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MANAGEMENT PERSPECTIVE

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. Sediment microbial communities can alter the state of these isotopes under certain environmental conditions. There is also evidence that lake sediment profile values will reflect environmental changes in the lake drainage basins over the past century. This study compares sediment downcore profiles of sulphur content, sulphur isotope values, diatom inferred pH and microbiological populations from several lakes north of Lake Superior of which two are near and/or 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 sediments (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%). It was evident from the study that the greater the abundance of sulphate reducers the greater is the surface sediment sulphate content and the degree of isotope fractionation in the anaerobic and organic rich sediments. The data from the surface sediments also revealed isotopic evidence of bacterial SO_4 reduction. The results of this study improve our understanding of lake acidification processes and associated microbiological processes. The study provides an insight into a mechanism of recovery of lakes experiencing acid stress.

PERSPECTIVE-GESTION

Le rapport des isotopes du soufre est utilisé de plus en plus pour déterminer les sources de soufre dans les études sur l'environnement. On a montré récemment que le rapport des isotopes du soufre présent dans les sulfates des eaux lacustres dans les régions éloignées reflète celui que l'on retrouve dans les précipitations acides globales au cours d'une année. Les populations microbiennes des sédiments peuvent, dans certaines conditions du milieu, modifier l'état de ces isotopes. Des données montrent également que le profil sédimentaire des lacs reflète les changements intervenus dans le milieu des bassins hydrographiques des lacs au cours du siècle dernier. La présente étude compare les profils de la teneur en soufre, le rapport des isotopes du soufre, le pH par inférence des diatomées et des populations microbiennes dans les sédiments de plusieurs lacs au nord du lac Supérieur dont deux sont situés près ou en aval de l'usine de frittage de Wawa et les autres, plus éloignés et en amont de l'usine. Les résultats indiquent que les valeurs des isotopes du soufre des sédiments les plus profonds (environ 60 ans B.P.) se rapprochent de celles que l'on mesure actuellement pour les sulfates dans les lacs. Toutefois, les valeurs isotopiques des sédiments superficiels ont tendance à être plus faibles (isotopes du soufre plus légers). Pour les lacs éloignés dont les eaux ne se mêlent pas à celles de l'océan, cette tendance est peu prononcée (1-4%) alors que pour les eaux qui se rapprochent de celles de l'océan, la tendance est plus beaucoup plus prononcée (12-14%). L'étude montre clairement que plus les réducteurs des sulfates sont abondants, plus la teneur en sulfates des sédiments superficiels et le degré de fractionnement des isotopes sont élevés dans les sédiments anaérobies et riches en matières organiques. Les données isotopiques des sédiments de surface révèlent également qu'il y a réduction du SO_4 par les bactéries. Les résultats de cette étude nous permettent de mieux comprendre les processus d'acidification des lacs et les processus microbiologiques associés et nous donnent un aperçu d'un mécanisme de récupération des lacs soumis à un stress acide.

ABSTRACT

Sulphur contents and sulphur isotope ratios (δ^{34} $S_0/_{00}$ values) in deep sediments (10-12 cms; circa 50-100 years before the present) and surface sediments (0-2 cm; circa 0-10 years before the present) from eight lakes located north of Lake Superior, Canada indicated that surface sediments had a significantly higher sulphur content (largely organic sulphur) per gram dry weight and a lower sulphur isotope ratio than the deeper layers.

The increased sulphur content and decreased sulphur isotope ratios (δ^{34} $S_0/_{00}$ values) in the surficial sediments were much greater for the lakes near and downwind from the Wawa sintering plant than for more remote lakes reflecting the impact of the sintering plant emissions on the lake environment.

A significant relationship was observed between the sulphate reducing bacterial populations and the magnitude of the isotope shift in the study lakes. It was evident from the data that the greater the abundance of sulphate reducers the greater was the surface sediment sulphate content and the degree of isotope fractionation in the anaerobic and organic rich sediments. The surface sediments of the eight study lakes revealed isotopic evidence of bacterial sulphate reduction. The deeper sediments, however, did not reveal such a condition due to the absence of sulphate reducers.

The rate of lake acidification as inferred from the downcore diatom inferred pH profile for each of the study lakes was not significantly correlated with the amount of sulphur in the lake sediments, nor was it correlated with the density of sulphate reducing bacteria or shifts in the sulphur isotope ratios (δ^{34} S).

