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Bacteria Sediment Diatoms and Sulfur  
Isotope Downcore Profiles.

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**EFFECTS OF LAKE ACIDIFICATION ON SEDIMENT BACTERIA,  
SEDIMENT DIATOMS AND SULFUR ISOTOPE DOWNCORE PROFILES**

by

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## EXECUTIVE SUMMARY

Sulphur isotope ratios are being used more and more to trace sources of sulphur in environmental studies. It has been shown recently that sulphur isotope ratios of lake water sulphates in remote areas reflect those of the annual bulk acid precipitation. There is also evidence that lake sediment core profile values will reflect environmental changes of the lake drainage basins over the past century. This study compares sediment downcore profiles of sulphur contents, sulphur isotope values, diatom inferred pH and microbiological populations from several lakes north of Lake Superior of which two are near and downwind from the Wawa sintering plant while others are more remote and upwind of the plant. The results indicate that sulphur isotope values for the deeper sediment (Circa 60 yrs. B.P) are close to those of the present day lake sulphate values. However, isotope values of the surficial sediments are shifted to lower values (toward isotopically light sulphur). For the remote non-plume lakes this shift is slight (1-4%) whereas for the near plume lakes the shift is much more dramatic (12-14%). The results of this study improve our understanding of lake acidification process and resulting changes in microbiological populations. The results also improve our ability to assess the impact of acid loadings on lake acidification processes.

Le rapport des teneurs isotopiques du soufre est de plus en plus utilisé, pour déterminer les sources de soufre, dans les études environnementales. Il a été montré récemment, que le rapport des teneurs isotopiques du soufre dans les sulfates des eaux lacustres des régions éloignées reflète celui des précipitations acides annuelles totales. De plus, des données indiquent que les valeurs de profil des chambres de sédiments lacustres reflètent les modifications environnementales des bassins versants des lacs au cours des cent dernières années. La présente étude compare les profils de teneur en soufre dans les carottes de sédiments, les valeurs isotopiques du soufre, le coefficient pH calculé d'après les diatomées et les populations microbiologiques de plusieurs lacs au nord du lac Supérieur, dont deux sont proches et en aval de l'usine de frittage de Wawa, tandis que les autres sont plus éloignés et en amont de l'usine. Les résultats indiquent que les valeurs isotopiques du soufre dans les sédiments profonds (environ 60 ans B.P.) se rapprochent des valeurs actuelles de sulfate dans les lacs. Cependant, les valeurs isotopiques des sédiments superficiels baissent vers un niveau inférieur (soit celui du soufre isotopiquement léger). Dans le cas des lacs éloignés qui ne subissent pas les effets du panache de fumée de l'usine, ce changement n'est pas important (1-4 %), tandis que pour les lacs rapprochés, soumis à l'effet du panache, l'écart est beaucoup plus radical (12-14 %). Les résultats de l'étude permettent de mieux comprendre les processus d'acidification des lacs et leurs répercussions sur les populations microbiologiques, ainsi que de mieux évaluer l'impact des charges acides sur ces mêmes processus.

## ABSTRACT

A comparison of sulphur contents and sulphur isotope ratios in 10-12 cm deep sediments (Circa 50-100 yrs. before the present) was made with surface sediments 0-2 cm deep (Circa 0-10 yrs. B.P.) from each of six lakes located north of Lake Superior, Canada.

The comparison indicated that the surface sediments had significantly higher sulphur contents (largely organic sulphur) per gram dry weight and significantly lower sulphur isotope ratios ( $\delta^{34}\text{S}^{\text{O}}_{\text{OO}}$  value) than the deeper sediments.

The increased sulphur content and decreased  $\delta^{34}\text{S}$  values in the younger sediments were much greater for the lakes near and downwind from a sintering plant than for the remote lakes reflecting the impact of the sintering plant on the lake environments.

The surface sediments revealed positive isotopic evidence of bacterial sulphate reduction (a shift to isotopically light sulphur) while the deeper older sediments revealed a virtual absence of bacterial sulphate reduction (no appreciable shift in  $\delta^{34}\text{S}$  relative to the lake sulphate).

A significant correlation between the density of sulphate reducing bacteria and the magnitude of the isotope shift was observed in the study lakes. This suggests that given sufficient organic matter, the greater is the sulphate content in the soft water lakes -- the greater is the number of sulphate reducing bacteria and the

greater is the isotope fractionation in the shallow anaerobic sediments.

The rate of lake acidification as inferred from the downcore pH profile for each of the study lakes was not significantly correlated with the amount of sulphur in the lake sediments, their density of sulphate reducing bacteria or their  $\delta^{34}\text{S}$  shifts.

The underlying geology and buffering action of the lakes which play a key role in their pH listing have little direct impact on the biological activity and isotope fractionation in sediments.

## RÉSUMÉ

La teneur en soufre et le rapport des teneurs isotopiques du soufre des sédiments à 10-12 cm de profondeur (environ 50-100 ans B.P.) ont été comparés à ceux des sédiments superficiels à 0-2 cm de profondeur (environ 0-10 ans B.P.) provenant de six lacs situés au nord du lac Supérieur, au Canada.

La comparaison a indiqué que les sédiments superficiels avaient une teneur en soufre (en grande partie du soufre organique) appréciablement plus élevée par gramme de poids sec, et un rapport des teneurs isotopiques du soufre considérablement plus faible (valeur de  $\delta^{34}\text{S}^{\circ}/\text{oo}$ ) que ceux des sédiments plus profonds.

L'accroissement de la teneur en soufre et la baisse des valeurs de  $\delta^{34}\text{S}$  des sédiments plus récents étaient beaucoup plus importants dans le cas des lacs proches et en aval d'une usine de frittage que dans celui des lacs éloignés, reflétant l'impact de l'usine sur les milieux lacustres.

Les sédiments superficiels ont donné la preuve isotopique évidente de la réduction des sulfates par les bactéries (un changement vers le soufre isotopiquement léger), tandis qu'une absence à peu près totale de ce type de réduction a été observée dans les sédiments plus anciens (aucune modification appréciable de  $\delta^{34}\text{S}$  par rapport aux sulfates lacustres).

Une corrélation significative entre la densité des bactéries réductrices de sulfates et l'importance du changement isotopique a été observée dans les lacs à l'étude. Ce phénomène indique que, s'il y a suffisamment de matières organiques, le nombre de bactéries réductrices de sulfates et le fractionnement

isotopique dans les sédiments anaérobies peu profonds augmentent avec la teneur en sulfates des lacs d'eau douce.

Le taux d'acidification lacustre, déduit à partir du profil du pH des sédiments carottés pour chacun des lacs étudiés, n'a pas présenté une corrélation significative avec la quantité de soufre dans les sédiments lacustres, leur densité de bactéries réductrices de sulfates ou les écarts de  $\delta^{34}\text{S}$ .

L'assise géologique et l'effet tampon des lacs, qui jouent un rôle clé dans l'établissement de leur pH, ont peu d'impact direct sur l'activité biologique ou le fractionnement isotopique dans les sédiments.



1. INTRODUCTION

Several lakes located north of Lake Superior have become acidified as a result of increased atmospheric loading of sulphuric and nitric acids (Fortescue et. al. 1981 and 1984; Kerr, 1982; Dickman et. al. 1984). It is therefore important that these lakes be examined in order to develop baseline information for monitoring changes which would be useful in developing criteria for management strategy.

The historical water pH data commonly used to evaluate the rate of lake acidification are frequently of dubious quality or are so sparse as to be of little value.

Two lakes may both have similar low pH and alkalinity but one may have been stable with these conditions for the last century or more while the other lake has been undergoing rapid acidification over the last thirty years. To distinguish between these two types of lakes a number of researchers have turned to a technique based on sediment diatom stratigraphic analyses.

This technique has been shown to be effective in estimating the rate of lake acidification in a number of regions throughout North America and Scandinavia (Davis & Berg, 1980; Renberg & Hellberg, 1982; Dickman et. al., 1984).

This is partly a result of the fact that diatoms are abundant in freshwater lakes, are silicious and preserve well in sediments and are sensitive to changes in lake pH (Batterbee, 1973). Whether a shift in diatom species composition is due directly to a shift in lake pH or whether it is due to changes associated with a shift in lake pH, has never been determined. Rao et. al. (1984) have indicated that sediment microbial populations and sediment microbial activity can be used to recognize differences between acid stressed lakes from non-acid stressed lakes and to trace historical changes in response of lakes to acification. Although independent studies of acidified lakes described above have provided much valuable information, no attempt has ever been made to integrate bacterial, diatom and sediment chemistry stratigraphic studies. The purpose of our research was to conduct such an integrated study. We examined the sediments of eight lakes in the Algoma district north of Lake Superior in order to reconstruct their pH history.

## 2. MATERIALS AND METHODS

### 2.1 Sediment Digestion and Diatom Preparation

An acid digestion technique was used for cleaning the diatoms. Small amounts of lake sediments (0.3 to 0.5 g) were placed in 100 ml beakers and 25 ml of concentrated sulphuric acid was added

to each beaker. The beakers were heated to boiling under a fume hood for 30 minutes. During the digestion, samples were stirred to avoid the accumulation of sediment on the bottom of the beakers. This acid digestion step was repeated until the digestion of the organic matter in the beakers was visibly completed. The beakers were then removed from the heating element and a small amount (0.3 to 0.5 g) of potassium dichromate was added to each beaker to oxidize any remaining organic matter.

After digestion, samples were washed into centrifuge tubes with distilled water and centrifuged for two minutes at 6,000 rpm. The supernatant was carefully decanted and the pellet was resuspended in distilled water. This rinsing process was repeated three times to remove all the acid. The diatoms were then transferred to labelled plastic vials.

The diatom concentrate in each sample was examined under the microscope and a further dilution was often made before placing the solution in Battarbee sedimentation plates (Battarbee 1973).

A measured volume (generally 5 to 7 ml) of well mixed (homogeneous) sample was poured into each Battarbee plate. After placing the sample in the plates, they were not disturbed until evaporation was completed. After 3-4 days when all the water has

evaporated, the diatom coated coverslips were mounted on glass slides using Hyrax mounting media.

## 2.2 Diatom Identification and Enumeration

Diatom identification was based on Hustedt (1930 and 1939), Hubber-Pestalozzi (1942), Cleve-Euler (1951-1955), Patrick and Reimer (1966, 1975), Foged (1979), Gerloff and Chohnoky (1970) and Germain (1981).

Eight hundred to a thousand diatom frustules were counted at each half centimeter depth interval using a Leitz inverted microscope equipped with Nomarski interference optics (1,250X magnification).

## 2.3 Bacteriological Procedures

Total and respiring bacteria in all water samples were estimated using the INT - formazan reduction technique (Zimmerman et. al. 1978). A 10 ml portion of each water sample was poured into previously cleaned and sterilized test tubes and 1 ml of 0.2% aqueous INT - dye (2 - para iodophenyl: 3 - p-nitrophenyl: 5 - phenyl tetrazolium chloride, Sigma Chemicals) was added to each of the tubes. After mixing, the samples were kept in the dark for 20 minutes at in situ temperature. The reaction was stopped by adding 0.1 ml of 37%

formaldehyde which also served as a preservative. The treated samples were then stored at 4°C. One ml of the treated sample was filtered through 0.1 µm poresize polycarbonate membrane (Nuclepore) which was presoaked for 24 hours in a 0.0066% solution of Sudan Black (Merck) in 5% ethanol. The filter while in the filter holder was stained with 0.01% acridine orange for three minutes, dried and examined under oil immersion for total bacteria using epifluorescence microscopy under U.V. light. After epifluorescence counts, respiring bacteria were counted on the same slide using a combination of U.V. and transmitted bright light illumination (Zimmerman et. al. 1978). Because of anaerobic conditions and microbial layers on particles, sediment samples were not suitable for this procedure.

#### 2.4 Bacterial Physiological Types

Sulphur cycle and Nitrogen cycle bacteria were estimated on all sediment samples using the five tube MPN procedure (Dutka, 1978). Nitrifying bacterial densities were estimated using Nitrosomonas broth. Alexander's media was used to test for denitrifying bacteria. Densities of sulphur oxidizing bacterial (Thiobacillus sp.) populations were measured using the postgate medium. Sulfate reducing (Desulfovibrio sp.) bacterial populations were enumerated using Starky's medium with an anaerobic incubation. For enumeration of bacteria that reduce organic sulphur to sulphide, an MPN medium

described by Gunkel and Openheimer was used combined with anaerobic incubation. All MPN tubes were incubated for 21 days at 20°C.

## 2.5 Chemical and Biological Activity in Sediments

Spectrophotometric method based on the quantitative reduction of dye resazurin by chemically reducing substances and by dehydrogenase activity in micro-organisms was followed. The method was essentially the same as that of Liu and Strachan (1981). The chemical and biological activities are differentiated by using m-cresol. Activity is expressed as  $\mu$  moles of resazurin reduced  $\text{h}^{-1}\text{g}^{-1}$  dry sediment. The sediment samples were processed within 24 hours of collection and the experiment was performed in duplicate, in a dark cabinet as resazurin is photosensitive.

## 2.6 Age Dating from Pollen Analysis

Five ml of cold 10% HCl was added to approximately 3 cc of wet sediment taken from the sediment core. The mixture was stirred for five minutes, centrifuged and decanted, rewashed, centrifuged and decanted. Next, 5 ml of 10% KOH was added and the mixture was boiled for five minutes, stirring continuously. The mixture was next centrifuged, decanted and washed with distilled water. Following this, the sample mixture 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 added to a beaker containing the above prepared sediment mixture and boiled for five minutes. After cooling, the mixture was centrifuged, decanted and washed with glacial acetic acid which was then 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. Three hundred pollen grains were counted and the number of Ambrosia pollen grains counted were recorded as a percentage of this total.

## 2.7 Diatom Counts

Diatom enumeration was based on a minimum count of 800 diatom 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), Foged (1979), Hustedt (1938), Patrick and Reimer (1966 & 1975), and Germain (1981).

## 2.8 Estimates of Precision

The precision of the diatom inferred pH technique was estimated by coding replicate slides of the sediment diatoms. These

slides were coded to avoid unconscious bias. Eight hundred frustules were counted per slide.

The results of these coded slide replicate tests were used to calculate the standard deviation about the mean. The diatom inferred pH variance (2 standard deviations) for any particular depth and core was within plus or minus three tenths of a pH unit of the mean. Variance was represented by a vertical line atop the histogram depth from which replicate counts were made.

## 2.9 Plankton Sampling Techniques

The zooplankton and phytoplankton occurring in each lake in mid-summer were sampled using methods described in Fortescue et. al. (1981). This permitted us to characterize the dominant species occurring in each lake. The dominant terrestrial vegetation and higher aquatic plants occurring in the watershed of each lake was also noted for purposes of comparison.

