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SULPHATE REDUCTION AND MICROBIAL MEDIATED ALKALINITY PRODUCTION IN AN ARTIFICALLY ACIDIFIED LAKE

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ABSTRACT

Three gravity cores were removed from near the deepest point in Lake 223 on June 9, 1984, eight years after the Experimental Lakes Area (ELA) staff began the artificial acidification of the lake with sulphuric acid. The first of these cores was analyzed for diatoms and pollen stratigraphy while the second and third were analyzed for downcore sulphur isotope ratios and downcore changes in sulphur reducing bacterial densities. Sediment core chronologies were based on lead-210 and cesium-137 data and the *Ambrosia* pollen rise.

Analysis of the first core to the depth of *Ambrosia* pollen rise (9 cm) indicated that diatom inferred pH in Lake 223 at the time of the *Ambrosia* rise (circa 1890) was 6.8 - 7.0. At a sediment depth of 3 cm the diatom inferred pH was 6.7. Thereafter diatom inferred pH began a decline culminating in the present day (observed) pH range for 1984 (5.3 - 5.5). At a sediment depth of 1 cm an increase in the abundance of two benthic alkalophilic diatoms occurred. The increase in the abundance of these diatoms was ascribed to an increase in hypolimnetic alkalinity following the artificial acidification of Lake 223. This is the first time that lake acidification has been linked to an increase in benthic alkalophilic diatoms associated with hypolimnetic alkalinity production following sulphate reduction.

Sulphur in the anaerobic (black) sediment layers (0 - 1.5 cm) was isotopically light relative to the sulphur in the deeper layers. This was due to sulphur isotope fractionation resulting from the bacterial reduction of sulphate to hydrogen sulphide in the anaerobic portion of the water column. A jet black FeS-rich layer in the uppermost 1.5 cm of the lake's sediments was associated with an increase in the abundance of sulphate reducing bacteria (e.g. *Desulfovibrio* spp).

RÉSUMÉ

Trois carottages par gravité ont été effectués près du point le plus profond du Lac 223 le 9 juin 1984, huit ans après le début de l'acidification artificielle du lac à l'acide sulphurique par le personnel de la région des lacs expérimentaux. La première de ces carottes a fait l'objet d'une analyse des des diatomées et d'une stratigraphie pollénique tandis que la seconde et la troisième ont fait l'objet d'une analyse des rapports isotopiques du soufre ainsi que des changements dans la densité des bactéries réductrices du soufre. La chronologie des carottes de sédiment était basée sur les données du plomb-210 et du césium-137 et la hausse de concentration du pollen Ambrosia.

L'analyse de la première carotte la profondeur de la hausse du pollen Ambrosia (9 cm) révèle que la valeur du pH établie en fonction des diatomées dans le lac 223 au moment de la hausse de Ambrosia (autour de 1890) était de à 6.8 - 7.0. A une profondeur de 3 cm, ce pH était de 6.7, puis a commencé à chuter pour atteindre à sa valeur actuelle (observé) en 1984 (5.3 - 5.5). À une profondeur de 1 cm, une augmentation dans l'abondance de deux diatomées alcalophiles benthiques se produit. Cette augmentation a été attribuée à une augmentation de l'alcalinité hypolimnique qui a suivi l'acidification artificielle du lac 223. C'est la première fois que l'acidification d'un lac est reliée à une augmentation des diatomées alcalophiles benthiques associée à la production d'alcalinité hypolimnique suivant une réduction des sulfates.

Le soufre présent dans les couches de sédiment anaérobies (noirs) (0 - 1.5 cm) affichait des valeurs isotopiques peu élevées comparativement au soufre des couches inférieures. Ce phénomène est attribuable au fractionnement isotopique du soufre résultant de la réduction bactérienne du sulfate en sulfure d'hydrogène dans la portion anaérobie de la colonne d'eau. Une couche noire de jais riche en FeS dans les premiers 1.5 cm de sédiments du lac a été associée à une augmentation de l'abondance des bactéries réductrices du sulfate (p. ex Desulfovibrio spp).

EXECUTIVE SUMMARY

The recent report of the National Acid Precipitation Assessment Program (NAPAP) concludes that acidic deposition is likely to have little or no effect on water, vegetation and human health in the next few decades, if ever. However, paleolimnologists have concluded that diatom inferred pH in acid sensitive lakes has decreased during the last two decades (Davis, 1987).

The present study confirms that diatom assemblages can be used as accurate indicators of lake pH. Furthermore, benthic diatoms (alkalophilic) increased in the sediments due to alkalinity generated during microbial sulphate reduction in the anaerobic zone. At a sediment depth of 1 cm, an increase in the abundance of two benthic alkalophilic diatoms occurred. This increase in the abundance of these diatoms was ascribed to an increase in the hypolimnetic alkalinity due to microbial sulphate reduction following the artificial acidification of Lake 223. This is the first time that the lake acidification has been linked to an increase in benthic alkalophilic diatoms following the hypolimnetic alkalinity production due to bacterial sulphate reduction. This study provides an insight into mechanisms of recovery of lakes experiencing acid stress.

RÉSUMÉ

Le récent rapport du Programme national d'évaluation des précipitations acides américain (NAPAP) conclut que les dépôts acides n'auront probablement pas sinon peu d'effet sur l'eau, la végétation et la santé humaine au cours des prochaines décennies. Ces conclusions viennent contredire les études à long terme sur la paléolimnologie des lacs. Les paléolimnilogistes ont conclu que le pH inféré à partir des diatomées dans les lacs sensibles à l'acidification a diminué au cours des deux dernières décennies (Davis, 1987).

Cette étude confirme que les assemblages des diatomées peuvent être utilisés comme indicateurs fiables du pH des lacs. En outre, les diatomées benthiques perturbées par l'alcalinité produite pendant la réduction microbienne du sulfate dans les sédiments anaérobies d'un lac augmentent en abondance pendant l'acidification du lac. Toutefois, si l'épilimnion du lac conserve un faible pH, la production de diatomées planctoniques y dépassera la contribution de diatomées benthiques alcalines et le pH global inféré à partir des diatomées se situera en deça de 0.3 dixième d'unité de pH du pH observé à la surface du lac.

INTRODUCTION

In the winter of 1976 personnel of the Freshwater Institute began acidifying Lake 223 each season with approximately 5,500 liters of technical grade sulphuric acid (Schindler et al. 1980a). A paleolimnological study of Lake 223 was carried out to determine how diatom populations respond to artificial acidification, 2) to test the precision and accuracy of the diatom inferred pH technique in a lake where pH has been carefully monitored for the last 15 years, and 3) to determine the relationship between downcore changes in sulphur isotope ratios and the anaerobic bacterial mediated rate of sulphate reduction.

Ambient lakewater alkalinity is not a good predictor of the buffering capacity of lake sediments. The principle source of abiotic acid neutralization is from the release of calcium ions (Schnoor and Stumm 1985). Sources of sedimentary Ca^{+2} fluxes vary from 0-130 $meq.m^{-2}.yr^{-1}$. These fluxes are the result of mineral weathering and advection of groundwaters. Porewater pH is confined to a narrow range close to the pK_1 of carbonic acid (H_2CO_3). Porewater pH is indicative of a balance between excess CO_2 resulting from diagnetic reactions and the kinetics of silicate weathering. The primary factor determining redox status of surficial sediments is the availability of organic matter. Unproductive lakes exhibit oxidized surficial sediment potentials above 200 mV while those of more productive lakes are typically less than 200 mV (Stahl, 1986). Sulphate consumption in sediments also contributes to alkalinity production (Ibid). A significant portion of lake sediment porewater alkalinity is associated with Fe^{+2}, Mn^{+2} and NH_4^{+1} (Schiff Personal Communication). Sulphate consumption rates range from 5 to 160 $meq.m^{-2}.yr^{-1}$. Permanent alkalinity from SO_4^{2-} requires sequestering of sulphur in sediments as organic sulphur or iron sulfides. Alkalinity production in the hypolimnetic layers is an important component of the resistance of softwater lakes to anthropogenic acidification.

METHODS

On June 9, 1984, three short gravity cores were removed from the centre of Lake 223. The first was 28 cm long, the second was 26 cm long and the third was 44 cm long. The three cores were sectioned at 1 cm intervals with the exception of one core in which the uppermost 0-5 cm was sectioned at 0.5 cm intervals for diatom inferred pH analysis. Sediment core preparation techniques were similar to those described by Dickman and Thode (1985).

Pollen Analysis

0.25 g dry weight of lake sediment was treated at 5 mL of KOH (10%) and the mixture was boiled for five minutes, stirring continuously. The mixture was then centrifuged, decanted and washed with distilled water. Following this, the sample mixture was

was dehydrated with 3 mL glacial acetic acid, centrifuged and decanted without washing the sediment. An acetolysis solution was prepared by adding one part concentrated sulphuric acid to nine parts acetic anhydride. Five mL of this solution was then boiled for five minutes. After cooling, the mixture was centrifuged, decanted and washed with glacial acetic acid which was then also decanted. The final mixture was twice washed with distilled water and decanted each time. The resulting sediment was mounted on glass slides using corn syrup so the pollen grains could be rotated beneath the coverslip if required for identification purposes. Four hundred pollen grains were counted and the number of Ambrosia pollen grains counted were expressed as a percentage of this total.

Diatom Counts

Diatom enumeration was based on a minimum count of 800 diatum frustules per slide. Procedures for cleaning, mounting and counting the diatoms were described by Dickman et al. (1984). References used in the identification of the diatoms and the assignment of pH indicator status include Beaver (1981). Cleve-Euler (1951-1955), Foged (1979), Hustedt (1938, 1939) Patrick and Reimer (1966, 1975), and Germain (1981).