RÉSUMÉ

La teneur en soufre et le rapport des isotopes du soufre (valeurs de $S_o/_{oo}\,\delta^{34}$) dans les sédiments profonds (10-12 cm; environ 50 à 100 ans avant l'Actuel) et les sédiments de surface (0-2 cm; environ 0-10 ans avant l'Actuel) provenant de huit lacs situés au nord du lac Supérieur, au Canada, ont indiqué que les sédiments de surface ont une teneur en soufre significativement plus élevée (en grande partie du soufre organique) par gramme de poids sec et un rapport plus faible des isotopes du soufre que les sédiments plus profonds.

L'augmentation de la teneur en soufre et la diminution du rapport des isotopes du soufre (valeurs de $S_o/_{oo}\,\delta^{34}$) dans les sédiments superficiels étaient beaucoup plus prononcées dans les lacs situés à proximité et en aval de l'usine de frittage de Wawa que dans les lacs plus éloignés, à cause de l'impact des émissions de l'usine de frittage sur l'environnement des lacs.

On a observé un rapport significatif entre les populations de bactéries réductrices de sulfates et l'ampleur de la diminution du rapport isotopique dans les lacs à l'étude. Les résultats ont montré clairement que plus les réducteurs des sulfates sont abondants plus la teneur en sulfates des sédiments et le degré de fractionnement des isotopes sont élevés dans les sédiments anaérobies et riches en matières organiques. Les sédiments de surface dans les huit lacs à l'étude ont révélé grâce aux isotopes qu'il y a réduction des sulfates par les bactéries. Toutefois, on n'a pas pu observer ce phénomène dans les sédiments plus profonds; il y a en effet absence de réduction des sulfates dans ces sédiments.

La vitesse d'acidification des lacs, estimée à partir du profil de pH des diatomées au coeur des sédiments pour chacun des lacs à l'étude, n'était pas corrélée de façon significative à la quantité de soufre dans les sédiments lacustres ni à la concentration des bactéries réductrices de sulfates ni à la diminution du rapport des isotopes du soufre ($S\,\delta^{34}$).

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 important that a data base for these lakes be established in order to monitor changes which would be useful for determining criteria for lake management.

The historical water pH data commonly used to evaluate the rate of lake acidification are frequently of dubious quality or are so sparce 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 30 years. To distinguish between such types of lakes, Rao et al. (1984) have indicated that sediment microbial populations and sediment microbial activity can be used to recognize differences between acid stressed and unstressed lakes. However, a number of other researchers have turned to a technique based on sediment diatom stratigrpahic analyses and chemistry stratigraphic studies (Davis & Barg, 1980; Renberg & Hellberg, 1982).

The diatom stratigraphic technique has been shown to be effective in estimating the rate of lake acidification in a number of regions throughout North America and Scandinavia (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 satisfactorily determined. Although these independent studies of acidified lakes have provided much valuable information, no attempt has ever been made to integrate bacterial, diatom sulphur isotope and sediment chemistry stratigraphic studies. We examined the sediments of some lakes in the Algoma district north of Lake Superior. The results of such an integrated study are presented in this article.

MATERIALS AND METHODS

Bacteriological Procedure

Counting of bacteria was performed using epifluorescence microscopy after staining with acridine orange. The staining of filters and solutions used follow Zimmerman *et al*. (1978).

Total bacteria were estimated using UV light. Numbers of bacteria were determined in 20 fields, each field with 25 rectangular occular fields. Generally, this resulted in a total count of 30-300 bacteria.

Sulphur cycle bacteria were estimated on all sediment samples using the five tube MPN procedure (Dutka, 1978). Densities of sulphur oxidizing bacterial (Thiobacillus sp.) populations were measured using the postgate medium. Sulphate 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 Openheiumer was used combined with anaerobic incubation. All MPN tubes were incubated for 21 days at 20°C.

Sediment Diatom Enumeration

An acid digestion technique was used for cleaning the diatoms (Dickman *et al*., 1985). 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.

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 Cholnoky (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).

Age Dating from Pollen Analysis

After cooling, the mixture was centrifuged, decanted and washed with glacial acetic acid which was then decanted. Three CC of wet sediment were treated with HCl, KOH and then acetolysed according to the procedures reported in Dickman et al. (1985). The final mixture was twice washed with distilled water and decanted each time. The resulting sediment was mounted on glass slides. Three hundred pollen grains were counted and the number of Ambrosia pollen grains counted were recorded as a percentage of this total.