## 2.10 Water Sampling

Dissolved oxygen (% saturation), temperature (degrees C), alkalinity (mg/l as  $\text{CaCO}_3$ ), specific conductivity (micromhos/cm), Secchi transparency (m), water colour as platinum-cobalt colour units,



pH and sulphate concentration (mg/l) were measured in each of the four lakes according to the methods described in Fortescue et. al. (1981). In addition, half litre nalgene bottles were filled with surface water from Crozier, Fenton and Rabbit Blanket Lakes. These samples were stored at room temperature at McMaster University until analyzed two to three months later as described in the following sections.

### 3. SEDIMENT ANALYSIS

#### 3.1 Sulphide Sulphur (HCl Soluble)

Acid soluble sulphur is extracted from weighed aliquots of crushed and ground dried sediment samples by treatment with dilute HCl. The  $H_2S$  released is converted in successive steps to  $CdS$ ,  $Ag_2S$  and  $SO_2$ , the latter compound being the gas used for isotopic analysis. The concentration of the acid soluble sulfide sulphur is determined gravimetrically at the  $Ag_2S$  step.

#### 3.2 Sulphate Sulphur

The water soluble sulphate sulphur is extracted from the original dried and ground sediment using a Soxhlet extraction apparatus. Ten - 15 grams of dried sediment is weighed into the cellulose extraction thimble and 100 ml of distilled water is poured

into the glass flask boiler. After a 24 hour extraction period, the dissolved sulphate in the glass boiler is precipitated as  $\text{BaSO}_4$ , filtered, washed, dried and weighed. The water soluble sulphur content of the sample is determined at this step. This sulphate sample is then reduced to  $\text{H}_2\text{S}$  with the reducing mixture ( $\text{HI-H}_3\text{PO}_2\text{-HCl}$  mixture) and converted to  $\text{Ag}_2\text{S}$  and finally to  $\text{SO}_2$  for sulphur isotope analysis.

### 3.3 Elemental Sulphur

Elemental sulphur, if present, is also extracted in a Soxhlet extraction apparatus. The same cellulose extraction thimble containing the residue from the water extraction, 3.2 above, is dried in a vacuum oven at  $\sim 65^\circ\text{C}$  and is used again. 100 ml of acetone is poured into the glass flask boiler containing 10 sq cm of Cu gauze. After the extraction is complete, the  $\text{CuS}$  formed on the Cu gauze is converted in successive steps to  $\text{H}_2\text{S}$ ,  $\text{CdS}$ ,  $\text{Ag}_2\text{S}$  and  $\text{SO}_2$  in the usual manner. The elemental sulphur content of the sample is determined gravimetrically at the  $\text{Ag}_2\text{S}$  step.

### 3.4 Pyrite + Organic Sulphate Sulphur

The dried residue in the cellulose extraction thimble from 3.3 is used for the extraction of pyrite sulphur. A complete separa-

tion of pyrite sulphur from carbon bonded sulphur is most difficult (Smith 1964, Monster 1978).

In our experience (Monster 1978) the 6N nitric acid method is the simplest and most satisfactory for ancient sediments where only highly refractory carbon-bonded sulphur is involved. The sample is treated with 80 ml of 6N  $\text{HNO}_3$  for 24 hours at room temperature. Under these conditions, the pyrite sulphur is oxidized to sulphate leaving the carbon bonded sulphur in the residue. The solution is filtered through a glass fiber filter pad using a Gooch crucible. The sulphate in the filtrate is precipitated as  $\text{BaSO}_4$ , washed, dried and weighed using standard techniques. The  $\text{BaSO}_4$  is then reduced to  $\text{H}_2\text{S}$  with the reducing mixture and converted in successive steps to  $\text{CdS}$ ,  $\text{Ag}_2\text{S}$  and finally to  $\text{SO}_2$  which is used for isotopic analysis.

### 3.5 Carbon Bonded Sulphur

The residue in the Gooch crucible from the pyrite extraction, 3.4 above, is dried in a vacuum oven at  $65^\circ\text{C}$ . The organically bound sulphur remaining in this residue is extracted as sulphate using the "Eschka" method, a method often used to determine the total sulphur in a sample. The dried ground residue is transferred to a porcelain crucible and well mixed and covered with "Eschka" mixture (65%  $\text{MgO}$ , 35%  $\text{Na}_2\text{CO}_3$ ). The conversion of the sulphur to sulphate

takes place in a furnace -800°C in ~3 hours. The sulphate produced in the crucible is dissolved in a beaker of distilled water at 100°C. The sulphate in the filtrate from this operation is precipitated as BaSO<sub>4</sub>, filtered, dried and weighed. The sulphate is then converted to SO<sub>2</sub> as before for isotope analysis.

### 3.6 Total Sulphur

The total sulphur is extracted from 1-2 grams of dried, crushed and ground lake sediment using the "Eschka" method as in 3.5 above. All forms of sulphur are converted to sulphate by this method. The sulphate produced is determined gravimetrically as BaSO<sub>4</sub> as before and finally converted to SO<sub>2</sub> for isotopic analysis.

## 4. MASS SPECTROMETRY

Isotopic analysis of SO<sub>2</sub> gas samples is 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  $\delta$  notation

$$\text{where } \delta^{34}\text{S}^0/00 = \left[ \frac{(^{34}\text{S}/^{32}\text{S})_{\text{sample}}}{(^{34}\text{S}/^{32}\text{S})_{\text{standard}}} - 1 \right] \times 1000$$

The standard ratio is that of troilite sulphur of the Canyon Diablo meteorite. Primary sulphur, magmatic sulphur, sulphur in Basic sills, have  $\delta$  values essentially equal to zero.

## 5. RESULTS AND DISCUSSION

Eight lakes were examined in order to determine whether a relationship existed between the rate of lake acidification and the sulphur isotope ratio in their surface (0-1 cm) and deeper (6-12 cm) sediments. Seven lakes were located between the Montreal River (north of Sault Ste. Marie) and Wawa in an area northeast of Lake Superior (Fig. 1). The eighth lake (Crawford Lake, Fig. 2) was chosen as a control lake. The buffering capacity of this Carbonate-rich lake (280 mg Ca CO<sub>3</sub>/l) was so high that acid rain would not have altered its pH.

The pH of the eight lakes (Table 1) ranged from 5.1 (Logger Lake) to 7.8 (Crawford Lake). Diatom inferred pH ranged from 4.9 (Logger Lake) to 8.4 (Crawford Lake, Table 6).

Only one of the eight study lakes was becoming more acid as indicated by downcore diatom inferred pH. Beaver Lake (Figure 11) had a diatom inferred pH of roughly 5.7 at the Cesium - 137 rise (circa 1954), while its present pH (5.3) and its surface sediment diatom

diatom inferred pH (5.2) indicate that a significant reduction in lake pH (0.16 of a pH unit per decade) has occurred in this lake. Although a similar reduction in diatom inferred pH has also occurred in Logger Lake (Fig. 12), its Ambrosia depth sediment (16 cm, circa 1890) had a diatom inferred pH of 4.7 - 4.8, which was not significantly different from its present day pH of 4.9 - 5.1. Therefore, the interpretation of the downcore shift in pH of Logger Lake is quite different from that of Beaver Lake where lake pH has been  $5.7 \pm 0.1$  over the last century, except for the last 30 years, during which time it fell to its present level (5.2 - 5.3, Fig. 11).

Table 2 summarizes microbiological data from seven Northern Ontario lakes and one lake in southern Ontario. The two lakes located closest to the Algoma Sintering Plant (Lakes WW1 and WW2) had the highest bacterial densities and the highest density of sulphate reducers. These lakes are within 15 km of a major sulphur source (300,000 tons/yr of  $\text{SO}_2$  is emitted by the Algoma Sintering Plant, Weizman 1980). The sulphur isotope ratio based on total sulphur analyses (Table 5) was also greater in these two lakes than in any of the others.

Based on the sediment biological activity (using the resazurin test), these lakes may be classified into three categories. Lake WW1 appears to be the least active (6%), while lakes WW2, Fenton

and Logger are moderately active (28 to 35%). Beaver Lake exhibited maximum microbiological activity.

Lake WW1 contained considerable densities of sulphate reducing bacteria. The relatively low sediment biological activity at the sampling time in June was puzzling. The presence of large populations of sulphate reducing bacteria in the sediment is probably related to the rather constant negative Eh values and the availability of carbonaceous energy source and sulphate (Dutka et. al. 1974). Concentrations of carbonaceous energy sources present in the lake sediment are generally adequate to support normal microbial populations and organic degradative processes, however, the local conditions in the lakes near Algoma Smelter appear to have suppressed or lowered the active population levels for bringing about the normal biodegradation processes. Similar circumstances were observed in some other Ontario lakes receiving acid precipitation (Rao et. al. 1984). The presence of large populations of sulphate reducers is also indicative of probable anoxia (Dutka et. al. 1974), thus reducing aerobic microbial biodegradation rates.

In lakes WW2, Fenton and Logger, the densities of sulphur cycle bacteria were high. Organic sulphur oxidizers and sulphate reducers being approximately in equal densities suggested that a ready supply of organic matter (primarily algae) was available as an energy source for sulphate reducing bacteria.

Lakes WW1 and WW2

Both WW1 and WW2 were located on siderite-rich greenstones at roughly 324 m above sea level. The combined catchment area for the two lakes was 0.24 square Km. The area of Lake WW1 was 3.5 ha and WW2 was 1.4 ha. Both lakes were shallow (< 4 m) and the water of Lake WW1 was clear while the water from WW2 had a yellow tinge. The Secchi disc was visible on the bottom of both lakes. The specific conductivity corrected to 25 degrees C. was 183 micromhos/cm for Lake WW1 and 189 micromhos/cm for Lake WW2. Large amounts of iron oxides and pyrite granules were found in the sediments of WW2. The top 2 cm of sediment from this lake were bright red while its deeper sediments (2 - 40 cm) were jet black. In Lake WW1 the 41 cm long core removed from the centre of this lake was brown in colour from top to bottom.

Aquatic plants in lakes WW1 and WW2 were dominated by the mosses growing on the bottom of both lakes. Water lilies (Nuphar), water shield (Brassenia), arrowheads (Sagittaria), Pickerelweed (Pontederia) and Cattails (Typha) were common in the outlet and inlet areas of both lakes.

The ambrosia pollen rise is indicated in the uppermost line in Figure 6. It is also denoted by the letter "A" at 15 cm just below the lead 210 profile (Fig. 6).



Diatom inferred pH in Lake WW1 has increased significantly from a low of 6.5 (19 - 20 cm) to a high of 7.0 at 2 and 4 cm (Fig. 6). The pH of the lake which we observed when we sampled it in 1982 and 1983 was 6.8. A Student's "t" test was performed on the mean diatom inferred pH for the period after and before the Cesium 137 rise (3.5 cm, Fig. 6). The t test indicated that the mean pH for the period 1954 (3.5 cm) to 1982 (0 cm) was significantly higher ( $P < 0.05$ ) than the period represented by the sediment depths of 3.5 - 20 cm.

Although WW1 receives considerable amounts of  $SO_2$  from the Algoma Ore Sintering Plant it may also receive substantial amounts of alkaline fly ash as indicated by snow samples reported by Weizmann (1980). In addition the acid rain enhanced weathering of the carbonate-rich greenstones which are everywhere exposed in the fume kill watershed occupied by lakes WW1 and WW2 may account in part for the increase in diatom inferred pH of this lake.

The downcore diatom inferred pH profile for Lake WW2 was very similar to WW1 with the exception that the peak in diatom inferred pH at 9 cm in Lake WW2 was significantly higher than in WW1 (Figs. 6 & 7). The Ambrosia rise inferred sedimentation rates in WW2 were lower than they were in WW1 (13 vs. 16 cm Ambrosia rise). However, in the recent past (0 - 5.5 cm) as reflected by the cesium

137 rise sedimentation rates have actually been greater in WW2 (Fig. 7).

#### Doc Grieg Lake

A relatively deep lake (17 m) which thermally stratifies in summer. Although the lake is not as close to the Trans Canada Highway as Crozier Lake, it is easily accessible from the highway. Specific conductivity ranges between 25 and 29 micromhos/cm. Lake pH ranges from 4.7 to 5.7. Alkalinity ranges from -0.3 to 3.4. The lake is located in a granitic basin. The depth of 1% surface light intensity was 13 m in June of 1984. The water had no detectable colour. According to Marcel Pelligrini (Algoma area Ministry of Natural Resources) the lake was stocked with rainbow trout in 1982 by Tony Quain and by himself in 1983.

The lake was cored on 7 June 1984. The sediments in the core were dark brown to black in colour from top to bottom. Numerous chironomids were observed in the surface sediment of the two cores.

The diatom inferred pH of the surface sediments of Doc Grieg Lake was 5.7. The observed pH of the lake in the summer of 1983 was 5.6 which was identical to the diatom inferred pH at the bottom (19 - 20 cm) of the Doc Grieg Lake sediment core (Fig. 5).

Ambrosia pollen increased from an average of 4 - 5 grains per hundred to 7 grains per hundred at 15 cm (Fig. 5B). As a result we concluded that the Ambrosia rise, circa 1890, occurred at 15 cm in Doc Grieg Lake (Fig. 5). The cesium 137 rise occurred at 3.5 cm and just below this depth we recorded the only significant decrease in diatom inferred pH (5.4; or - 0.2 of a pH, Fig. 5). The horizontal lines at 3, 4, 9 and 13 cm in Fig. 5 represent 2 standard deviations about the mean ( $n = 3$ ). We concluded that the diatom inferred pH of Doc Grieg Lake (5.7 at 0.0 - 0.5 cm) had not decreased significantly from that of the Ambrosia rise (5.7, 14 - 15 cm).

#### Crozier Lake

According to the Ministry of Natural Resources, Crozier Lake has a maximum depth of 20 m. Two cores were removed from the centre of the lake on 8 June 1984 where the water was 17 m deep. Specific conductivity ranged from 195 micromhos/cm at the surface to 266 at the bottom. The lake's hypolimnion was not anaerobic in June (minimum dissolved oxygen was 1.7 mg/l). The lake was also cored in the summer of 1982 and 1983 when its hypolimnion was anaerobic. Ph ranged between 7.2 and 7.6 and alkalinity ranged between 60 and 67 mg/l. The lake was thermally stratified at 4 m in June 1984 and 1% surface light intensity was recorded at a depth of 11 m.