The precision of the diatom inferred pH technique was estimated by making nine replicate slides of the sediment diatoms (3 from 2 cm, 3 from 3 cm and 3 from 7 cm). These slides were then coded to avoid

Age-Dating Using Lead-210 and/or Cesium-137 Analysis

Lead-210 per unit dry weight was measured at 1 cm intervals over the length of one of the three cores. The "total" lead-210 was measured by determining the granddaughter Polonium-210 by means of isotope dilution (Nriagu et al. 1982).

The cesium-137 activity was determined by gamma counting of an oven dried subsample from each depth interval. A Lithium-drifted germanium detector multi-channel analyzer was used. The basic technique was similar to that described by Pennington et al. (1973) and Edgington and Robbins (1976). Bioturbation factors such as those described by Fisher et al. (1980) were also considered.

Sulphur Content and Isotope Ratio Measurement

Standard methods were used to determine the sulphur content and sulphur isotope ratios of lake water sulphate. In general the sulphur content was determined gravimetrically either as $BaSO_4$ or as Ag_2S. The latter compound was converted to SO_2 gas for isotope analysis in the mass spectrometer.

In the case of the sediment samples, the total sulphur was extracted and determined using the "Eschka" method. The samples of sediment, vacuum dried at 60°C and ground, are placed in a porcelain crucible well mixed with Eschka mixture (65% mgO, 35% Na_2CO_3). The conversion of all forms of sulphur to sulphate then takes place in a furnace at 800° in three hours. The sulphate produced was dissolved in ater at 100°C, and precipitated as $BaSO_4$ from the filtered solution. Finally, the sulphate was converted in steps as indicated above to SO_2 gas for isotope analysis. Again, the sulphur content was determined gravimetrically either as $BaSO_4$ or as Ag_2S.

Isotopic analyses of SO_2 gas samples were performed using a high precision isotope ratio mass spectrometer described by Thode et al. (1961) and modified by Beaver (1973). Sulphur isotope ratios are expressed in terms of a notation where

$$^{34}S‰ = \frac{(^{34}S/^{32}S \text{ sample})}{(^{34}S/^{32}S \text{ standard})} - 1 \times 1000$$

The standard ratio is that of troilite sulphur in the Canyon Diablo meteorite. On this scale primary sulphur or magnetic sulphur have ^{34}S values of essentially zero.

RESULTS

Light attenuation (Table 1A) is presented as the % of the surface light intensity. Light was not detectable on the lake bottom (14 m). Secchi disk transparency (10.4 m) was measured on the sediment coring date (June 9, 1984). Specific conductivity, dissolved oxygen, pH and temperature were measured at 1 m intervals near the centre of Lake 223 (Tables 1 and 2). For more extensive water chemistry data, see Schindler et al. (1980a) and Cook and Schindler (1983).

Lake 223 Sediment Core Stratigraphy

The uppermost layer of sediments (0 - 14 m) in all three sediment cores was jet black. Below this depth (14 - 33 mm) the sediments were blackish brown. Below this depth (33 - 120 mm) the sediments were brown. Microscopic analysis of these 33 - 120 mm deep sediments indicated that they were composed primarily of algal gyttja. From 120 - 200 mm a transition to less organic lighter brown materials occurred. The sediments at the base of the gravity core (200 - 340 mm) were brown and richer in clay than any of the overlaying sediments.

Chronologic Information for Lake 223

During the last decade of the 1800's, ragweed (Ambrosia) became abundant in the Kenora area due to the disturbance of the natural vegetation by Europeans settling in that general region. This increase in Ambrosia pollent was detected in the sediments of Lake 223 by its increase above background levels (2 - 5 grains per thousand). The first significant increase in Ambrosia pollen (8 grains per thousand) occurred at a depth of 9 cm (Fig. 2).

The Ambrosia rise depth was used to calculate a mean sedimentation rate (0.8 mm/yr) for comparison with the cesium-137 (Fig. 3) and lead-200 (Fig. 4) generated sedimentation rates. The lead-210 generated sedimentation rate was 0.54 mm/yr while the cesium-137 generated sedimentation rate was 1.33 mm/yr.

Downcore Bacterial Analysis

The surface sediments of Lake 223 contained 2,300 sulphate reducing bacteria per mL. This is considerably higher than for any of the control lakes in the Wawa study area (Dickman, Rao and Thode 1985). Heterotrophic bacteria (640,000/mL) and sulphur oxidizing bacteria (48 per mL) were also observed in the surface sediments (0 - 0.5 cm) taken from core no. 3.

Sulphur Contents and Isotope Ratios

The sulphur contents and isotope ratios were determined for Lake 223 sediment samples selected from 0 to 14 cm in depth. The sediment profiles of these values are plotted in Figure 5 together with the Lake 223 water column data of Cook (1980), Cook and Schindler (1983) for purposes of comaprison. A single water column sample taken in June 1984 at a depth of 5 m gave a sulphate concentration of 10 PPM and a ^{34}S value of +13% also included in Figure 5.

Diatom Inferred pH

The downcore pH for Lake 223 was inferred from the ratio of acid to alkaline diatoms in the sediments of this lake (Table 2). The log of this ratio (log alpha, Merilainen 1967 and 1969) was modified by Renberg and Hellberg (1982) and Dickman et al. (1984) and referred to as Index B.

$$(\text{Index B} = \frac{(\%\ \text{Circumneutral diatoms}) + (5 \times \%\ \text{acidophilic diatoms}) + (40 \times \%\ \text{acidobiontic diatoms})}{(\%\ \text{Circumneutral diatoms}) + (3.5 \times \%\ \text{alkaliphilic diatoms}) + (108 \times \%\ \text{alkalibiontic diatoms})}$$

No alkalibiontic diatoms were observed in the sediments of Lake 223. Although it is frequently difficult to distinguish between circumneutral and pH indifferent diatoms, the latter contribute little to the interference of lake pH and should be ignored as they increase the variance without increasing the precision of the diatom inferred pH estimates (Dickman et al. 1984).

The Log B diatom inferred pH was calculated from the equation: diatom inferred pH 6.4 - 0.85 Index B.

Diatom Stratigraphy

Major downcore changes in the relative abundance of acidobiontic, acidophilic, circumneutral and alkalophilic diatom taxa were primarily the result of changes in the percentage composition of 11 dominant taxa (Figs. 6 - 21). The majority of the diatoms in the sediments of Lake 223 belonged to a single taxon, Cyclotella stelligera (Fig. 17).

Downcore changes in the relative abundance of the most common alkalophilic diatoms were of two types: 1) Benthic alkalophilic taxa which displayed a general upcore decrease with a statistically significant ($P < 0.05$) increase at 1.5 cm Achnanthes peragali (Figs. 11 and 1.0 cm (Achnanthes bicapitata, Fig. 12) following the artificial acidification of Lake 223 and, 2) planktonic alkalophilic taxa which decreased in relative abundance after the artificial acidification of Lake 223 (Figs. 10 and 13). The alkaliphilous, planktonic, Melosira italica subspecies subarctica (Fig. 20) also decreased significantly ($P < 0.05$) after the initiation of acidification. Shallow water taxa such as Nitzschia gracilis (Fig. 20) also decreased upcore.

The most abundant acidophilic diatom in the sediments of Lake 223 (Asterionella ralfsii var. americana Fig. 16) increased dramatically after the lake's acidification. This diatom increased most strikingly in the top 1.5 cm of the sediment core from Lake 223 while the pH indifferent diatom Asterionella formosa increased at 1.0, 1.5, 3.0, 4.0 and 4.5 cm (Fig. 19). Acidophilic and acidobiontic taxa (e.g. Asterionella ralfsii var. americana, Eunotia vanheurkii (not figured), Tabellaria quadriseptata and Eunotia exigua Figs. 14, 15 and 16) all increased in their relative abundance following the artificial acidification of Lake 223.

DISCUSSION

Sulphate Reduction and the Generation of Alkalinity

Schindler et al. (1980a) reported that after the addition of sulphuric acid to Lake 223 in 1976 the freshly introduced sulphur was reduced by sulphate reducing bacteria. Based on our observations of the increase of <u>Desulphovibrio</u> spp. in Lake 223 sediment cores, we have concluded that some of this reduced sulphur quickly combined with ferrous ions in the anaerobic portion of the lake's hypolimnion to form a FeS-rich black sediment layer.

The stoichiometric relationship for Fe^{+++} reduction during the microbial utilization of organic matter can be written as:

$$CH_2O + FeOOH + 8 \text{ Protons} \qquad CO_2 + 4Fe^{+++} + 7H_2O.$$

Alkalinity is generated by virtue of the fact that eight protons are consumed for every mole of organic carbon (CH_2O) which is oxidized to CO_2 and H_2O. This equation can be rewritten to include biocarbonate:

$$4Fe^{+++} + O_2 + 8HCO^{-1} \qquad 4FeOOH + 8CO_2 + 2H_2O.$$

In an iron-dominated lake such as Lake 223 were Fe^{++} at 14 m was 1.6 mg/L in July of 1983 (Schindler, Pers. Comm.), the above equations represent important alkalinity producing and consuming reactions that occur during stratification and overturn. Redox reactions involving manganese and nitrogen also occur, but they are secondary, as is the alkalinity production that occurs as the result of H_2S build-up in the anoxic hypolimnion of this lake during late summer and fall. It should be noted that pyrite formation will also generate alkalinity. Unfortunately, only qualitative (light microscope and SEM) information exists about the presence of pyrites in the surficial sediments of Lake 223.