Sulphur Content and Isotope Ratio Measurements

Water samples from eight Algoma Lakes were collected and analysed for sulphate content and sulphur isotope ratios. Acid soluble sulphur was extracted from weighed aliquots of crushed and ground dried sediment samples by treatment with dilute HCl. The H_2S released was 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 was determined gravimetrically at the Ag_2S step. The water soluble sulphate sulphur was extracted from the original dried and ground sediment using a Soxhlet extraction technique (Dickman et al., 1985).

Elemental sulphur was extracted in a Soxhlet extraction apparatus. The dried residue in this apparatus was next used for the extraction of pyrite sulphur. A complete separation of pyrite sulphur from carbon bonded sulphur was most difficult (Smith, 1964; Monster, 1978). The pyrite and ester sulphate were extracted together using 6N nitric acid. The residue from the pyrite extraction was dried in a vacuum oven at 65°C. The organically bound sulphur remaining in this residue was extracted as sulphate using the "Eschka" method. Total sulphur was extracted from 1-2 grams of dried, crushed and ground lake sediment using the "Eschka" method as described in Dickman et al. (1985). All forms of sulphur were converted to sulphate by this method. The sulphate produced was determined gravimetrically as $BaSO_4$ and this was ultimately converted to SO_2 for isotopic analysis using a high precision mass spectrophotometer (Thode et al., 1961; Beaver, 1973).

Sulphur isotope ratios were expressed in terms of δ notation

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

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

Dissolved oxygen (% saturation), temperature (degrees C), alkalinity (mg/l as $CaCO_3$), specific conductivity (micromhos/cm), Secchi transparency (m), water colour as platinum-cobalt colour units. pH and sulphate concentration were measured in each of the lakes according to the methods described in Fortescue et al. (1981).

RESULTS AND DISCUSSIONS

General characteristics of the lakes studied are given in Table 1. The study acidified lakes are located between the Montreal River and Wawa in an area northeast of Lake Superior (Fig. 1). Crawford Lake in southern Ontario was chosen as a control lake. The buffering capacity of this carbonate-rich lake (280 mg Ca CO_3/1) was so high that acid rain has not altered its pH.

The pH of these lakes 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, Fig. 2a). In Crawford Lake, the *Ambrosia* pollen was two to three times more abundant than it was in the Algoma area lakes and the sedimentation rates in Crawford Lake were substantially greater than any observed for the Algoma area lakes (i.e. the *Ambrosia* rise Circa 1856 was at 21 cm (Fig. 2A). This was deeper than in any of the Algoma area lakes. The well marked light and dark coloured varves in this lake made it possible to estimate the cores age at six depths by counting its varves under a dissecting microscope. These age estimates were compared with those carried out by Boyko (1978).

Table 2 summarizes bacteriological data from some of the study lakes. The two lakes WW1 and WW2 located closest to the Algoma Sintering Plant had the highest sediment bacterial densities and the highest density of sulphate reducers. 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 a carbonaceous energy source and presumably high sulphate loading (Dutka <u>et</u> <u>al</u>., 1974). Concentrations of carbonaceous energy sources present in the lake sediments are generally adequate to support normal anaerobic or facultative anaerobic microbial populations and their organic degradative processes, however, the local conditions in the lakes near the Algoma scintering plant appear to have suppressed or lowered the active aerobic population levels thereby suppressing the normal aerobic biodegradation processes. Similar circumstances were observed in some other Ontario lakes receiving acid precipitation (Rao <u>et</u> <u>al</u>., 1984). The presence of relatively large populations of sulphate reducers is also indicative of probable anoxia (Dutka <u>et</u> <u>al</u>., 1974), thus reducing aerobic microbial biodegradation processes.

In lakes WW2 and Fenton, 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.

The sediments of WW1 and WW2 lakes also showed greatest upcore increase in total sulphur content and largest upcore decrease in ^{34}S of the lakes studied. These lakes are within 15 km of a major sulphur source (140,000 metric tons/yr of SO_2 is emitted by the Algoma Sintering Plant, Weizman, 1980). The sulphur isotope ratio based on total sulphur analyses (Table 3-6) was also greater in these two lakes than in any of the others.