The top 2 cm of the KB Cores from Crozier Lake was dark brown in colour. Diatom inferred pH was 7.3 at the Ambrosia rise (15 cm, Fig. 9B) and 7.2 at the surface (0.0 - 0.5 cm, Fig. 9). In the early 1900's the pH of the lake fell to 6.7 (11 - 13 cm). The reasons for this are not known although the Algoma logging records indicate that the lake was logged in the first half of this century.

#### Beaver Lake

Beaver Lake with an area of 0.3 square Km was long relative to its width. Granite bedrock outcrops were visible on both sides of the lake's watershed. The lake which is nameless on the NTS map of the area received its name from an old beaver dam which occupied its outlet at the north end of the lake. Beaver Lake is located 407 m above sea level at 48 degrees 4 minutes north latitude and 85 degrees 1 minute west longitude. Surficial deposits of glacial overburden were observed in low lying areas near both its inlet and outlet but were rare on the steep sided rock uplands within the lake's small watershed (watershed area = 3 square km).

Temperature corrected specific conductivity of the lake (23 micromhos/cm) was lower in this lake than in any other study lake. Its alkalinity was 3.2 mg/l and its epilimnetic pH was 5.2 in the summer of 1982. The bottom of the lake (maximum depth < 4 m) was

covered with dense patches of aquatic moss. The lake was slightly humic (15 Pt. Co. units) and a Secchi disc was visible on the lake's bottom near its centre in 3.5 m of water.

Beaver Lake displayed three times the bacterial activity of the other seven study lakes. The reason for this is probably associated with the fact that the initial isotope and diatom analyses were made on cores taken from the centre of Beaver Lake in 1982. Financial constraints made it impossible to return to the lake via helicopter. As a result a canoe was used to portage into the lake via its inlet stream. Bacteriological samples were taken from the stream rather than the lake in 1983 (and so labelled) when it became too dark to proceed with the portage.

The sedimentation rate in Beaver Lake as inferred from its Ambrosia rise at 12 cm (Fig. 11B) was one of the lowest in the Algoma area study lakes. Diatom inferred pH (5.8, Fig. 11). This was a statistically significant decrease ( $P < 0.01$ ). The reasons for the change have been ascribed to the proximity of the lake to the Algoma iron ore sintering plant which discharges approximately 300,000 metric tons of  $SO_2$  each year (Weizman, 1980).

Logger Lake

This lake was also nameless on the NTS map at 47 degrees 16 minutes north latitude and 84 degrees 0 minutes west longitude. The name "Logger" Lake was arbitrarily assigned to it because Mr. Len Oliphant, a prominent forester in the area had shown us his logging records. These indicated that the lake had been logged in the early 1900's.

The lake is situated on granitic bedrock 440 m above mean sea level. Its area is 0.05 square km and its catchment was 0.8 square km in area according to the NTS map.

The chemistry of the lake is similar to Beaver Lake. The specific conductivity of Logger Lake was 44 micromhos/cm and its alkalinity was 1.2 mg/l as  $\text{CaCO}_3$ . The observed pH of the lake in the summers of 1982 and 1983 respectively was 4.9 and 5.1. The major difference between the two lakes was in their epilimnetic sulfate concentrations which were significantly higher in Beaver Lake (Table 4).

Logger Lake was very slightly humic (colour = 15 Pt. Co. units) and muskeg was evident in the area adjacent to the lake's inlet. Most of the shoreline of the lake was dominated by rocky (granitic) outcrops.

The diatom inferred pH at the Ambrosia rise (16 cm, Fig. 12B) was never estimated as the core from Logger Lake was only sectioned to a depth of 15 cm. The diatom inferred pH at the bottom of the core (15 cm) was 4.75 (+  $\pm$  or - 0.1 of a pH unit, Fig. 12). The diatom inferred pH at the top of the core was 4.9 +  $\pm$  or - 0.1 of a pH unit. Thus there was no significant difference between the present day pH and the pH of the lake in the early 1900's. However, above a depth of 13 cm, diatom inferred pH in Logger Lake started to increase until it reached a pH of nearly 5.2 at 7 cm. Thereafter its pH fell until it reached its present level (Fig. 12). This was a statistically significant shift in diatom inferred pH. Its implications are discussed in a later section of this paper.

#### Crawford Lake

This 21 m deep lake has a pH of 7.8 to 8.2 and its alkalinity is so high that during summer calcium carbonate forms a precipitate in its water column causing the lake to appear a milky green colour. The lake was chosen for study as a control because of its high alkalinity and because its profundal sediments are varved making age determinations fairly reliable. In addition, the anaerobic sediments of this meromictic lake are free from bioturbation. The lake has been well studied by numerous limnologists as reviewed by Dickman (1984). Details of the lakes' limnology were also summarized by Dickman (1984).

The sedimentation rates in Crawford Lake were substantially greater than any observed for the Algoma area lakes. The Ambrosia rise at 21 cm (Fig. 10B) was deeper than in any of the Algoma area lakes. The well demarked light and dark coloured varves in this lake made it possible to estimate the cores age at six depths (Fig. 10) by counting its varves under a dissecting microscope. The Ambrosia pollen was two to three times more abundant in Crawford Lake than it was in the Algoma area lakes (Figs. 5B - 12B).

The downcore diatom inferred pH profile for this well buffered lake was surprisingly varied (Fig. 10). The pH ranged from a low of 7.6 (5 - 6 cm) to a high of 8.4 at 12 cm. These differences were significant ( $P = < 0.01$ ) as indicated by the horizontal lines which represent two standard deviations ( $n = 3$ ) at 0, 8, 11 and 19 cm (Fig. 10).

#### Fenton Lake

Fenton, like Crozier and Doc Grieg is accessible from the Trans Canada Highway. All three occupy granitic basins and all three lakes are located in or near the Lake Superior Provincial Park. The pH of Fenton Lake was similar to Crozier (7.3 - 7.7). In most respects Fenton and Crozier Lakes are very similar. However, the hypolimnion of Fenton Lake has always been very well oxygenated.



Diatom inferred pH varied very little downcore in this well buffered oligo to mesotrophic lake. It ranged from a high of 7.4 to a low of 7.2 (Fig. 8). We concluded that there were no significant changes in diatom inferred pH in this lake. The pH at the Ambrosia rise (15 cm, Fig. 8B) was 7.3 (Fig. 8). The observed pH of Fenton Lake at the time it was cored in June of 1983 was 7.5 (Table 6).

#### 6. LAKE SULPHATE

Water samples from three lakes upwind from the Wawa Smelter, Doc Grieg Lake, Fenton Lake and Crozier Lake were collected and analyzed for their sulphate content and sulphur isotope ratios. The results are given in Table 3.

These lakes south of the Smelter have sulphate contents and  $\delta^{34}\text{S}$  values of 9.0 to 12.2 ppm and  $3.8^{0}_{00}$  to  $4.6^{0}_{00}$  respectively, (Table 3). These values are almost identical with those reported for the poorly buffered lakes some 60 to 90 Km N.E. of Sudbury (Nriagu and Coker, 1978A), and are thought to be regulated by influx of sulphate from the atmosphere via precipitation and runoff from the watershed. The average annual  $\delta^{34}\text{S}$  values for bulk precipitation for remote stations north of the Great Lakes of  $4.6^{0}_{00}$  would seem to confirm this (Nriagu and Coker 1978B). Thus the  $\delta^{34}\text{S}$  sulphate values for the three lakes upwind from the Wawa Smelter may be considered to be the

values for the bulk precipitation in the area in the absence of the smelter.

## 7. LAKE SEDIMENTS

The sulphur contents and isotope ratios have been obtained for the various forms of sulphur in sediment samples from Logger and Beaver Lakes upwind from the Wawa Smelter and lakes WW1 and WW2, near and downwind from the smelter. In each case, the sediment samples were taken from Ekman Dredge samples at depths of 10-12 cm and 0-2 cm. The results are given in Tables 4 and 5.

The  $\delta^{34}\text{S}$  (Py + Org. $\text{SO}_4^{=}$ ) levels in the 10-12 cm depth core samples from Logger and Beaver Lakes (Table 2), upwind from the smelter, are seen to be  $3.83\text{‰}$  and  $3.95\text{‰}$  respectively, almost identical with those found for the sulphate in the three upwind lakes (av.  $-4.0\text{‰}$ ) (Table 3). This result indicates: 1) that the av.  $\delta^{34}\text{S}$  level in the atmospheric precipitation and in the lake sulphate has not changed significantly in the area upwind from the smelter over the past 80 years, and 2) that no sulphur isotope fractionation occurred during this period due to the bacterial reduction of lake sulphate. This means that either this latter process did not occur, or it occurred under extreme conditions of very low sulphate concentrations (Harrison and Thode 1958). The  $\delta^{34}\text{S}$  (Org-S) values for

the deep cores of Logger and Beaver Lakes are seen to confirm little or no change in the  $\delta^{34}\text{S}$  levels in the upwind part of the basin over the past 80 years. However, the  $\delta^{34}\text{S}$  ( $\text{Py} + \text{Org.SO}_4^-$ ) in the shallow core samples (0-2 cm) average age ~10 years of Logger and Beaver Lakes show a decrease from that of the lake sulphates, Table 3, of  $5.0^0/00$  and  $1.5^0/00$  respectively. This suggests the possibility of some bacterial sulphate reduction and isotope fractionation or some new source of organic sulphur with negative  $\delta$  values in these recent sediments.

The sediments in lakes WW1 and WW2 near and downwind from the Wawa Smelter show similar  $\delta^{34}\text{S}$  patterns. The changes in  $\delta^{34}\text{S}$  ( $\text{Py} + \text{Org.SO}_4^-$ ) and  $\delta^{34}\text{S}$  ( $\text{Org.}$ ) values in the older samples 10-12 cm are again essentially those considered representative of the basin upwind from the smelter  $-4.0^0/00$ . However, the  $\delta^{34}\text{S}$  ( $\text{Py} + \text{Org.SO}_4^-$ ) and  $\delta^{34}\text{S}$  ( $\text{org.}$ ) in the shallow sediment samples (0-2 cm) have values of  $-11.4^0/00$  and  $-7.6^0/00$ , respectively, Table 5.

The  $\delta^{34}\text{S}$  values obtained for lake WW2 sediment samples, Table 5, also downwind from the smelter show a similar pattern to those of lake WW1.  $\delta^{34}\text{S}$  ( $\text{Py} + \text{Org.SO}_4^-$ ) shifts from  $0.75^0/00$  to  $-13.8^0/00$ , in going from the deep to the shallow sediment samples.

These large shifts in  $\delta^{34}\text{S}$  for sulphur in the surficial sediments, and the corresponding increases in sulphur contents in these sediments near the Wawa Smelter, indicate a marked change in the sedimentation environment over the past 40 years due in some way to anthropological input.

The  $\delta^{34}\text{S}$  levels of the sulphur in the Wawa Smelter effluent or their effect on the levels of the sulphate in the lakes downwind from the smelter have yet to be determined. However, the  $\delta^{34}\text{S}$  values for the sulphides in the siderite ores at Wawa have been measured (Goodwin et. al. 1976). The values are highly variable and average close to zero. It seems highly unlikely that the negative  $\delta^{34}\text{S}$  values of the recent surficial sediments are reflecting a smelter source. Nriagu (in press) has reported negative  $\delta$  values in shallow sediments in lakes downwind from the Sudbury Smelter (effluent with  $+\delta^{34}\text{S}$  values).

The large shifts in  $\delta^{34}\text{S}$  of about  $15^0/_{00}$  toward negative values, indicate: 1) either extensive bacterial reduction and isotope fractionation of sulphur, in the recent anaerobic sediments, the biological activity being stimulated by anthropological input of sulphur and other nutrients or 2) the unlikely possibility of some new source of sulphur added to the drainage basin with negative  $\delta^{34}\text{S}$  values.

8. CONCLUSIONS

1. The diatom inferred pH downcore profiles for the 8 study lakes can be classified into two basic groups: 1) those in which no significant shift in downcore diatom inferred pH occurred (e.g. Logger, Fenton and Doc Grieg Lakes) and 2) those with significant downcore changes in diatom inferred pH.

This latter group of five lakes can be further subdivided into three lakes where the surface sediment diatom inferred pH was significantly different from that at the Ambrosia rise (e.g. WW1, WW2 and Beaver Lakes). The remaining two study lakes, Crozier and Crawford displayed significant downcore shifts in diatom inferred pH. However, there were no significant differences between the diatom inferred pH at the Ambrosia rise and at the sediment surface.

2. Changes in downcore pH profiles for Crozier and Crawford Lakes were difficult to interpret. Both lakes have anaerobic hypolimnia and therefore they may generate considerable alkalinity from the reduction of sulphate (Cook and Schindler, 1983). In addition, both lakes have been altered by man during the last century: Crozier Lake by the construction of the Trans Canada Highway and Crawford Lake by the settlement of the

Crawford family on its shores. For these reasons it was particularly difficult to interpret downcore changes in diatom inferred pH for these two lakes.

3. Beaver Lake was the only study lake in which a significant reduction in diatom inferred pH could be reasonably ascribed to lake acidification. Beaver Lake (observed pH of 5.2) is located in a granitic basin less than 25 km from the Algoma Sintering Plant which annually produces 300,000 tons of SO<sub>2</sub> (Weizman, 1980). The nearby Lake B is also acidifying (Dickman et al., 1985).
4. Lakes WW1 and WW2 are also located near the Algoma Sintering Plant. However, both are located on carbonate-rich greenstones. The significant increase in diatom inferred pH which was observed upcore in these two lakes may therefore be the result of acid rain enhanced weathering of the carbonate-rich materials in their watershed. Unlike Beaver Lake, WW1 and WW2 are within the sinter plume vegetation-free zone (i.e. the zone in which large trees are absent). There was speculation by some that alkaline fly ash may enter both of these lakes.

5. The lakes which were located furthest from the sintering plant (Logger, Crozier, Fenton and Doc Grieg Lakes) had sulphate concentrations in their surface waters which were similar to many lakes located in remote areas.
6. Lakes receiving the heaviest influxes of sulphur had the highest densities of sulphate reducing bacteria and demonstrated the largest downcore shifts in their sulphur isotope ratios.
7. The sulfur isotope values for organic sulphur, sulphate and pyrite in the deeper sediments (10 - 12 cm) of each of the four lakes which were analyzed for sulphur isotopes were similar. The absence of isotopic evidence of bacterial reduction of sulphate in the older sediments implies very low sulphate concentrations resulting in little or no reduction, or a very low isotope effect or both in these deeper sediments. Sulphur isotope ratios in the deeper sediments approached those of the lake's water ( $-4.0$  ‰).
8. It is important that upcore shifts in sulphur isotope ratios which chronicle past changes in the environment be confirmed and investigations be extended. Further measurements of deep core samples could provide base level  $\delta^{34}\text{S}$  values for drainage basins before the advent of anthropogenic sulphur inputs.