Estimates of Sedimentation Rate

We have hypothesized that the addition of 5,500 litres of concentrated sulphuric acid (Schindler et al. 1980a) to the epilimnion of Lake 223 in the winter of 1976 stimulated the formation of FeS in the lake's hypolimnion and shortly thereafter this material entered the lake's bottom sediments forming a black layer there. The sedimentation rate over the last eight years (1976-1984) as judged from the depths of the relatively uncompacted FeS-rich black layer at 14 mm would have been 1.75 mm/yr.

The question of the relative degree of mixing and bioturbation of the recently deposited sediments of Lake 223 is critical to any stratigraphic analysis (Edgington and Robins 1976, and Fisher et al. 1980). We hypothesized that the presence of pyrite framboids and FeS at a sediment depth of 14 - 33 mm indicated that some of the material deposited during the last eight years in the top 14 mm has been mixed (principally by chironomid bioturbation) to a depth of 33 mm.

Microbial Populations

The presence of large populations of sulphate reducing bacteria which were observed in the recently deposited sediments of Lake 223 were correlated with the large quantities of introduced sulphuric acid, the negative eH values of the lake's black sediments and the availability to these bacteria of a carbonaceous energy source.

Concentrations of carbonaceous energy sources present in the sediments of most acid lakes is generally considered adequate to support considerable microbial populations such as sulphur reducing bacteria (Dutka et al. 1974). The presence of large populations of sulphate reducers in the sediments of a number of Canadian Shield lakes following sulphur deposition is correlated with hypolimnetic anoxia. This increases the importance of aerobic microbial biodegradation processes during those months when the lower hypolimnion of these lakes is anaerobic. In the case of Lake 223, its deepest waters (10-14 m) become anoxic in July during most years, and remain anoxic until lake overturn occurs in November or early December (Cook and Schindler, 1983).

Sediment Sulphur

The sulphur content (% dry weight) was higher in the surface sediments (0-2 cm) of Lake 223 than in the deeper layers (12-14 cm) by a factor of 2.4 (Fig. 5). The big increase (circa 50%) which occurred between 2-4 and 0-2 cm depth parallels in part a 2.5 to three-fold increase in the lake's epilimnetic sulphate concentration following its artificial acidification with technical grade sulphuric acid. Cook (1980) reported an even higher sulphur content in the surficial samples (1 cm) for a Lake 223 core taken several years earlier.

Our ^{34}S (Total S) sediment profiles obtained for Lake 223 were plotted together along with the water column ^{34}S profiles, obtained from the data of Cook (1980), see Figure 5. ^{34}S in the deeper sediment layers is fairly constant at 2.4% and the sulphur is isotopically light relative to the lake water sulphate (epilimnion), prior to the lake acidification in 1976. The upcore shift in ^{34}S appears to be toward more positive values going from 2.4% in the deeper layers to 6.2% for the surface sediments 0-2 cm. However, the acidification of the lake with sulphuric acid, $^{34}S_{H\ SO} = +16.3\%$, increased the ^{34}S value for the sulphate in the lake surface waters from 5.0% to 12.8%, see Figure 5. Thus in effect the upcore shift in ^{34}S is toward lower values and the sulphur in the surficial sediments is isotopicaly light by 7.2% relative to the 1984 lake water sulphate value. This upcore shift in ^{34}S obtained for Lake 223 is not unlike those reported for the soft water Algoma Lakes or Turkey Lakes with similar lake water sulphate concentrations (Thode et al. 1987, Nriagu and Soon 1985). The magnitude of these changes appears to be related to the increase in sulphate loading of the lakes since Ambrosia times.

The artificial loading of Lake 223 from about 3.0-4.0 PPM to 9-10 PPM sulphate produced about the same ^{34}S shift in the surficial sediments as that of Fenton Lake in the Algoma Lake area with a present day sulphate loading of 8.2 PPM.

Nriagu and Coker (1978, 1983) first reported increasing sulphate contents and lower ^{34}S values for the surficial sediments in lakes downwind from the Sudbury smelters. The question as to the source of the isotopically light sulphur in the very recent sediments has been discussed by Dickman et al. (1983); Thode et al. (1986); Nriagu and

Coker (1983); and Nriagu and Soon (1985). In our opinion, the main source of isotopically light sulphur is the result of in-lake reductions of sulphate to sulphide as discussed below.

The absence of isotopically light sulphur in the various external sources of sulphur obtained from the Algoma Lake drainage area and the ^{34}S distribution patterns obtained for the lake sediments suggest an internal lake source for the isotopically light sulphur. We conclude therefore that the shift in sediment ^{34}S values must be due to sulphur isotope fractionation resulting from the bacterial reduction of lake sulphate to hydrogen sulphide at or near the sediment water interface. This biogenic process was very likely stimulated by introduction into the lake of increasing amounts of anthropological sulphur, via acid (rain) since Ambrosia times in the case of the Algoma and Turkey Lakes, and in addition via the direct addition of technical grade sulphuric acid since 1976 in the case of Lake 223.

This sulphur reduction to H_2S carried out anaerobically in the shallow sediments or in the lower hypolimnion for Lake 223 during summer stratification, in a partially open system, could account for the observed upcore shift in sulphur isotope ratios and sulphur content found for the lakes studied. The microbiological data obtained for the Algoma Lakes and Lake 223 are in acord with this conclusion (Thode et al. 1987). The Algoma Lakes' shallow sediments (0-2 cm) which showed the largest shift in ^{34}S displayed the highest concentrations of "sulphate reducers" and the highest sulphur loading. On the other hand, the shallow sediments of lakes which showed only small shifts in ^{34}S had relatively low concentrations of sulphate reducers (Thode et al. 1987).

It has been known for many years that sulphur isotopes are fractionated in the bacterial reduction of sulphate to hydrogen sulphide, the latter being depleted in ^{34}S (isotopically light) (Thode et al. 1963). This process accounts for the isotopically light sulphur usually found in marine sediments where the requirements for this biogenic process (1) the absence of oxygen, (2) the presence of sufficient sulphate and (3) the availability of organic substrate with easily assimilated low molecular weight compounds are easily is easily met. In marine sediments, the bulk of the isotopically light hydrogen sulphide generated is unlikely to be immediately tied up by iron and other metals, but rather escapes to the oxygenated part of the environment where it undergoes rapid oxidation. Some of this isotopically light sulphur becomes incorporated in the various organic compounds in the sediments through the cycles of biologically mediated reactions (Thode et al. 1960).

It has been generally assumed that the reduced sulphur in the sediments of soft water lakes of low sulphate concentrations is largely derived from the decomposition of organic matter, its isotopic ratio reflecting that of the lake water sulphate, since there is little or no sulphur isotope fractionation in plant (algae) metabolism of sulphate (Ishii 1953, Kaplan et al. 1963, Mekhtiyeva and Pankina 1968). However, recent studies of Lakes 223 and 227 in the experimental lakes area (ELA) of northwestern Ontario by Cook and

Schindler (1983) indicate that extensive bacterial sulphate reduction and isotopic fractionation occurs in anoxic zones of these lakes with sulphate concentrations as low as 30-40 moles/liter (3 to 4 PPM of $SO_4=$) contributing up to 70% of the total reduced sulphur in these sediments.

They suggest, however, that sulphate reduction may no longer be energetically favourable at sulphate concentrations below 20-30 mol/liter since these were the lowest concentrations of sulphate found in the bottom and pore waters of Lake 223 where bacterial reduction had occurred.

However, this seems unlikely since sulphate reduction by pure cultures of sulphate reducers <u>Desulphovibrio</u> <u>desulphuricans</u> has been reported at these low concentrations (Harrison and Thode, 1985). The minimum sulphate concentrations reported in these sediment pore waters could be due to oxidation of H_2S during sampling and in analytical procedures.

A more likely possibility is the competition between methanogens and "sulphage reducers" for the organic nutrients present. A model for the distribution of sulphate reduction and methane production in fresh water lake sediments developed by Lovley and Klug (1986) indicates that a sulphate concentration <30 m/liter 3.0 PPM, methanogens prevent "sulphate reducers" from growing because of the dual limitations of low sulphate concentrations and organic nutrient consumption by methanogens. The small apparent sulphur isotope fractionation in the deeper sediments (10-12 cm) of the Algoma Lakes and Lake 223 therefore suggests sulphate concentrations close to this threshold value, 20 m/L (2-3 PPM) some 60 to 80 years ago.

Downcore Diatom Inferred pH

When Lake 223 log B downcore diatom inferred pH was plotted against sediment depth, it became apparent that at a sediment depth of 1.5 cm a dramatic shift in the diatom inferred pH occurred. At a sediment depth of 1.5 cm, both log B and log alpha suddenly shifted from negative to positive values (Figs. 22 and 24). This resulted in a statistically significant decrease in diatom inferred pH from above pH 6 to below pH 5.5 as the B index dropped (Fig. 23). This was consistent with the reported observations of pH in Lake 223 following its artificial acidification (Cook and Schindler 1983).

After the acidification of Lake 223, there was a differential response in the planktonic and benthic diatom communities. The planktonic alkalophilous and circumneutral species such as Nitzschia graciles (Fig. 22), Rhizosolenia eriensis and Synedra acus (not figured) were replaced by acidophilous taxa, primarily Tabellaria quadriseptata and Asterionella ralfsii (Figs. 14 and 16 respectively). Similar observations were made by Davidson (1986). Benthic diatoms, on the other hand, responded quite differently. Those deep dwelling taxa which were exposed to anoxic conditions from time to time were dominated by alkaliphilic taxa rather than the anticipated acidophilic ones. The reasons for this are provided in the following section.