Beaver Lake was becoming more acid as evidenced by downcore diatom inferred pH. Beaver Lake 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 inferred pH (5.2) indicated that a significant reduction in lake pH (0.16 of a pH unit per decade) had occurred in this lake during the last 30 years. Because of these circumstances, the lakes near the scintering plant showed signs of greater bacterial inhibition and presumably associated biochemical processes.

Crozier Lake (Fig. 1 and 2B) is seasonally stratified and becomes anoxic in its hypolimnion during the summer and fall and as a result anaerobic and/or facultative anaerobic bacteria, sulphate reducers and photosynthetic sulphur oxidizers, can and do operate in the lower water column during these periods and lead to special $\delta^{34}S$ distribution patterns in both the water column and sediments of Crozier Lake. Even though the surface water pH values range from 7.3-7.5 (Fig. 2B), the stable aerobic heterotrophic bacterial populations were relatively small in size due to the impact of hypolimnetic anoxic conditions which commonly occur during the summer and fall.

The top 2 cm of the KB cores from Crozier Lake were dark brown in colour. Diatom inferred pH was 7.3 at the Ambrosia rise (15 cm) and 7.2 at the surface (0.0-0.5 cm, Fig. 2B). In the early 1900's (11-13 cm) the diatom inferred pH of the lake fell to 6.7. The Algoma logging records indicate that the lake was logged during this period in the first half of the century. Logging has been correlated with changes in diatom inferred pH (Dickman and Fortescue, 1984).

Doc Grieg Lake, a 17 m deep lake located in Lake Superior Provincial Park (Fig. 1) in a granite basin upwind of the scintering plant, was thermally stratified in summer. Specific conductivity fell between 25 and 29 micromhos/cm. Lake pH ranged from 4.7 to 5.7. Alkalinity ranged from -0.3 to 3.4 mg $CaCo_3$/L. 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 sediments of the two replicate cores which were taken near the deepest point in Doc Grieg Lake indicating the potential for bioturbation processes.

The diatom inferred pH of the surface sediments of Doc Grieg Lake was 5.7 (Fig. 2C). The observed pH of the lake in the summer of 1983 was 5.6 which was similar to the diatom inferred pH at the bottom (19-20 cm pH 5.5-5.6) of the Doc Grieg lake sediment core (Fig. 2C). Bacterial population in this lake is somewhat similar to that of Crozier Lake, thus implying that hypolimnetic anoxic conditions even though they existed precluded an aerobic biodegradation process similar to WW2 Lake.

precluded essential aerobic biodegradation processes.

Ambrosia pollen increased from an average of 4-5 grains per hundred to 7 grains per hundred at 15 cm. As a result we concluded that the Ambrosia rise, circa 1890, occurred at 15 cm in Doc Grieg Lake (Fig. 2C). The cesium 137 rise occurred at 3.5 cm and just below this depth we recorded the only significant ($p < 0.05$) decrese in diatom inferred pH. The horizontal lines at 3, 4, 9 and 13 cm 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 (Fig. 2C).

The observed pH of the surface waters of Beaver Lake ranged between5.2 and 5.3 during the summers of 1982 and 1983 (Fig. 2D). Diatom inferred pH at 0.5 cm was 5.2 ± 0.1 (n=3). At the depth of the Cesium rise (2.5 cm) the diatom inferred pH was 5.7. Below the depth, diatom inferred pH ranged from a low of 5.6 to a high of 5.8. We concluded that after the Cesium-137 rise (i.e. during the last 30 to 40 years) the lake has acidified going from a mean pH of 5.7 to he present day observed and diatom inferred pH (0.5 cm) of 5.2. This drop in pH was statistically significant ($p < 0.01$, n=3) at four replicate depths 0.5, 2.0, 4.0 and 12.0 cm).

This shift in diatom inferred pH was interpreted as an indication that the buffering capacity of the lake had been overwhelmed by an influx of acid material. A similar conclusion was reached for the nearby Lake B (Fortescue et al., 1984, p. 91.

In Logger Lake (Fig. 1 and 2E) the diatom inferred pH at the bottom of the core (15 cm, Circa 1900) was between 4.7 and 4.8. The diatom inferred pH at the top of the core was 4.9±0.1. Although there was no significant difference between the present day pH and the pH of the lake in the early 1900's, the diatom inferred pH at 7-9 cm (mid 1900's) reached a maximum of 5.2. This shift was ascribed to logging activity in the lake's watershed and its subsequent reforestation.