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## TABLE CAPTIONS

- Table 1 General characteristics of the eight study lakes including lake depth and area, water colour, specific conductivity, pH, alkalinity and Secchi transparency. In addition sediment core data concerning the 137 Cesium rise, Ambrosia rise and diatom inferred pH at the surface and Ambrosia rise depth within the core or provisia?
- Table 2 Bacterial abundance in the sediments and water columns of eight study lakes in Ontario, Canada.
- Table 3 Sulphur content and isotope ratios in lake water sulphates (Wawa Smelter Area) upwind.
- Table 4 Sulphur content and isotope ratios in lake sediment cores (Wawa Smelter Area) upwind.
- Table 5 Sulphur content and isotope ratios in lake sediment cores (Wawa Smelter Area) downwind.
- Table 6 A comparison of the observed and diatom inferred pH estimates for each of the study lakes

TABLE 1.

Lake Name	Lake Area (Hectares)	Lake pH	Alkalinity (as mg/l Ca CO <sub>3</sub> )	Conductivity (micromhos/cm)	Secchi Transparency (Depth in meters)	Colour	Undergoing Acidification	Lake Depth (m)	General Observations
WW1	3.5	5.2 -6.8	14	171 -183	*VOB	Clear 4***	No		Brown Homogenous Sediment
WW2	1.4	6.7 -6.8	17	162 -189	VOB	Yel-low 1***	No	2	0-2 cm = red sediments 2-20 cm = black sediments
Fenton	17.5	7.5	45	79	4.4	Green 5	No	17	Rivularia "Bloom" (Mesotrophic Lake)
Logger	3	4.9 -5.1	12	24	7.6	Clear 1	No	8	Headwater Lake
Beaver	3	5.2 -5.3	2	23 -26	5.0	Brown 15	Yes	3.8	Acidifying over the last 25 years
Doc Grieg	21	5.6	2	24	7.8	Clear	No	17	Fish mortality by S. err(1982)
Crozier	19	7.5	119	169	7.1	Pale Brown 6	No	20	Anaerobic below 1cm (Black sediment)
Crawford	3	7.8	280	480	6.2	Green 4	No	22	Eutrophic Meromictic Lake (Water Anaerobic below 15 m)

\* V.O.B. = Visible on Bottom (Secchi Disc)  
 \*\* "----" = Cesium - 137 data proposed for 1984 study  
 \*\*\* Colour = platinum-cobalt units

TABLE 2.

BACTERIAL ABUNDANCE IN THE SEDIMENTS AND WATER COLUMNS  
OF EIGHT STUDY LAKES IN ONTARIO, CANADA

Lake Name	Mean Water Column	Lake Sediment	
	Total Bacterial Density* ( $\times 10^7$ /ml)	Sulphate Reducers** ( $\times 10^3$ /ml)	Sulphur Oxidizers** ( $\times 10^3$ /ml)
WW1	2.1	4.9	2.2
WW2	7.8	2.8	1.7
Crawford	1.03	2.36	1.3
Fenton	1.4	0.95	.021
Logger	---	---	---
Crozier	1.9	---	---
Doc Grieg	1.7	---	---
Beaver	0.7	0.005	.069

\* Acridine Orange INT-Formazan Reduction Technique (Zimmerman et. al. 1978).

\*\* MPN (Most Probable Number) Procedure.

--- No data.



TABLE 3.

SULPHUR CONTENT AND ISOTOPE RATIOS  
IN LAKE WATER SULPHATES  
(WAWA SMELTER AREA) UPWIND

Lake*	[Sulphate] in ppm	[Sulphur] in ppm	$\delta^{34}\text{S}^0/00$
Rabbit Blanket	9.0	3.0	3.4
Fenton	12.0	4.0	4.6
Crozier	12.5	4.2	-

\* Site of lakes and Wawa Smelter (see map).

TABLE 4.

## SULPHUR CONTENT AND ISOTOPE RATIOS IN LAKE SEDIMENT

## DRIVE CORES (WAWA SHELTER AREA) UPWIND\*

Lakes	Sample No.	Core Depth (cm)	Sulphate		Pyrite+(Org. SO <sub>4</sub> <sup>2-</sup> )		Org.-S (Carbon-Bonded)		Total S	
			[S] ppm	$\delta^{34}\text{S}/\text{‰}$	[S] ppm	$\delta^{34}\text{S}/\text{‰}$	[S] ppm	$\delta^{34}\text{S}/\text{‰}$	[S] ppm	$\delta^{34}\text{S}/\text{‰}$
Logger	9A	10-12	140	-	1900	3.65	600	3.53	2800	2.10
	9B	10-12	-	-	1700	4.01	610	1.30	(2450)**	
Logger	9A	0-2	200	-0.58	1600	-1.99	440	-1.38	1990	-1.31
	9B	0-2	200	1.56	1800	-0.53	570	-1.81	(2570)**	
Beaver	12A	10-12	110	3.98	1040	3.06	415	3.82	1840	4.06
	12B	10-12	100	-	750	4.9	420	4.00	(1270)**	
Beaver	12A	0-2	240	2.39	1840	2.29	620	0.26	3100	1.83
	11B	0-2	215	2.58	1530	-	550	0.14	(2300)**	

\* Although procedures were carried out for the determination of HCl soluble sulphide (FeS) and elemental sulphur, (S<sup>0</sup>), no significant amounts were found.

\*\*Values calculated.

TABLE 5.

## SULPHUR CONTENT AND ISOTOPE RATIOS IN LAKE SEDIMENT

## DRIVE CORES (WAWA SHELTER AREA) DOWNWIND\*

Lakes	Sample No.	Core Depth (cm)	Sulphate		Pyrite+(Org.S <sub>4</sub> <sup>m</sup> )		Org.-S		Total S	
			[S] ppm	δ <sup>34</sup> S <sup>0</sup> /00	[S] ppm	δ <sup>34</sup> S <sup>0</sup> /00	[S] ppm	δ <sup>34</sup> S <sup>0</sup> /00	[S] ppm	δ <sup>34</sup> S <sup>0</sup> /00
			(Carbon-Bonded)							
WW1	1	10-12	780	2.0	6790	1.2	1230	3.5	8800	3.3
	2	10-12	650	2.4	6300	3.4	1180	4.3	8100	3.0
	3**	0-2	2390	-9.4	9250	-11.4	1600	-6.0	-	-11.0
	4	0-2	1920	-6.2	9500	-11.3	1780	-9.2	13000	-11.9
WW2	5	10-12	420	1.48	4200	-0.5	720	1.2	5200	-0.78
	6	10-12	530	4.1	5300	1.0	880	2.6	5600	-0.56
	7	0-2	540	-7.6	5700	-14.9	730	-	6500	-13.8
	8	0-2	440	-5.0	5100	-12.7	700	-5.4	7300	-10.1

\* Although procedures were carried out for the determination of HCl soluble sulphide (FeS) and elemental sulphur, (S<sup>0</sup>), no significant amounts were found.

\*\*Values calculated.

TABLE 6.

Lake Name	Observed Lake pH	Bedrock Type	Surface Sediment DI pH*	Ambrosia Rise DI pH	Ambrosia Surface Diatom	Max DI pH	Max DI pH	pH Spread
WW1 <sup>3</sup>	6.8	Greenstone+ Siderite	6.8	6.6	0.3	7.0	6.5	.5
WW2 <sup>3</sup>	6.7	Greenstone+ Siderite	6.8	6.6	0.2	7.0	6.5	.5
Fenton <sup>1</sup>	7.5	Carbonate-rich overburden on Granite	7.2	7.3	0.1	7.4	7.2	.2
Logger <sup>1</sup>	4.9-5.1	Granite	4.9	4.75	0.15	5.15	4.7	.45
Beaver <sup>3</sup>	5.2-5.3	Granite	5.2	5.7	0.5	5.8	5.2	.6
Doc Grieg <sup>1</sup>	5.6	Granite	5.8	5.7	0.1	5.85	5.4	.45
Crozier <sup>2</sup>	7.3-7.5	Carbonate overburden on Granite	7.2	7.3	0.1	7.3	6.7	.6
Crawford <sup>2</sup>	7.8	Dolomite	7.8	7.8	0.0	8.4	7.6	.8

<sup>1</sup> = Maximum DI pH spread was less than half a pH.

<sup>2</sup> = No significant difference between DI pH at top and bottom of core.

<sup>3</sup> = Lakes in which the present pH differs substantially from Ca 100 YBP.

\* Diatom Inferred pH.

## FIGURE CAPTIONS

- Figure 1     The study area north of Lake Superior, near Wawa, Ontario. The black dots represent the locations of the study lakes.
- Figure 2     Crawford Lake located on the Niagara Escarpment near Toronto, Ontario.
- Figure 3     The relationship between the observed pH of 28 lakes and their surface sediment diatom log alpha.
- Figure 4     Relative composition of five pH indicator diatom classes from each of the 28 study lakes located in the Algoma area north of Lake Superior.
- Figure 5     Downcore diatom inferred pH over the Grieg Lake vertical bars at 3,4,9 and 11 cm represent two standard deviations ( $n = 3$ ).
- Figure 5B    Percent Ambrosia pollen from selected depths in Doc Grieg Lake. At a sediment depth of 20 cm. For example, 12 grains of Ambrosia pollen were counted in a total pollen count of 300 grains.

- Figure 6 Downcore diatom inferred pH, Lead-210, and Ambrosia pollen percentage abundance for lake WW1.
- Figure 7 Downcore diatom inferred pH, Lead-210, and Ambrosia pollen percentage abundance for lake WW2.
- Figure 8 Downcore diatom inferred pH profile for Fenton Lake.
- Figure 8B Percent Ambrosia pollen for Fenton Lake.
- Figure 9 Downcore diatom inferred pH profile for Crozier Lake. The cm long core segment from Crozier Lake represents a period of approximately 95 years.
- Figure 9B Percent Ambrosia pollen in the Crozier Lake Core. the first increase in Ambrosia above background levels occurred at 15 cm. See text and Figure 5B for details.
- Figure 10 Downcore diatom inferred pH for Crawford Lake. Dates in years before present (YBP are based on varve counts which were made in 1980 (Dickman, 1984)).
- Figure 10B Percent Ambrosia pollen from selected depths in the Crawford Lake Sediment Core (see text and Figure 5B for explanation).

Figure 11 Downcore diatom inferred pH over the last 130 years for Beaver Lake.

Figure 11B Percent ambrosia pollen from selected depths in the Beaver Lake sediment core (see text and Figure 5B for explanation).

Figure 12 Downcore diatom inferred pH for Logger Lake. The 15 cm core segment from this lake represents a time period of approximately 95 years.

Figure 12B Percent Ambrosia pollen at selected depths from the Logger Lake Core (see text and Figure 5B for explanation).