Hypolimnetic Alkalinity and Diatom Species Composition

A number of benthic alkaliphilic taxa such as *Achnanthes peragali* and *A. bicapitata* decreased in relative abundance after the artificial acidification of Lake 223 and then increased at 0 and 1.5 cm (A. Peragali, Fig. 11) and at 1 cm (*A. bicapitata*, Fig. 12). These statistically significant increases ($p < 0.05$) were interpreted as indicated short term (e.g. August - November) anoxia and enhanced hypolimnetic alkalinity.

In addition, meroplanktonic alkalophilic taxon; *Melosira italica* subsp. *subarctica* increased suddenly at 0.5 cm, Fig. 20). This too was ascribed to the observed increase in the lake's hypolimnetic alkalinity following the onset of hypoxia in August - November.

The following hypothesis is advanced in an attempt to explain the observed short term increase in some alkaliphilous diatoms following the acidification of Lake 223. According to Cook and Schindler (1983) the addition of sulphuric acid to Lake 223 increased the penetration of light by precipitating humic matter. In addition, the abundance of planktonic algal taxa was reduced. Both of these factors increased the depth of light penetration in Lake 223. Thus benthic diatoms could grow at greater depths in Lake 223 after its acidification due to increased light penetration. Acidification also resulted in an increase in sulphate reduction rates from 3 to 10 x 10^{-4} mol m^{-2} d^{-1} (Cook and Schindler 1983). This in turn caused the bottom tenth of Lake 223's hypolimnion to become anoxic and more alkaline.

It is our belief that some of the benthic, meroplanktonic or tychoplanktonic, alkalophilic diatoms in Lake 223 were responding to this increase in hypolimnetic light and alkalinity. To the best of our knowledge, this is the first report of an observed response of benthic alkaliphilic diatoms to an increase in hypolimnetic alkalinity resulting from the addition of sulphuric acid to a natural lake.

CONCLUSIONS

Visual inspection of the sediments removed from the three gravity cores which were taken from Lake 223 in June of 1984 indicated that the top 14 mm of the sediments in Lake 223 were jet black. This was attributed to FeS production following sulphuric acid introductions to Lake 223. Bioturbation was implicated in the downcore distribution of the FeS-rich material to a depth of 3 cm.

Lead-210 and Ambrosia pollen analyses of the uppermost 20 cm of sediment from Lake 223 indicated that this lake has an extremely low sedimentation rate (0.54 - 0.85 mm/yr for lead-210 and Ambrosia respectively). Using the Ambrosia rise as an indication of sedimentation rate over the last 100 years and the 0-14 mm thick black layer as an indication of the commencement of artificial acidification of Lake 223, it was possible to conclude that the sedimentation rate in Lake 223 during the last eight years was approximately 1.75 mm/yr.

The log B index diatom inferred pH for Lake 223 from 1890 to 1967 ranged from pH 6.0 to pH 7.0. In 1976 when Lake 223 was acidified, diatom inferred pH suddenly began to decline. The pH of Lake 223 at the time the sediment cores were taken in June 1984 was 5.1-5.3 at the surface and 5.7 near the mud-water interface. The diatom inferred pH from the uppermost sediment layers (0.0-0.5 cm) was 5.3.

The artificial acidification of Lake 223 resulted in an increase in the relative abundance of acid indicator planktonic diatoms. Alkaline indicator benthic diatoms were rare relative to the planktonic taxa. Nevertheless, it was concluded that the generation of alkalinity by sulphate reduction in the anaerobic portions of Lake 223 and the increase in lake transparency following its artificial acidification stimulated the growth and reproduction of some benthic, meroplanktonic and tychoplanktonic alkaline indicator diatoms during periods of hypolimnetic oxygen depletion (August - November).

The upcore shifts in sulphur content and sulphur isotope ratios which chronicle past changes in lake sulphate loading were confirmed by the Lake 223 study. Our observations of upcore increases in the abundance of Desulphovibrio spp. were correlated with 2 to 3 fold upcore increases in the percentage dry weight of sulphur in the uppermost (0 - 2 cm) sediment layers. In addition, the sulphur in these uppermost sediment layers was isotopically light relative to the deeper layers. We've interpreted this to support the hypothesis that during period of hypolimnetic hypoxia the Desulphovibrio reduced sulphate to sulphide and by so doing, generated isotopically light sulphides. Previous studies (Dickman et al. 1985, Thode et al. 1987) have reported this phenomenon in lake sediments, but this is the first report of its occurrence in the water column of a lake.

ACKNOWLEGEMENTS

The authors are grateful to P. Hayes of Brock University who assisted in the diatom enumeration, Mark Taylor of Waterloo University and Roger Sweets of Indiana University who assisted in the diatom identification, and Ben Baliat of McMaster University who assisted in the sulphur isotope ratio analyses. We are also grateful to the S.E.M. staff at East Carolina University in Greenville, North Carolina for permission to use their S.E.M. facility and to NSERC for funding this research in the form of an operating grant to M. Dickman.

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Table 1 The relationship between depth (m) and percentage surface light intensity (% SLI), specific conductivity (Micromhos/cm) and dissolved oxygen (mg/l) for Lake 223 on 9 June, 1984.

Depth (m)	Light (%SLI)	Conductivity (Micromhos/cm)	Dissolved Oxygen (mg/l)
0	100	40	9.3
1	67	40	9.2
2	60	40	9.2
3	50	40	9.3
4	47	40	9.3
5	40	40	9.7
6	35	40	9.7
7	27	39	10.4
8	21	38	10.4
9	17	38	9.9
10	13	38	8.7
11	10	38	7.9
12	05	38	6.1
13	03	38	5.0
14	N.D.	39	0.2

SLI = Surface Light Intensity
N.D.= Not detected

Table 2 The relationship between depth (8 depths) and dissovled ogygen (mg/l) on 13 June 1983, pH and temperature (9 June 1984), Chlorophyll A and alkalinity on 13 June 1983 and 7 October 1983. Data from 1983 were provided by D. Schindler (pers. comm.).

Depth	D.O. 13/6/83	pH	Temperature Degrees (C°)	Chlorophyll A 6/83	Chlorophyll A 10/83
0	9.1	5.3	15.3	0.5	2.4
1		5.3	15.3		
2		5.3	15.3		
3		5.3	15.3		
4	9.6	5.4	15.3	0.4	2.0
5		5.4	14.8		
6		5.4	13.8		
7		5.6	11.6		
8	11.9	5.7	9.9	2.1	1.9
9		5.7	9.0		
10	9.4	5.7	8.5	11.2	
11	6.6	5.7	8.2	14.5	23
12	4.9	5.7	7.9	15.1	27
13	3.1	5.7	7.6	17.3	29
14	2.3	5.7	7.7		

Depth (m)	Alkalinity (microequiv/l) 6/83	10/83*
1	-10	-2
2		
3		
4		
5	- 9	-2
6		
7		
8	- 3	+3
9		
10	11	48
11	24	40
12	27	674
13	24	857

Chlorophyll was reported as micrograms/l.

*The high alkalinity in October was associated with anaerobic hypolimnetic conditions.

FIGURE CAPTIONS

Figure 1 The location of the experimental lakes area with inset of a morphometric map of Lake 223 (Modified from Cook and Schindler 1983).

Figure 2 Downcore (0-15 cm) *Ambrosia* pollen grain abundance expressed per thousand pollen grains. The *Ambrosia* rise (9 cm Circa 1890) was statistically significant ($p < 0.05$).

Figure 3 The downcore sediment profile for Cesium-137 in Lake 223. the Cesium-137 generated sedimentation rate was 0.083 cm/yr.

Figure 4 The downcore sediment profile for lead-210 in Lake 223. The lead-210 estimated sedimentation rate was 0.054 cm/yr.

Figure 5 Lake 223 water column and sediment core. Profiles of sulphur concentration and isotope ratios ($\delta^{34}S$). Water column data taken from Cook (1980). Sediment data and 1984 water column data - this work.

Figure 6 Histogram of the percent abundance of acidophilic diatoms at 0.5 cm intervals downcore in the sediments of Lake 223.

Figure 7 Histogram of the percent abundance of acidobiontic diatoms at 0.5 cm intervals downcore in the sediments of Lake 223. To convert x axis to sediment depth divide by 2.

Figure 8 Histogram of the percent abundance of the alkalophilic diatoms at 0.5 cm intervals downcore in the sediments of Lake 223.

Figure 9 Histogram of the percent abundance of the circumneutral diatoms at 0.5 cm intervals downcore in the sediments of Lake 223.

Figure 10 The relative abundance of the benthic alkaliphilic diatom *Achnanthes perigali* in the surficial sediments of Lake 223.

Figure 11 The relative abundance of the planktonic alkaliphilic diatom *Fragilaria construens* in the surficial sediments of Lake 223.

Figure 12 The relative abundance of the benthic alkaliphilic diatom *Achnanthes bicapitata* in the surficial sediments of Lake 223.

Figure 13 The relative abundance of the alkaliphilic planktonic diatom *Fragilaria brevistriata* in the surficial sediments of Lake 223.

Figure 14 The relative abundance of the acidobiontic diatom *Eunotia exigua* in the surficial sediments of Lake 223.

Figure 15 The relative abundance of the acidophilic diatom *Tabellaria quadrisepta* the surficial sediments of Lake 223.