The diatom inferred pH of Fenton Lake (Fig. 2F) was similar to Crozier (7.2-7.4). However, the hypolimnion of Fenton Lake is well oxygenated. The well oxygenated hypolimnetic waters not only supported significant aerobic bacterial populations, but showed signs of inhibition of anaerobes such as sulphate reducers (Desulfovibrio sp.). This situation may have important implications in the overall limnological features of the lake. Diatom inferred pH varied very little downcore in this well buffered oligo-mesotrophic lake. It ranged from a high of 7.4 to a low of 7.2 (Fig. 4). We concluded that there were no significant downcore changes in diatom inferred pH in this lake. The observed pH of Fenton Lake at the time it was cored in June of 1983 was 7.5.

SUMMARY AND CONCLUSIONS

The following are the major conclusions from the study:

- The Lakes which are located farthest from the sintering plant (Logger, Crozier, Fenton and Doc Greig) had SO_4 concentrations in their surface waters characteristic of the remote lakes described by Nriagu and Cocker (1978B).
- The lakes which are under the direct influence of the sinter plume and receiving the heaviest influx of sulphur (e.g. Beaver Lake and WW1 and WW2) showed the highest densities of sulphate reducing bacteria in their surface sediments. These lakes also

demonstrated the largest upcore shift in sulphur isotope ratios. This was accompanied by a significant increase in the upcore diatom inferred pH.

- The diatom inferred pH downcore profiles for the study lakes can be classified into two basic groups: 1) those in which no significant shift in downcore diatom inferred pH occurrd (e.g. Logger, Fenton and Doc Grieg Lakes) and 2) those with significant ($p < 0.05$) downcore changes in diatom inferred pH (e.g. Crozier, WW1, WW2, Crawford and Beaver Lakes). The surface sediment diatom inferred pH was significantly different from that at the <u>Ambrosia</u> rise for WW1, WW2 and Beaver Lakes. Crozier and Crawford Lakes displayed significant downcore shifts in diatom inferred pH. However, there were no significant differences between the diatom inferred pH at the <u>Ambrosia</u> rise and at the sediment surface (0-1 cm).
- Changes in downcore pH profiles for logger Crozier and Crawford Lakes displayed maxima in diatom inferred pH during the early to mid part of this century. These lakes had anaerobic hypolimnia and therefore they may generate considerable alkalinity from the reduction of sulphate (Cook and Schindler, 1983). In addition, these lakes were considerably altered by man during the last century as a result of logging, the construction of the Trans Canada Highway (Crozier Lake) and by the settlement of the Crawford family in the early 1900's (Crawford Lake).
- The sulphur isotope values for -organic sulphur SO_4 and pyrite in the deeper sediments (10-12 cm) indicated no evidence of

significant bacterial SO_4 reduction, i.e. the shift in the isotope ratio to -ve? $\delta^{34}S$ did not occur or, if it occurred, it was under extremely low SO_4 concentrations (Harrison and Thode, 1958).

- The results also suggest that the average $\delta^{34}S$ levels in the atmospheric precipitation and in the lake SO_4 had not changed significantly in the study area upwind or remote from the smelter over the past 80 years and no sulphur isotope fracitonation occurred during this period due to bacterial reduction of lake sulphate.
- Measurements of deep core samples provide baseline level of $\delta^{34}S$ values for drainage basins before the advent of anthropogenic sulphur inputs.