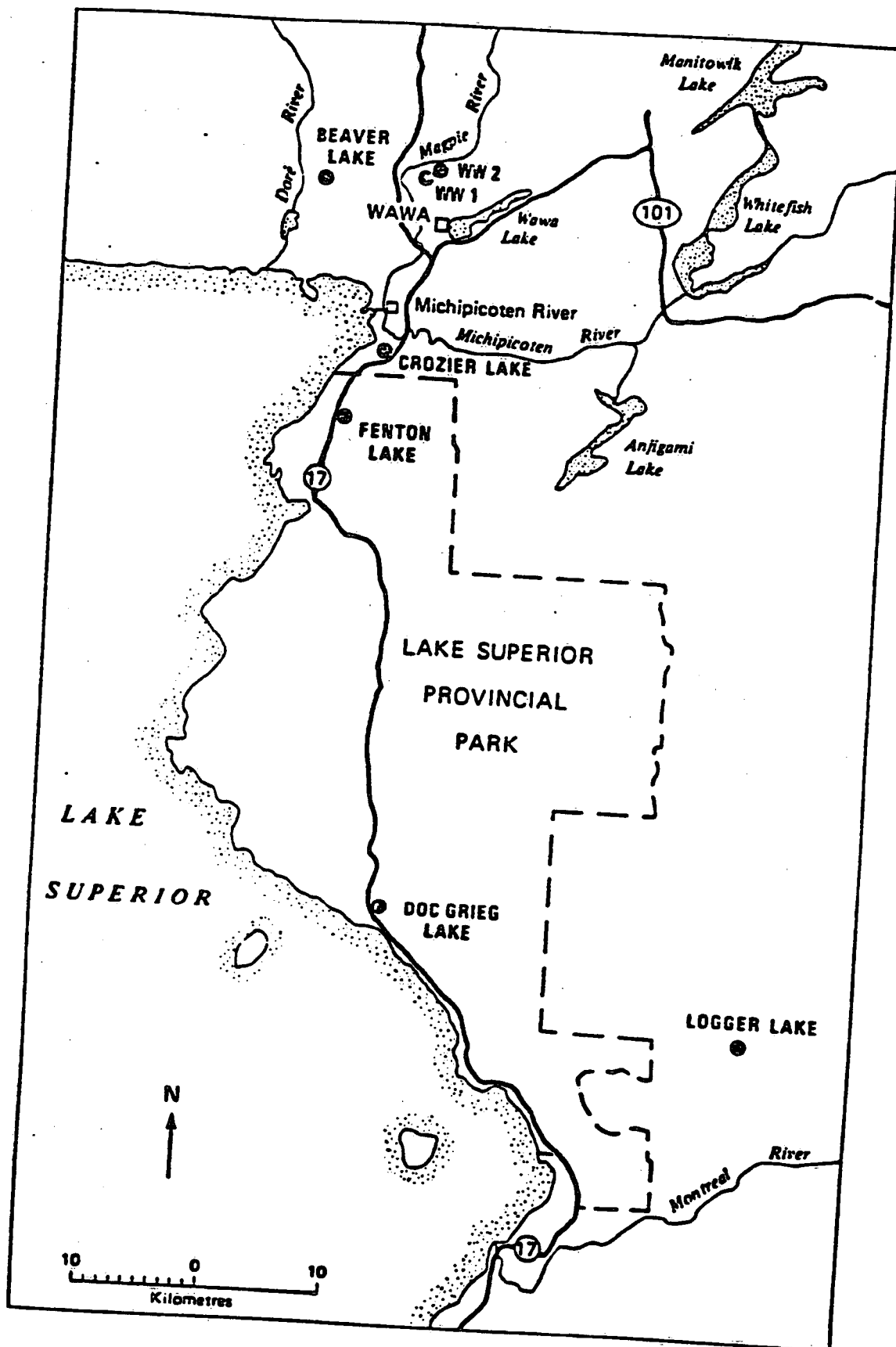


Fig. 1



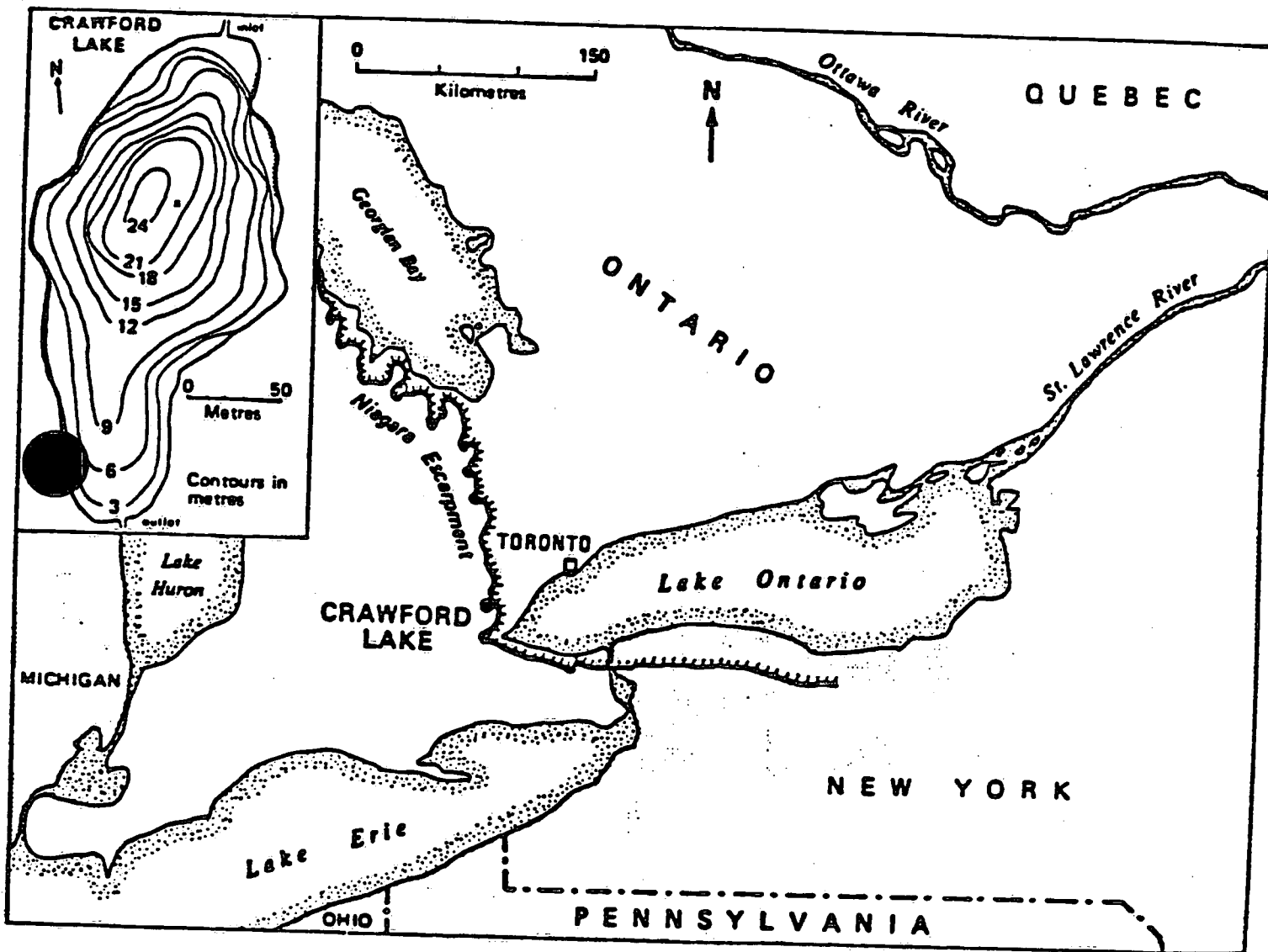


Figure 2

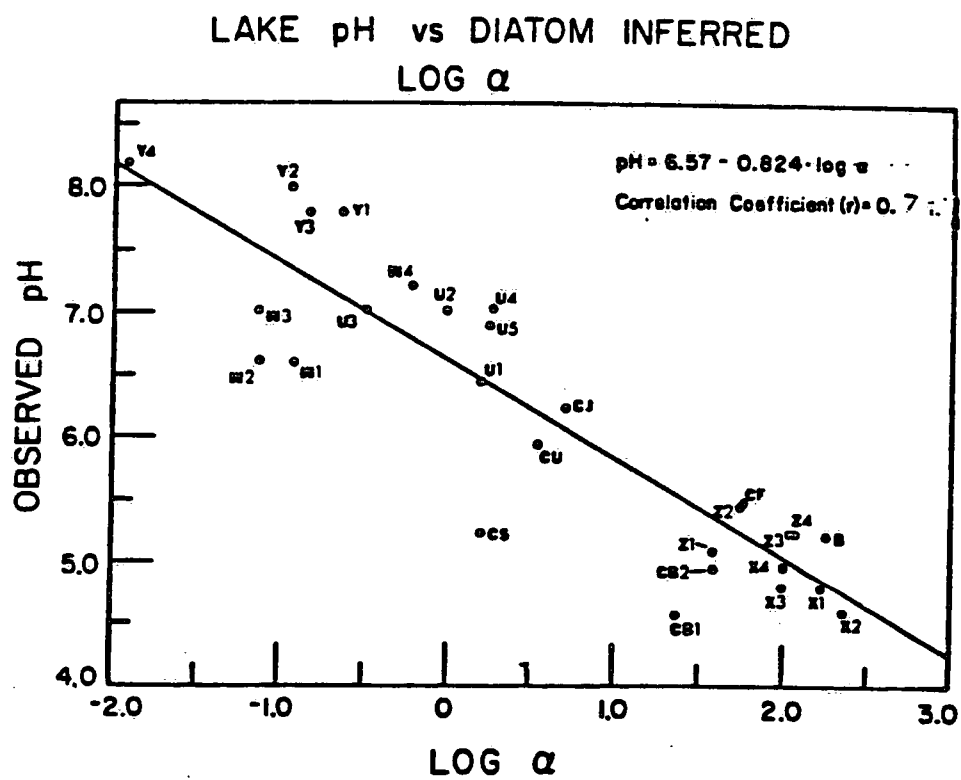


Figure 3



# DOC GRIEG LAKE

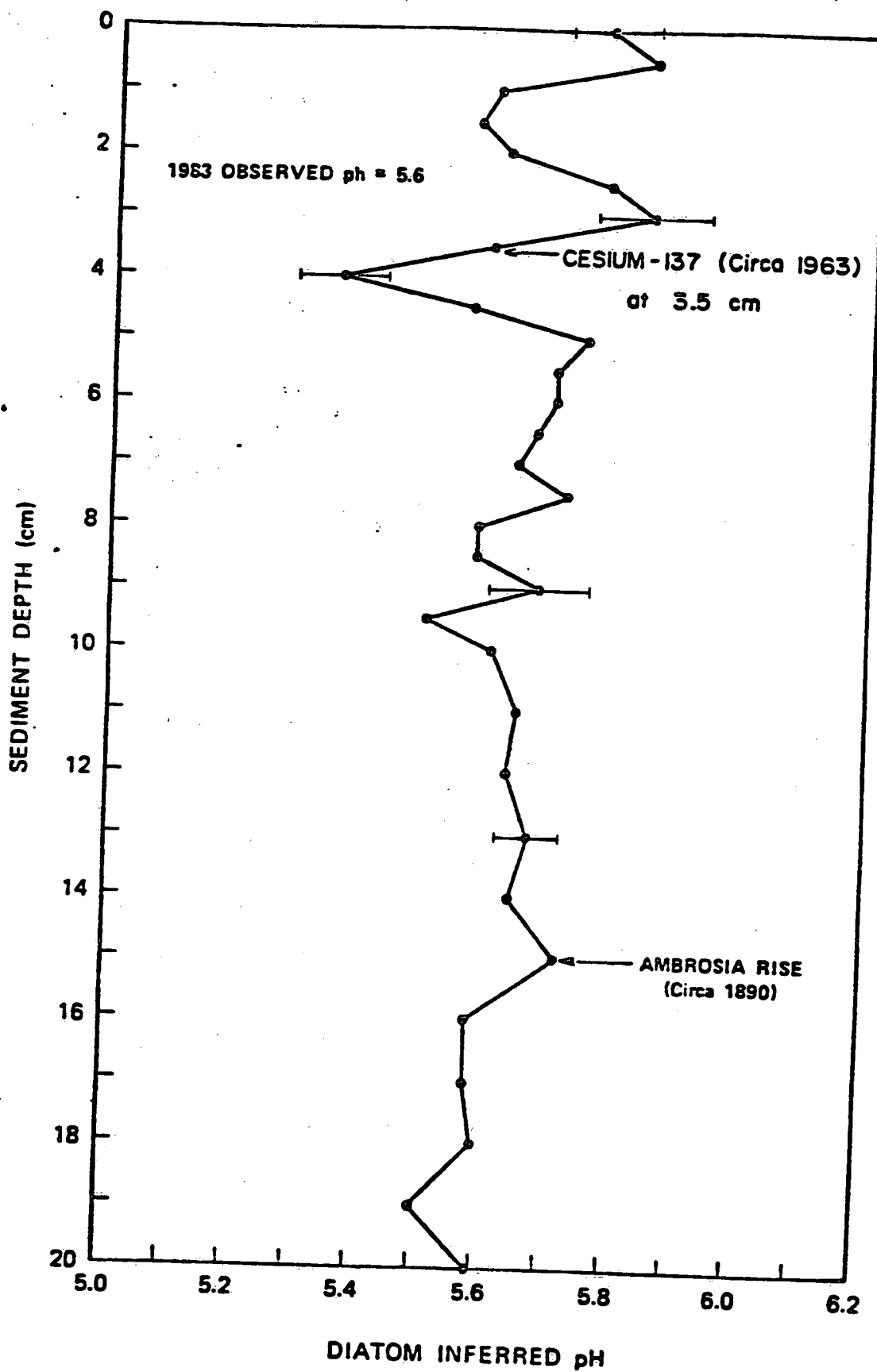


Fig. 5

# DOC GRIEG LAKE

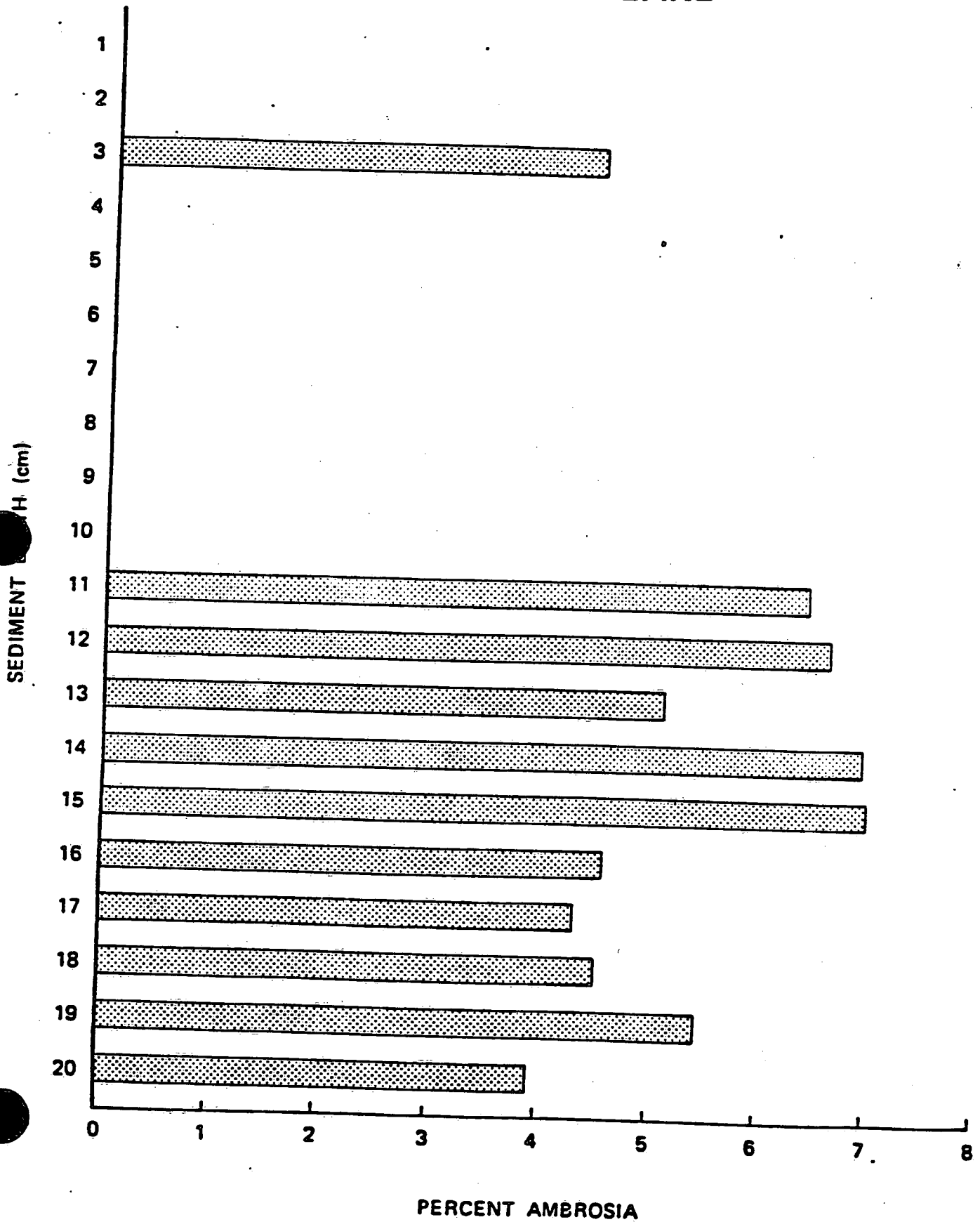
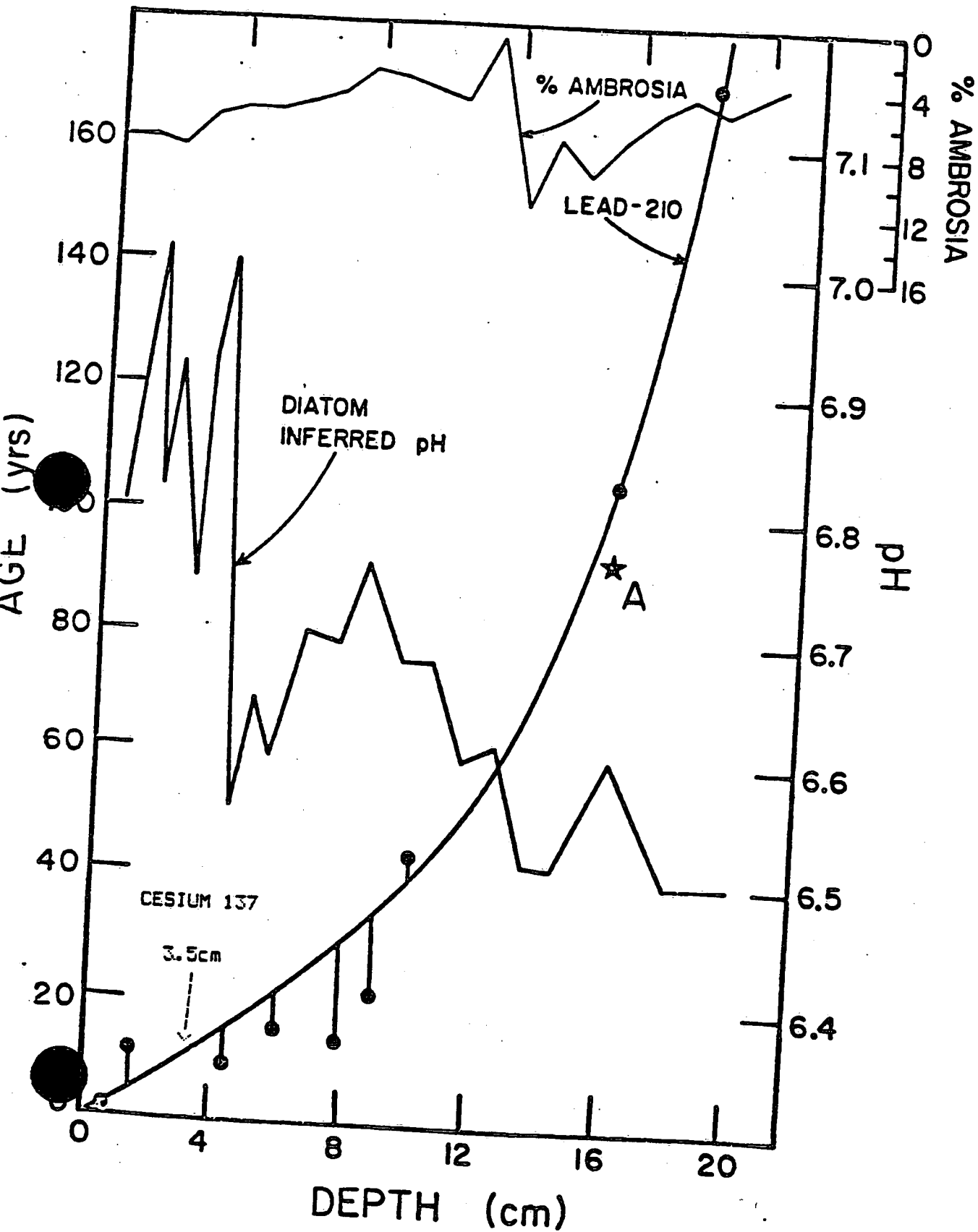