Figure 16 The relative abundance of the acidobiontic diatom *Asterionella ralffsii var Americana* in the surficial sediments of Lake 223. Dashed line portions of the histogram (e.g at 1.5 cm) in this and subsequent figures represent the maximum range (m=3).

Figure 17 The relative abundance of the circumneutral diatom *Cyclotella stelligera* in the surficial sediments of Lake 223.

Figure 18A Scanning electron micrograph (1,600 x magnification) of the common diatoms and chrysophyte cysts and scales found in the sediments of Lake 223. 1) *Pinnularia* sp. 2) *Cyclotella* sterlligeria, 3) *Dinabryon* cyst, and 4) *Tabellari quadriseptata*.

Figure 18B Scanning electron micrograph (1.600 x magnification) of common diatoms from Lake 223.

Figure 19 The relative abundance of the pH indifferent diatom *Asterionella formossa* the surficial sediments of Lake 223.

Figure 20 The relative abundance of the alkaliphilic planktonic diatom *Melosira italica* subspecies *subarctica* in the surficial sediments of Lake 223.

Figure 21 The relative abundance of the alkaliphilic littoral zone benthic diatom *Nitzschia gracilis* in the surficial sediments of Lake 223.

Figure 22 Log (base 10) of index B as a function of sediment depth for the surficial sediments of Lake 223.

Figure 23 Index B as a function of depth for the surficial sediments of Lake 223.

Figure 24 The relationship between Log alpha generated diatom inferred pH and sediment depth.

Figure 25 Log B generated diatom inferred pH versus sediment depth for the surficial sediments of Lake 223. Dashed line portion of the 1.0 and 3.5 cm histograms represents maximum range on replicate counts.

Figure 26 The relationship between observed lake pH and surficial sediment (0-0.5 cm) diatom inferred Log B for 13 lakes located north of Lake Superior (Correlation Coefficient = 0.87, $P < 0.01$).

Fig 1

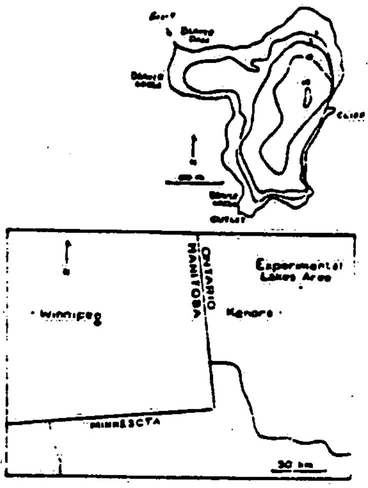


Fig 2

AMBROSIA DOWNCORE PROFILE (LAKE 223)

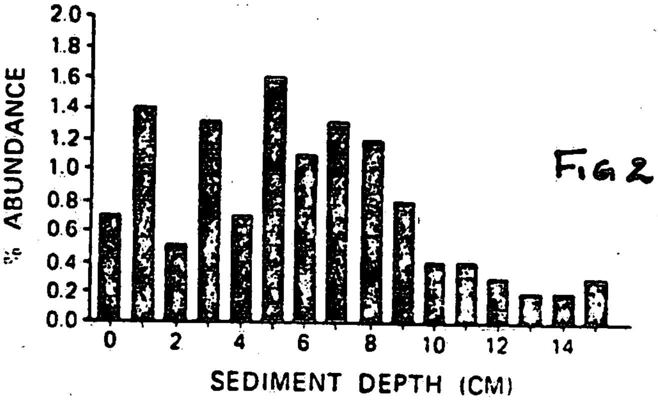


Fig 3.

137 CESIUM PROFILE (LAKE 223)

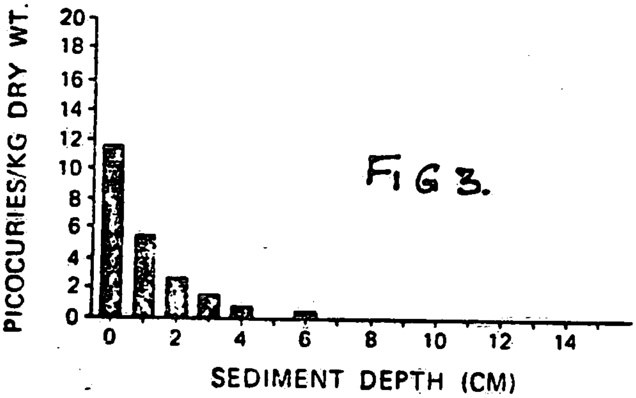
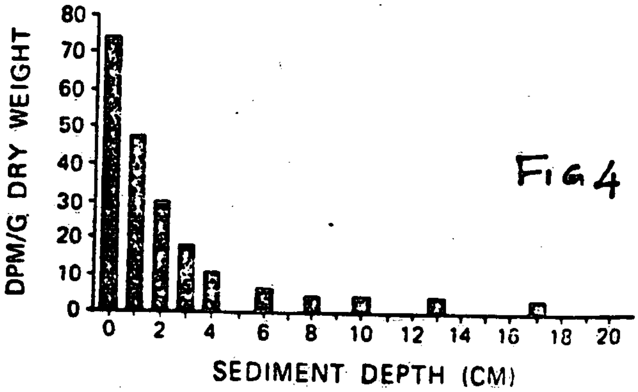


Fig 4

LEAD-210 DOWNCORE PROFILE (LAKE 223)



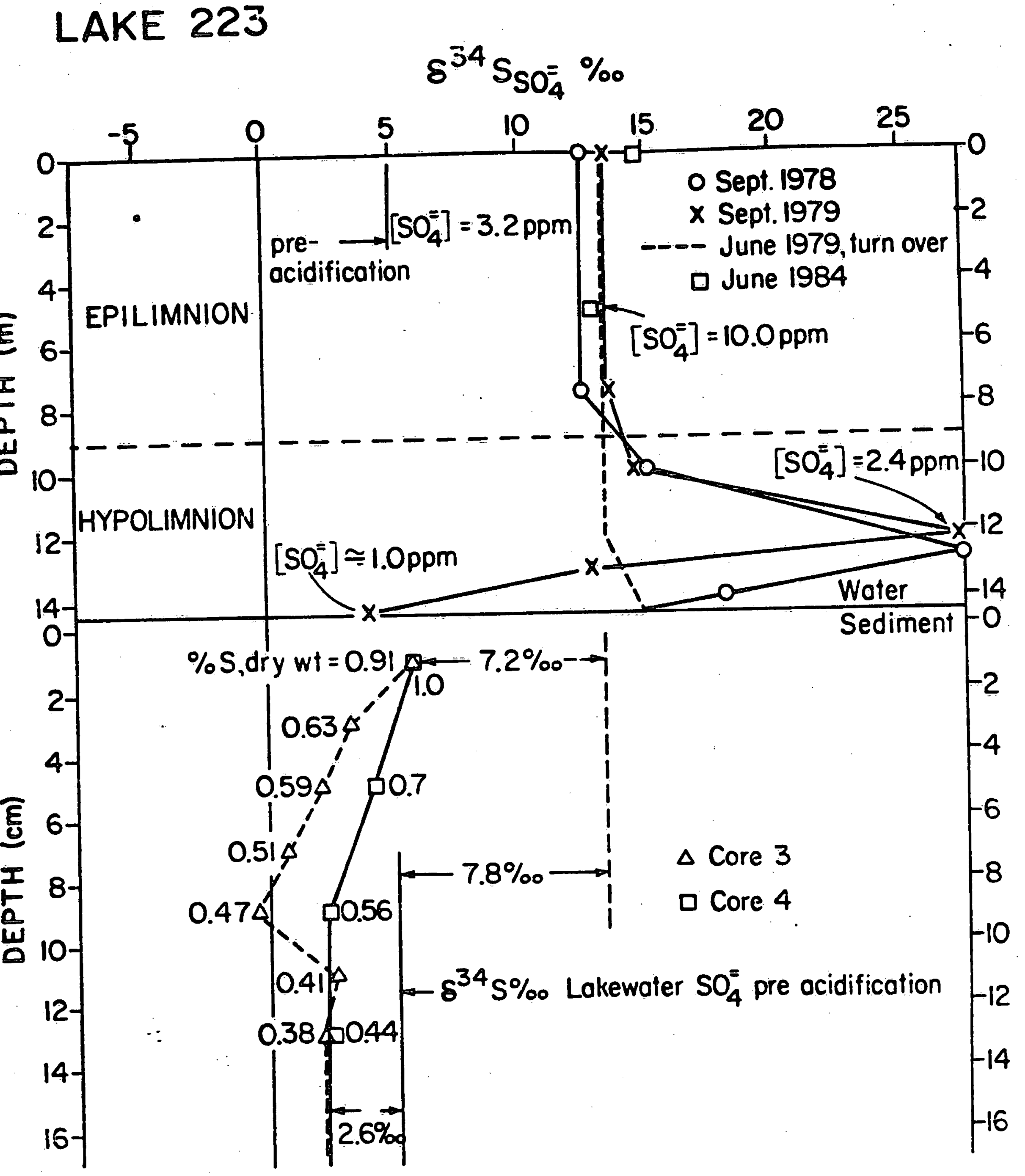
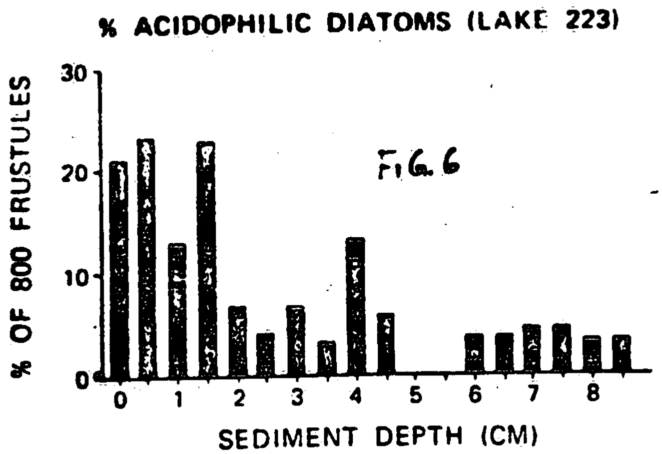
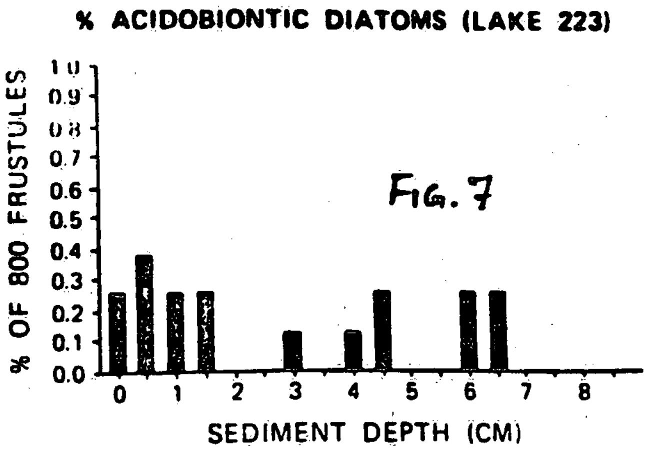

