimentary chlorophyll derivatives to sedimentary carotenoids remains characteristic of its original condition.

This interpretation of the paleoecology of Shagawa Lake, based on the stratigraphy of fossilized pigments, agrees with that of Bradbury and Waddington (1973), which is based on the stratigraphy of diatoms and Cladocera.

PAPERS AND PUBLICATIONS RELATED TO RESEARCH

International Limnological Congress, Winnipeg, 1974.

E. Gorham and J.E. Sanger--Fossil pigments in Minnesota Lake sediments, and their bearing upon the balance between terrestrial and aquatic inputs to sedimentary organic matter.

R.F. Wright, J.C.B. Waddington, S.J. Tarapchak, and J.P. Bradbury, --The impact of a forest fire on a wilderness lake in northeastern Minnesota.

American Society of Limnology and Oceanography, Halifax, 1975.

E. Gorham and J.E. Sanger--Fossil pigments as stratigraphic indicators of cultural eutrophication in Shagawa Lake, Northeastern Minnesota.

W.E. Dean, Jr., and E. Gorham--Chemical stratigraphy of Kirchner Marsh, Minnesota--correlation with paleobotanical evidence.

J.P. Bradbury and T.C. Winter--Diatom sedimentation in Lake Sallie, Minnesota.

Proc. Int. Congr. Limnol., in press. E. Gorham and J.E. Sanger. Fossil pigments in Minnesota lake sediments and their bearing upon the balance between terrestrial and aquatic inputs to sedimentary organic matter.

Geol. Soc. Amer. Bull., submitted for publication. E. Gorham and J.E. Sanger. Fossil pigments as stratigraphic indicators of cultural eutrophication in Shagawa Lake, Northeastern Minnesota.

Geological Soc. America, Memoirs, in press. Bradbury, J.P. Diatom stratigraphy and human settlement in Minnesota.

Proc. Int. Congr. Limnol., in press. Bradbury, J.P., S.J. Tarapchak, J.C.B. Waddington, and R.F. Wright. The impact of a forest fire on a wilderness lake in northeastern Minnesota.

Manuscript to be submitted to Limnology and Oceanography. Bradbury, J.P., and T.C. Winter. Distribution and stratigraphy of the diatomaceous sediments of Lake Sallie, Minnesota.