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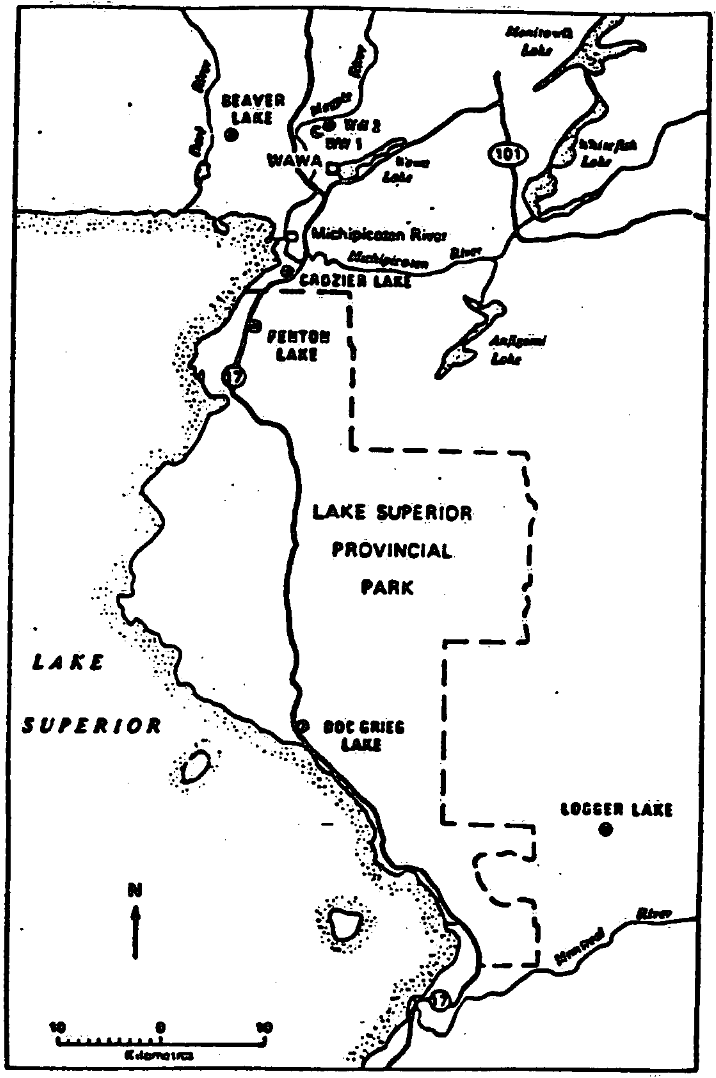

Fig. 1

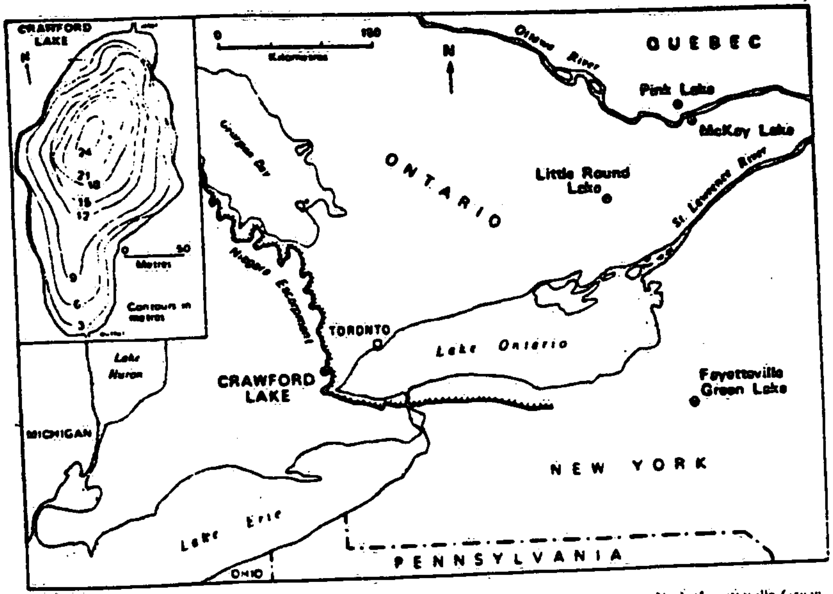

Fig. 1. Five meromictic lakes located between southern Quebec (Pink Lake) and northern New York (Fayetteville Green Lake) with an inset of Crawford Lake's bathymetric profile (after Boyko, 1978). Sediment trap sites were located near [illegible] (station A) and the '2' in 24 (station B)