Figure 5B

# LAKE WW I



# LAKE WW2

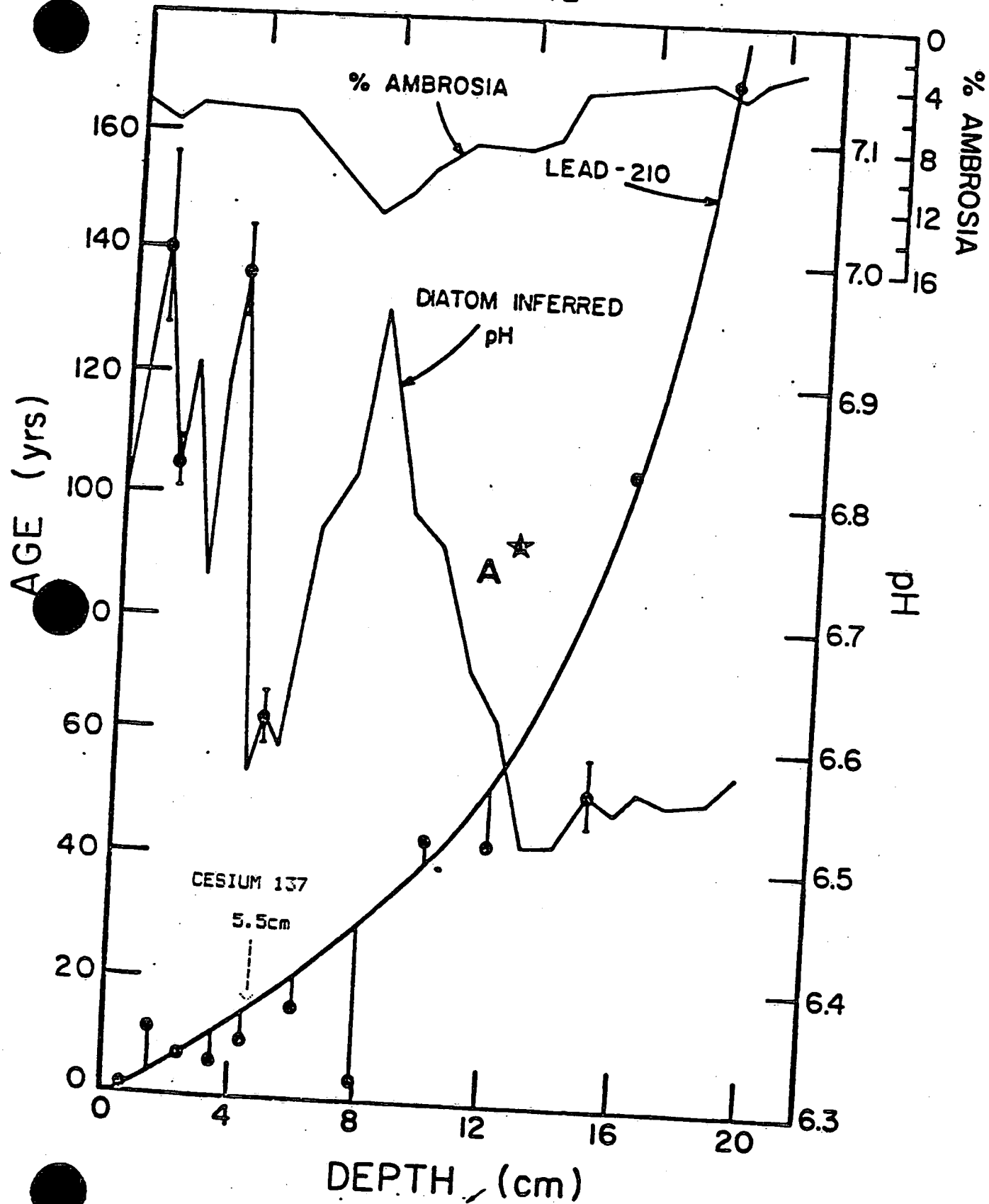
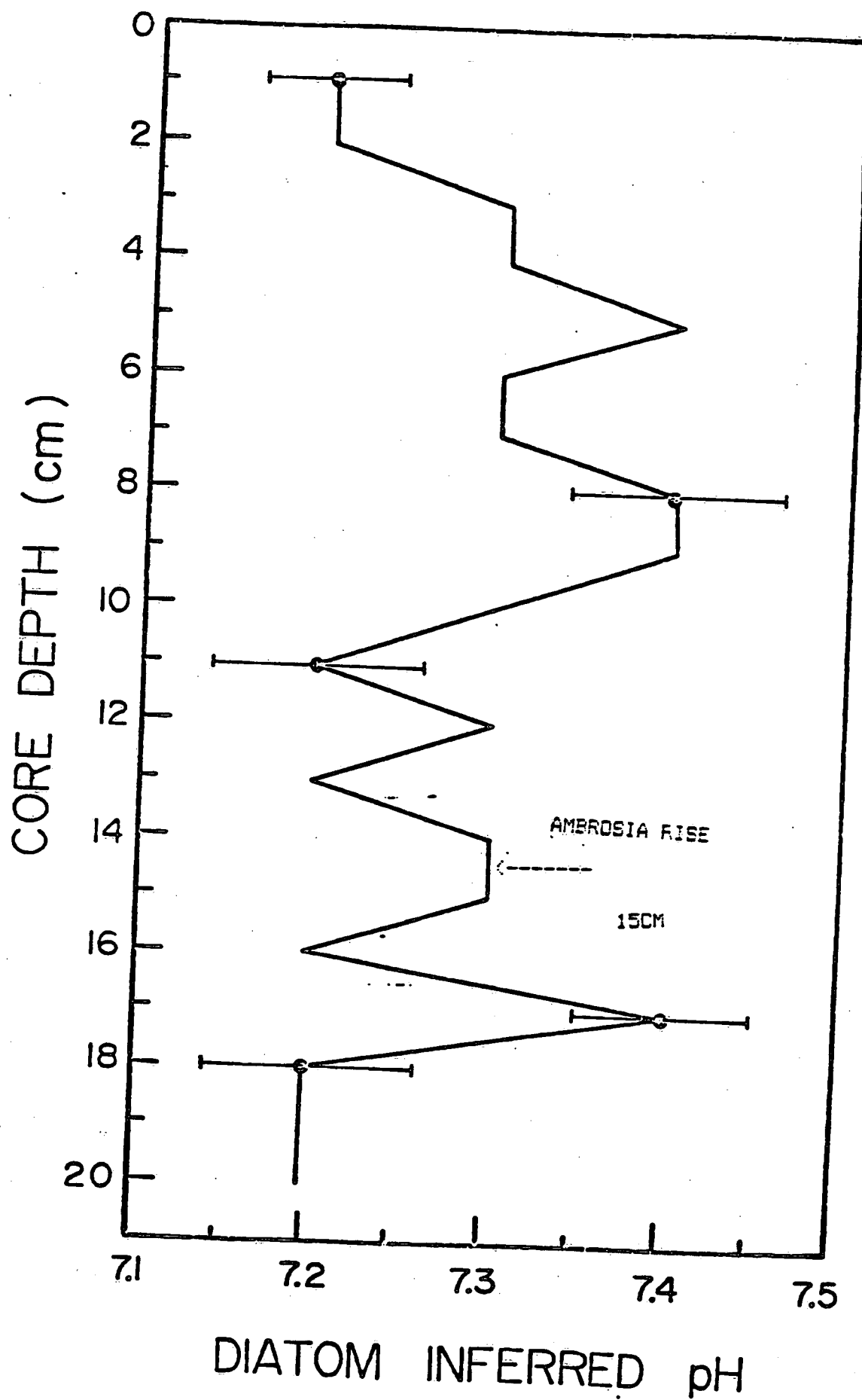