LAKE 223
$\delta^{34}S_{SO_4^=}$ ‰
-5
0
5
10
15
20
25
DEPTH (m)
0
2
4
6
8
10
12
14
EPILIMNION
HYPOLIMNION
pre-acidification
$[SO_4^=] = 3.2$ ppm
$[SO_4^=] = 10.0$ ppm
$[SO_4^=] = 2.4$ ppm
$[SO_4^=] \approx 1.0$ ppm
○ Sept. 1978
x Sept. 1979
---- June 1979, turn over
□ June 1984
Water
Sediment
DEPTH (cm)
16
%S, dry wt = 0.91
1.0
7.2‰
0.63
0.59
0.7
0.51
0.47
0.56
7.8‰
0.41
0.38
0.44
2.6‰
$\delta^{34}S$‰ Lakewater $SO_4^=$ pre acidification
△ Core 3
□ Core 4

Fig. 5



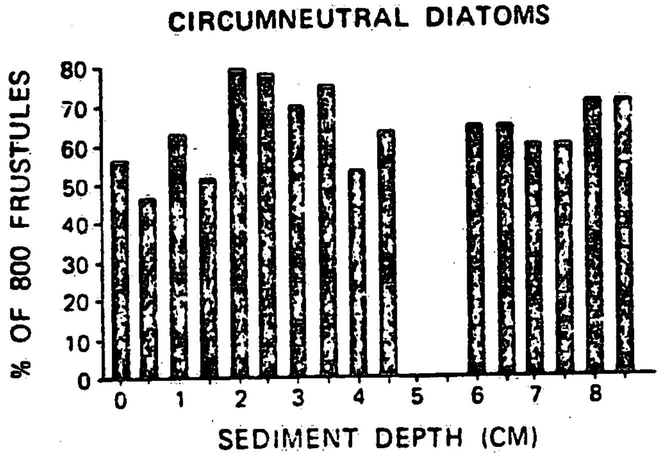
% ACIDOPHILIC DIATOMS (LAKE 223)

FiG.6



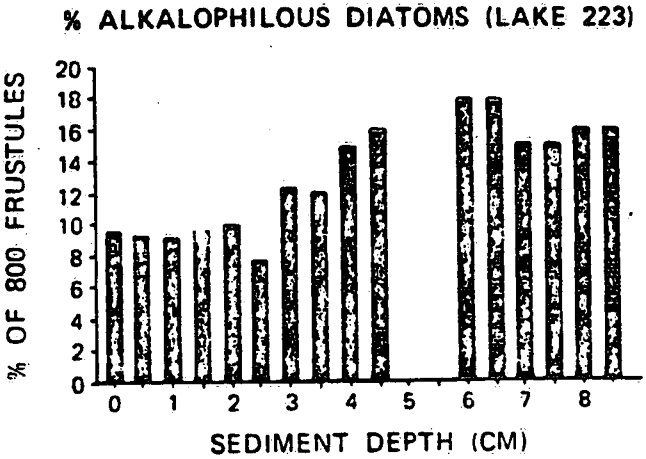
% ACIDOBIONTIC DIATOMS (LAKE 223)

FiG.7



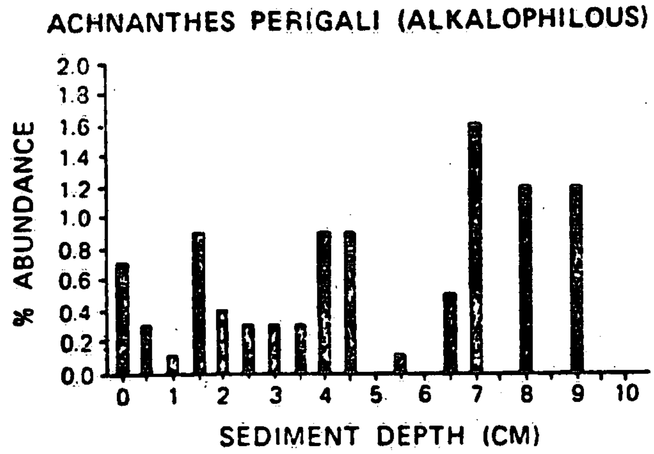
CIRCUMNEUTRAL DIATOMS

FiG.9



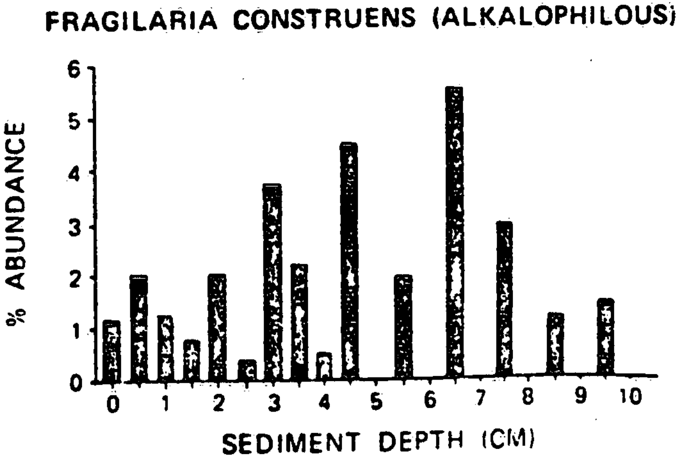
% ALKALOPHILOUS DIATOMS (LAKE 223)

FiG.8



ACHNANTHES PERIGALI (ALKALOPHILOUS)

FiG. 10



FRAGILARIA CONSTRUENS (ALKALOPHILOUS)

FiG. 11

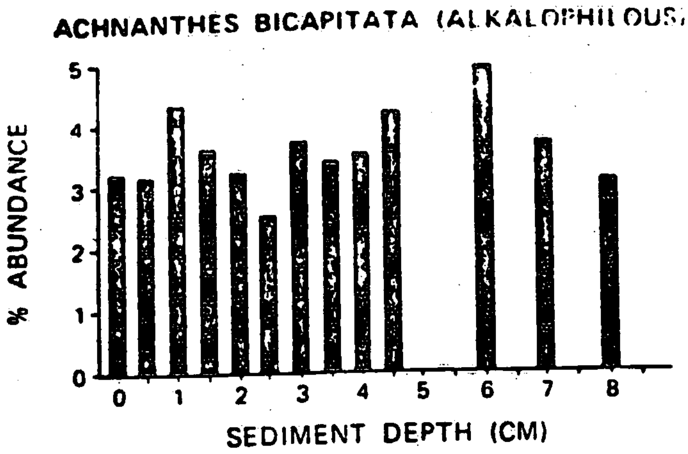

ACHNANTHES BICAPITATA (ALKALOPHILOUS)

FIG. 12

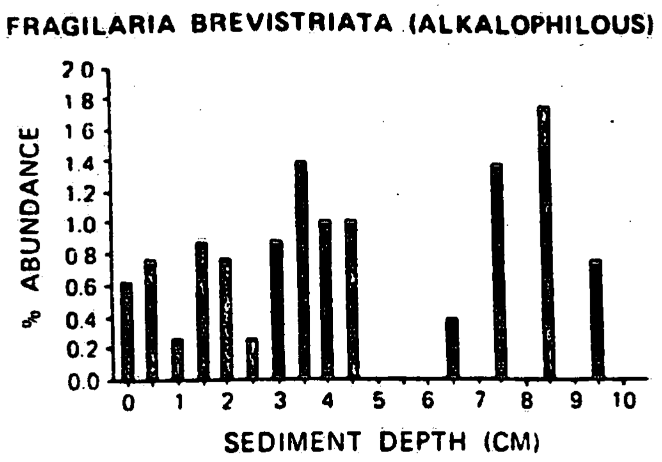

FRAGILARIA BREVISTRIATA (ALKALOPHILOUS)