Figure 7

# DOWNCORE PROFILE LAKE FENTON





# FENTON LAKE & ANODONTA POLLEN

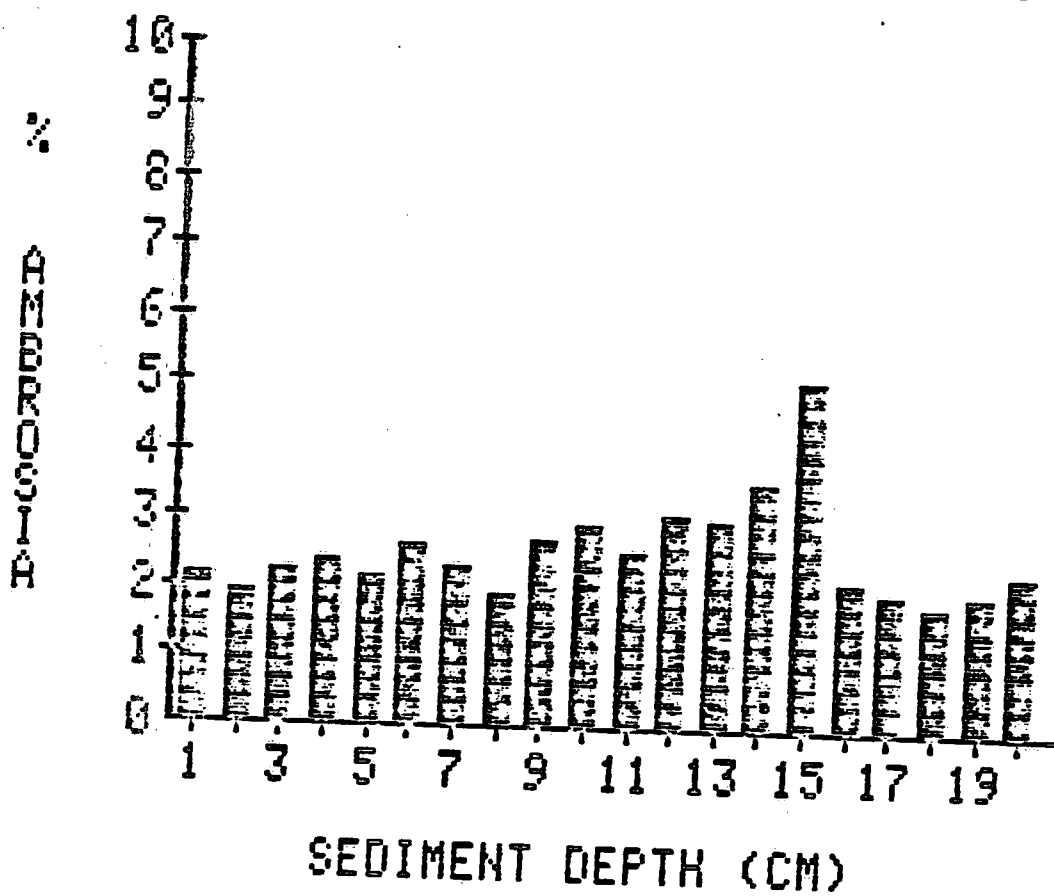


Figure 8.8

# CROZIER LAKE

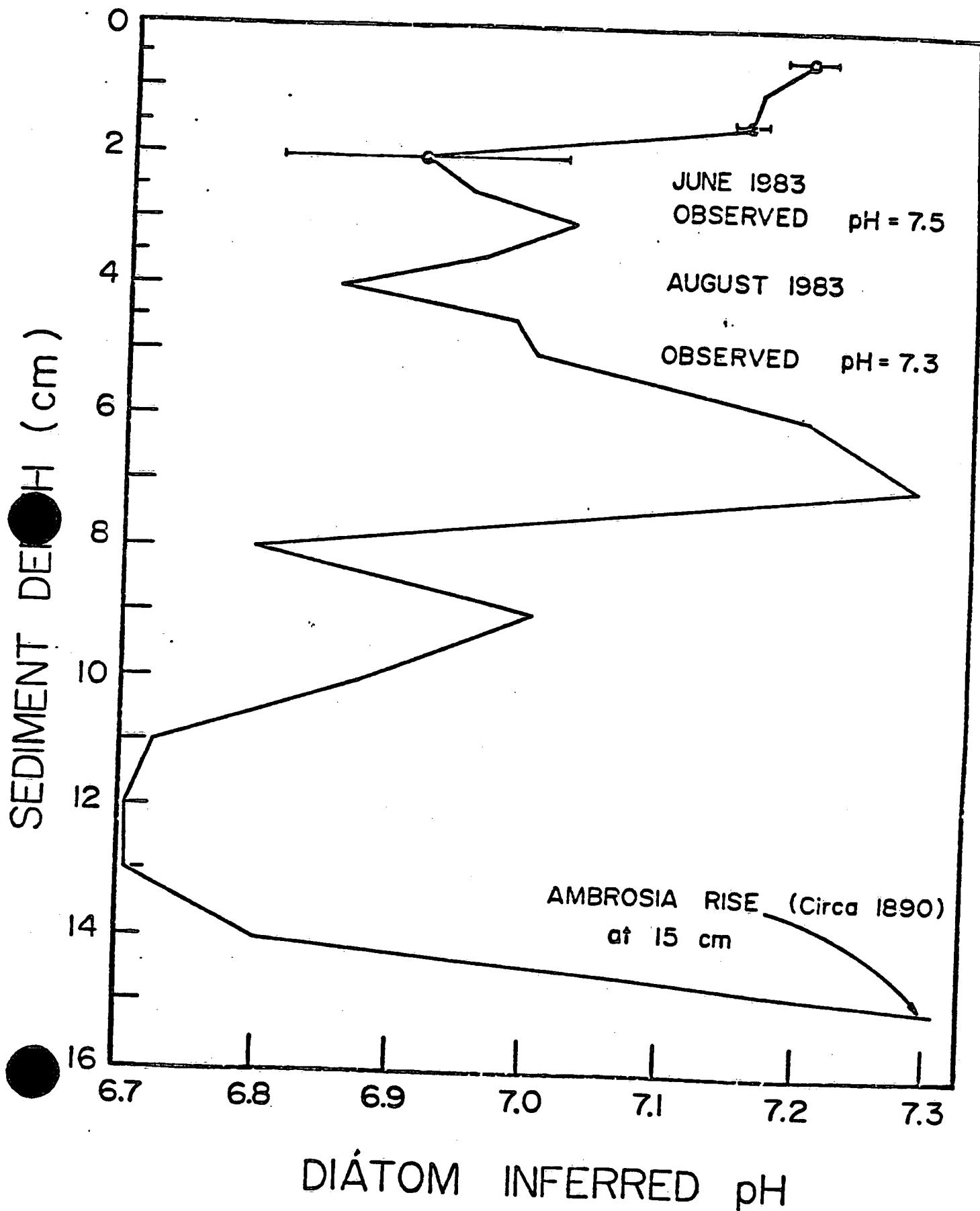


Figure 9

# CROZIER LAKE

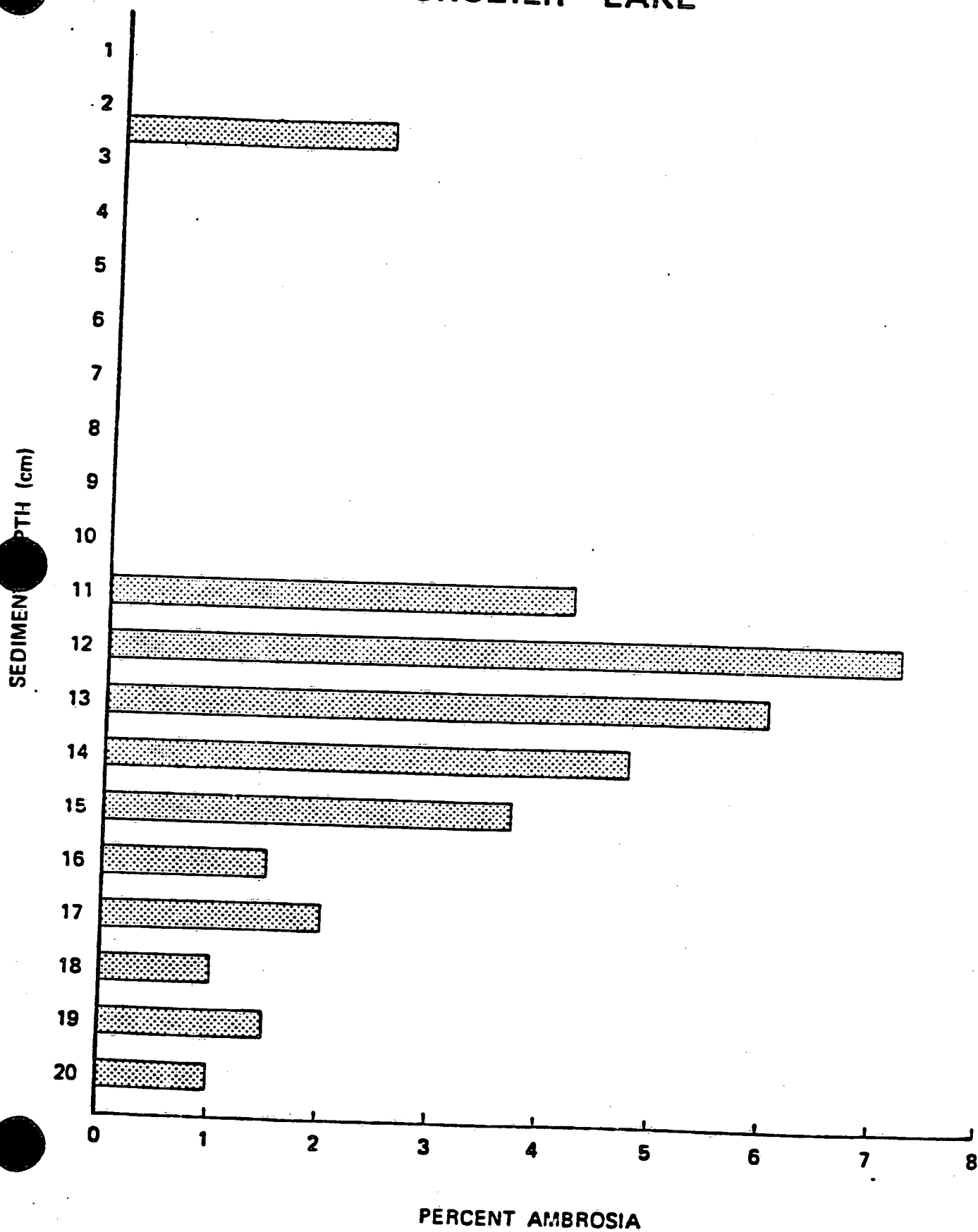


Fig. 9B

# CRAWFORD LAKE

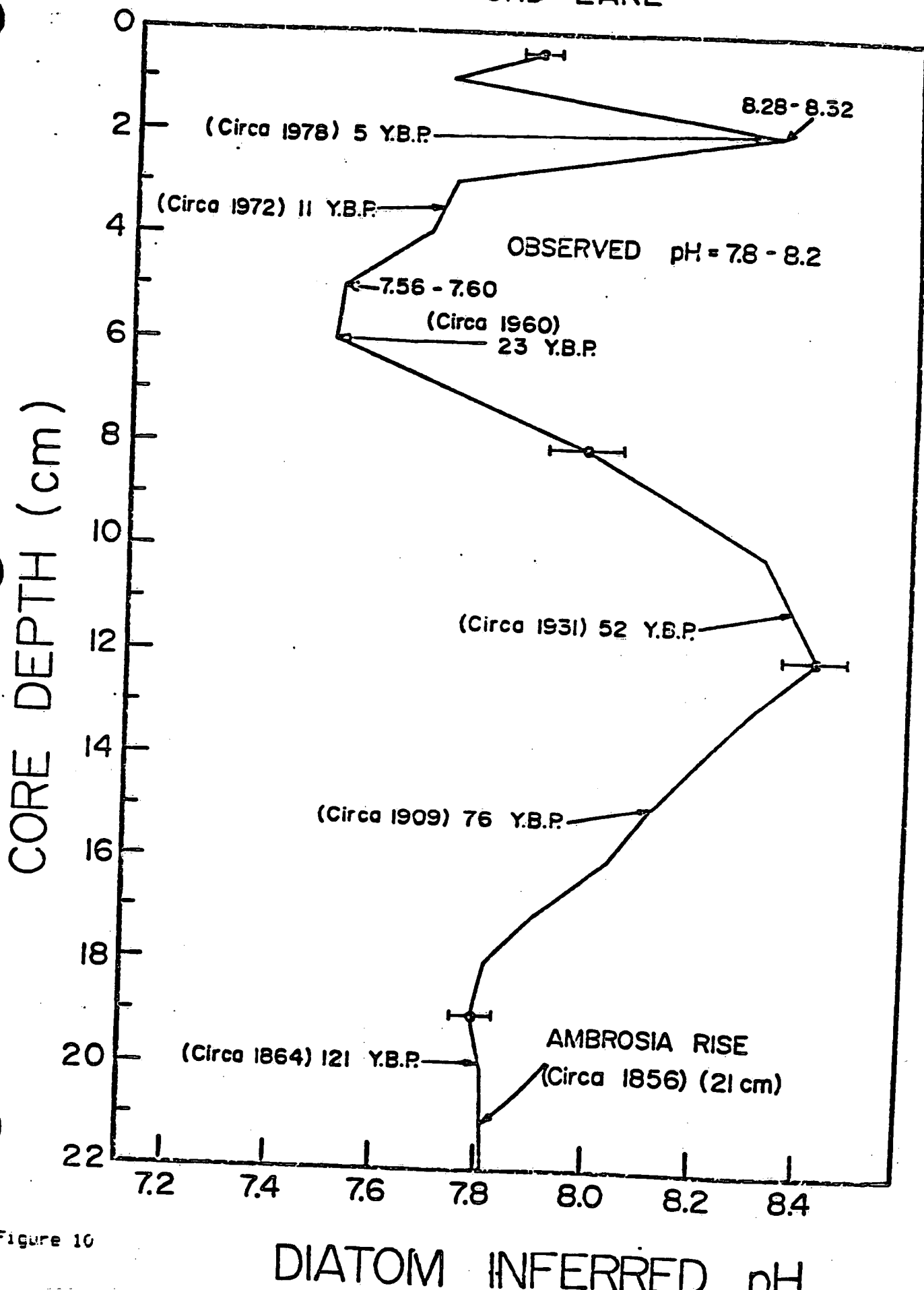


Figure 10

DIATOM INFERRED pH

# CRANFORD LAKE & ANERGOSIA FOLLER

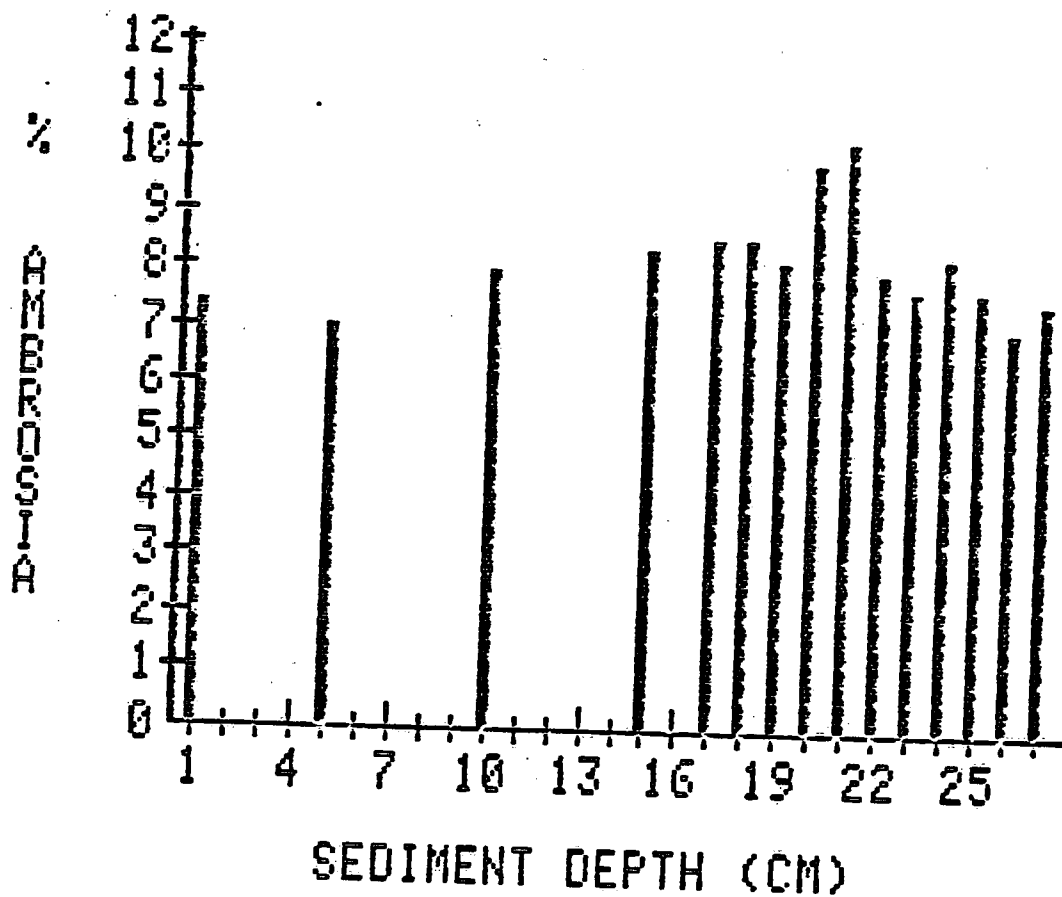


Figure 10B

# BEAVER LAKE

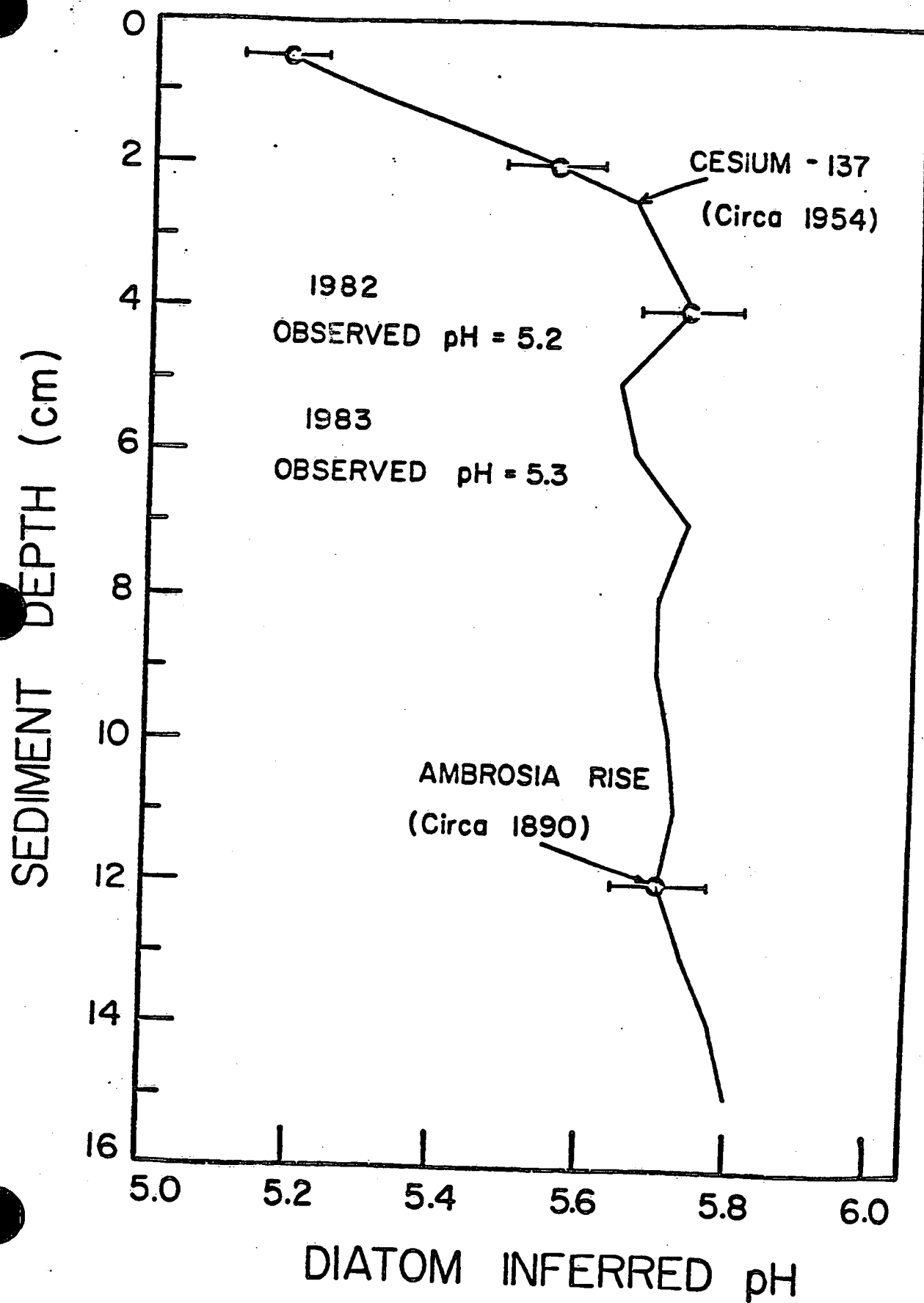


Figure 11

# BEAVER LAKE

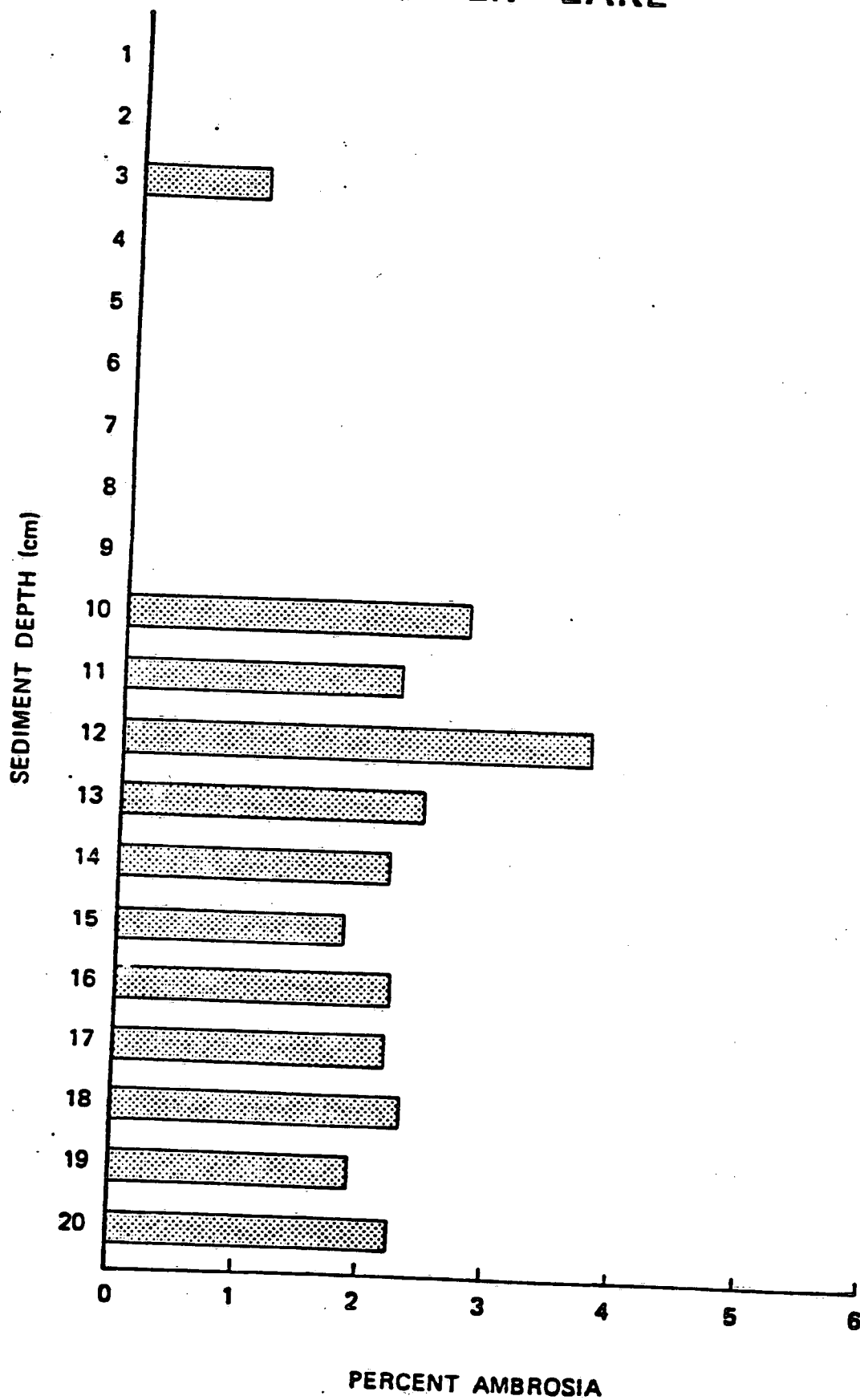


Figure 11E

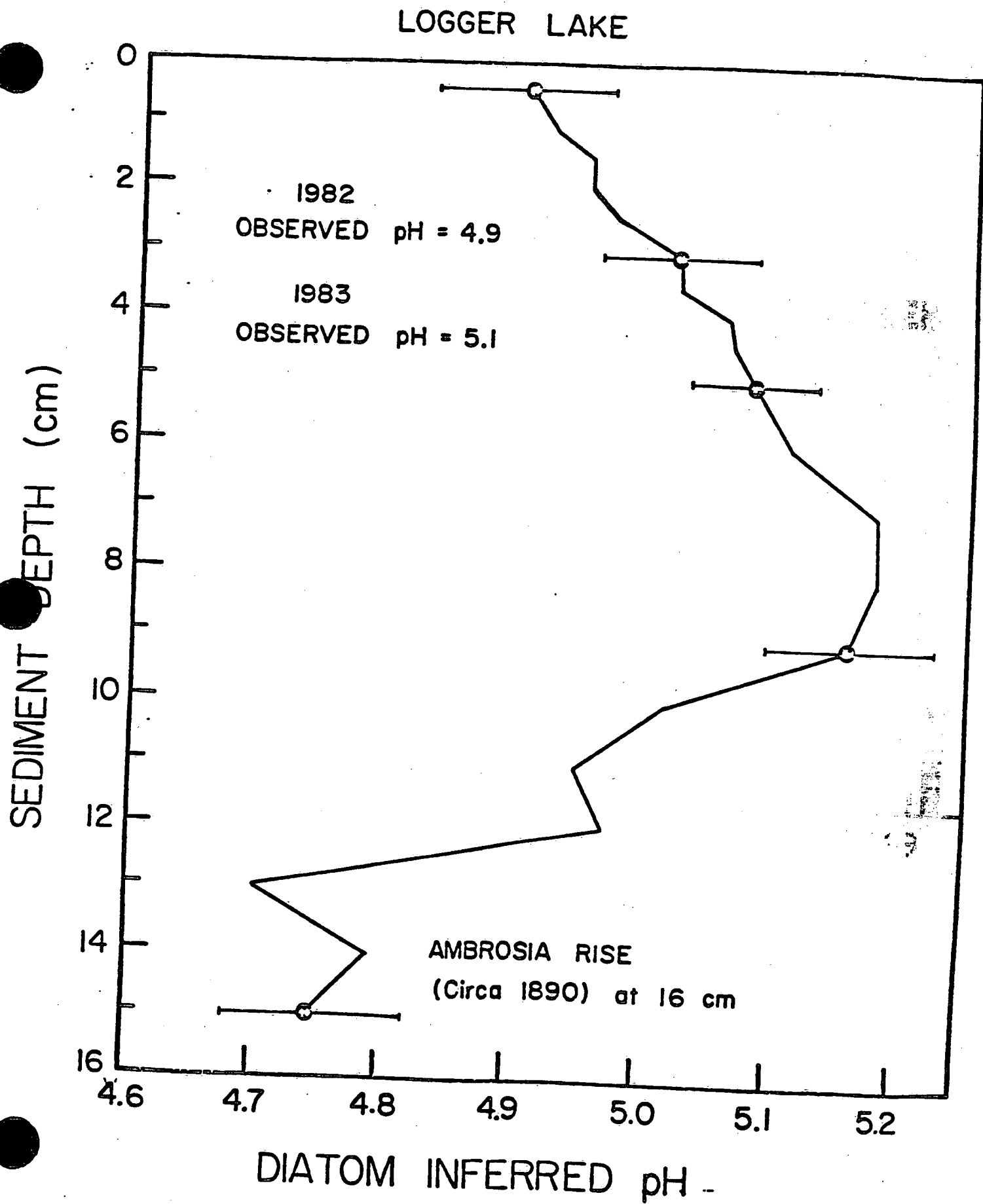


Figure 12



# LOGGER LAKE

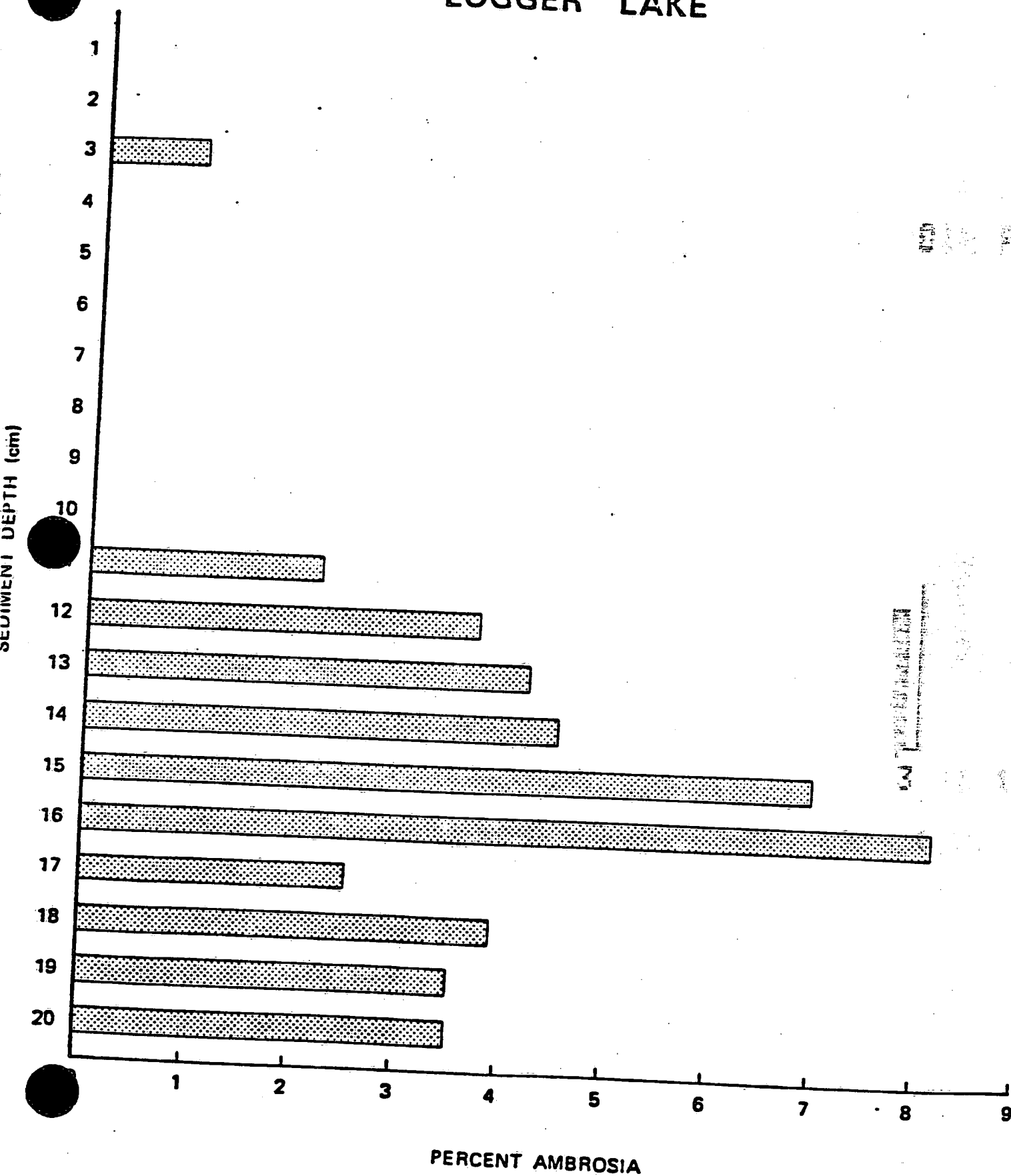


Figure 12b