FIG 13

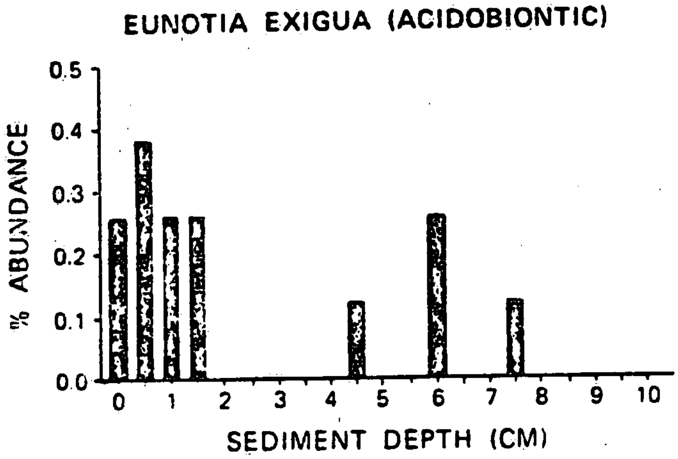

EUNOTIA EXIGUA (ACIDOBIONTIC)

FIG 14

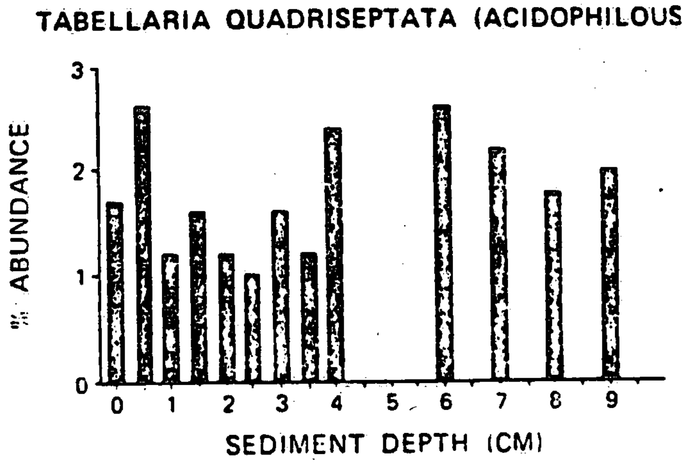

TABELLARIA QUADRISEPTATA (ACIDOPHILOUS)

FIG 15

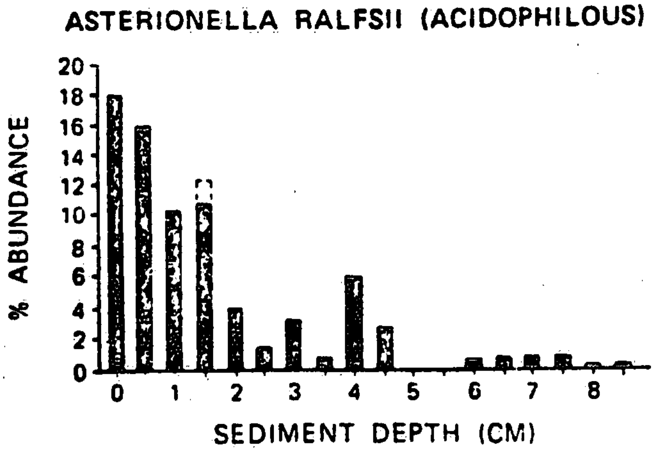

ASTERIONELLA RALFSII (ACIDOPHILOUS)

FIG 16

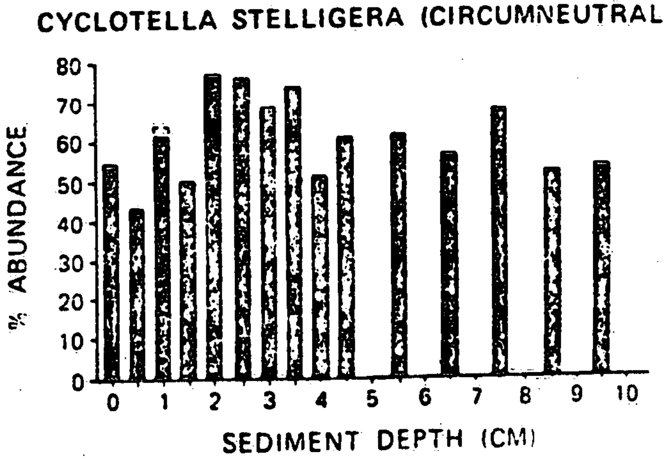

CYCLOTELLA STELLIGERA (CIRCUMNEUTRAL)

FIG. 17

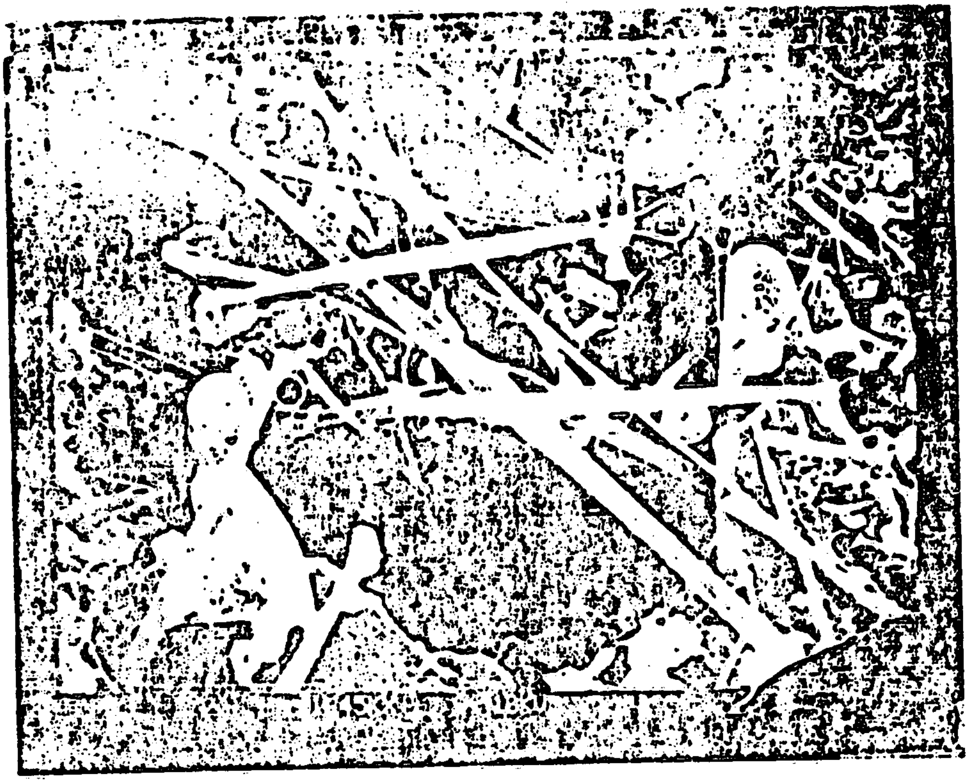


FIG 18a

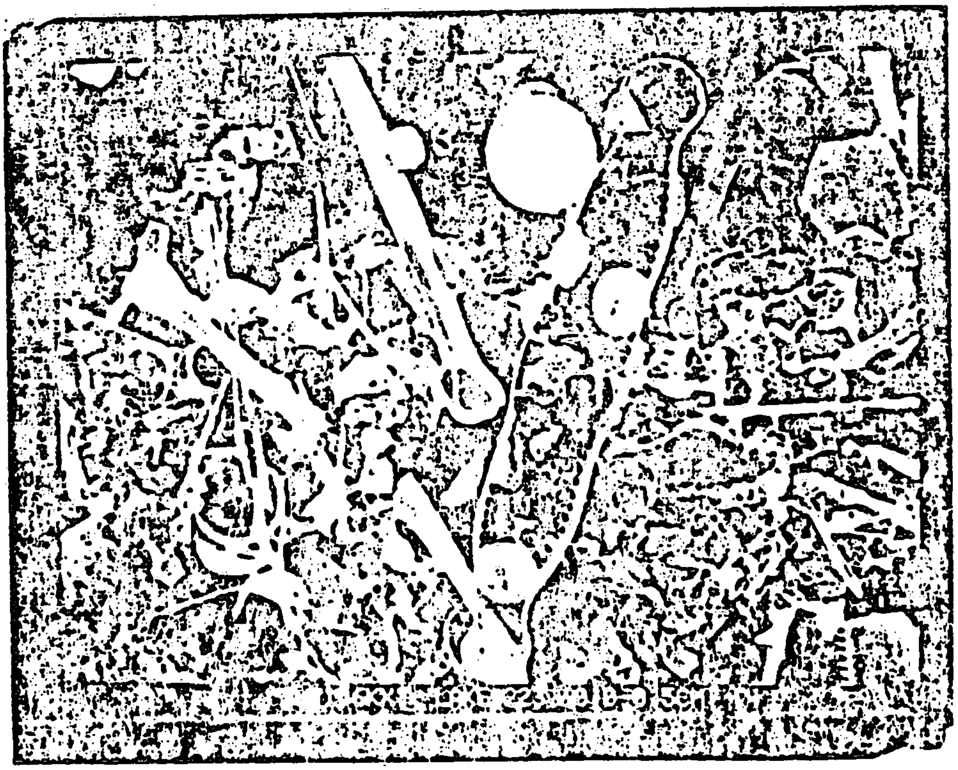


FIG 18b

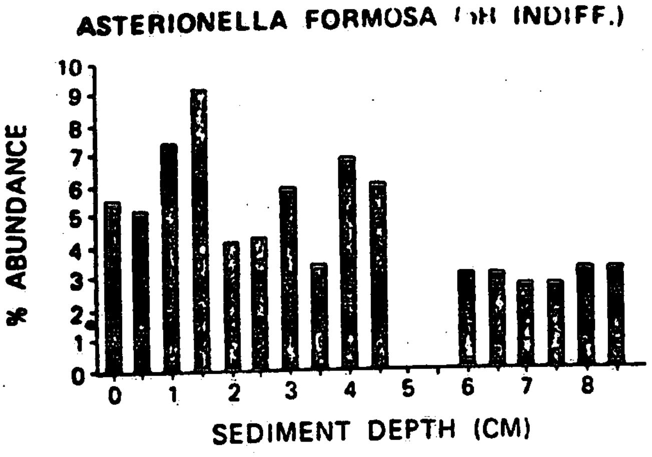

ASTERIONELLA FORMOSA (pH INDIFF.)

FIG 19

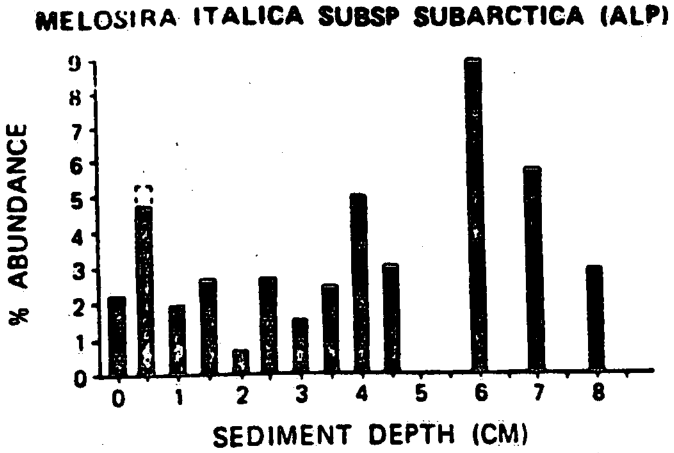

MELOSIRA ITALICA SUBSP SUBARCTICA (ALP)

FIG. 20

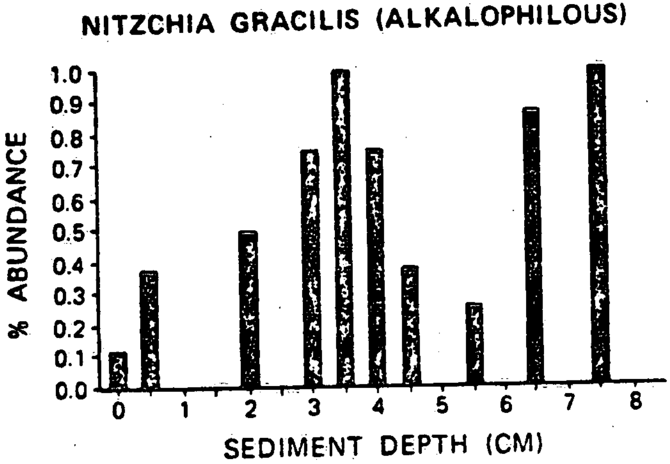

NITZCHIA GRACILIS (ALKALOPHILOUS)

FIG. 21.

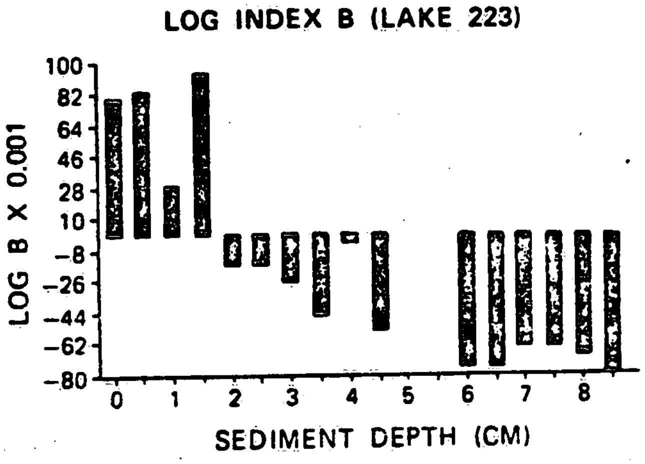

LOG INDEX B (LAKE 223)

FIG. 22

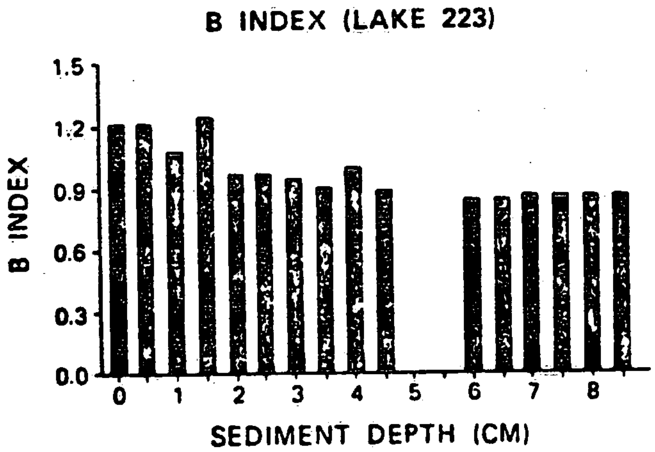

B INDEX (LAKE 223)

FIG 23

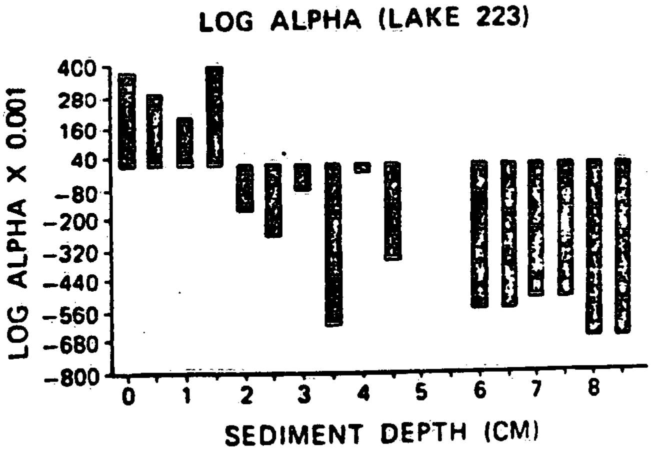

LOG ALPHA (LAKE 223)

FIG. 24

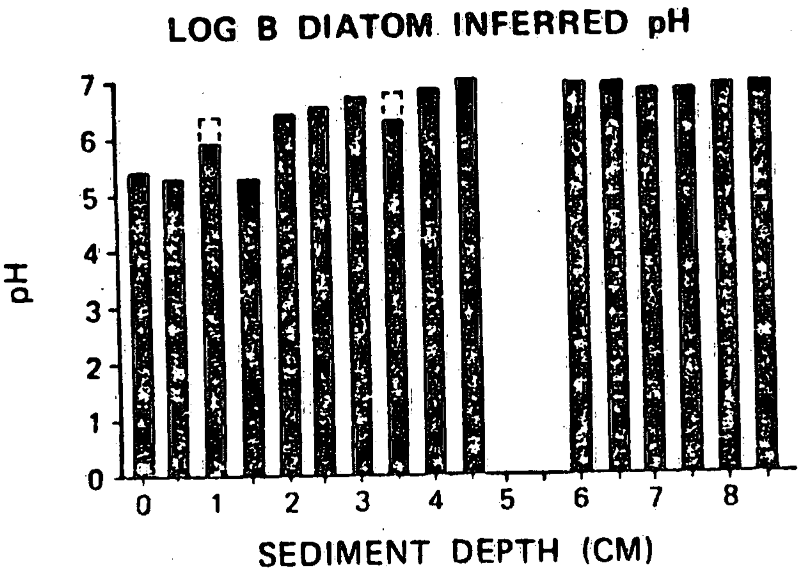

LOG B DIATOM INFERRED pH
pH
7
6
5
4
3
2
1
0
0
1
2
3
4
5
6
7
8
SEDIMENT DEPTH (CM)

FIG. 25.

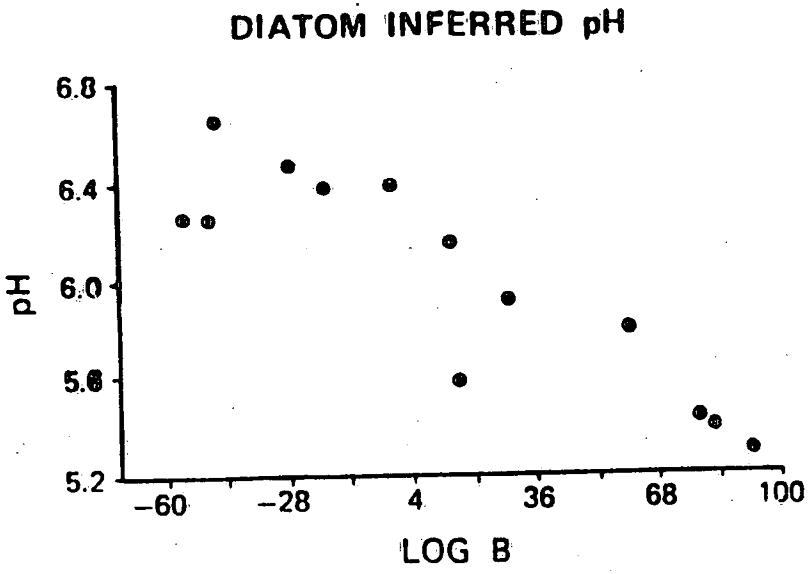

DIATOM INFERRED pH
pH
6.8
6.4
6.0
5.6
5.2
−60
−28
4
36
68
100
LOG B

FIG. 26.