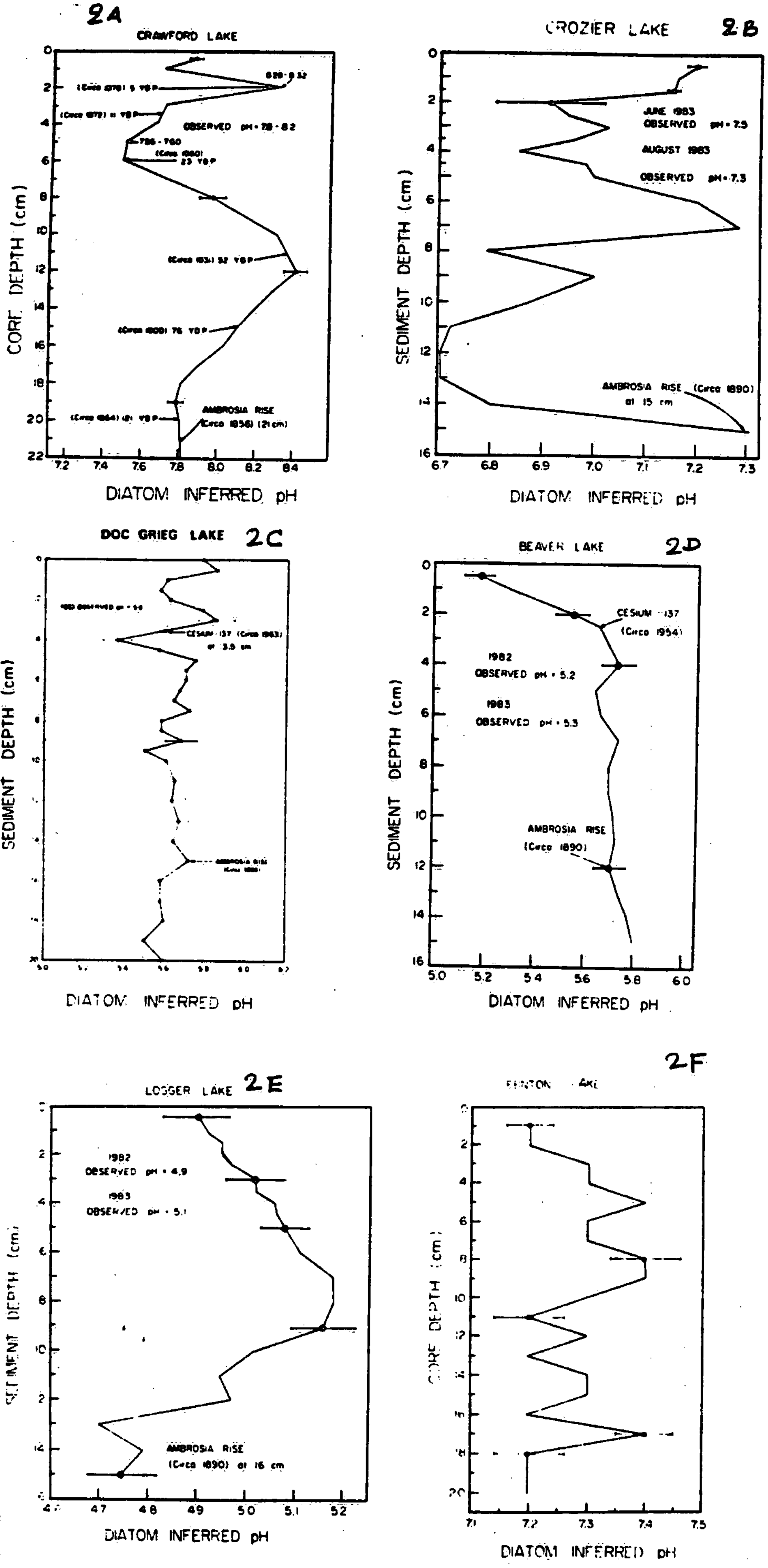

FIG 2: A-F

Fig. 2a → F

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.
Table 2	Bacterial abundance in the sediments and waters of study lakes in Ontario, Canada.
Table 3	Sulphur content and isotope ratios in lake water sulphates (Wawa Smelter Area).
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.

TA[illegible] 1.

Lake Name	Lake Area (Hectares)	Lake pH	Alkalinity (as mg/l Ca CO_3)	Conductivity (micromhos/ cm)	Secchi Transparency (Depth in meters)	Colour	Lake Depth (m)	General Observations
WW1	3.5	5.2 -6.8	14	171 -183	*VOB	Clear 4***		Brown Homogenous Sediment
WW2	1.4	6.7 -6.8	17	162 -189	VOB	Yel-low 1***	2	0-2 cm = red sediments 2-20 cm = black sediments
Fenton	17.5	7.5	45	79	4.4	Green 5	17	<u>Rivularia</u> "Bloom" (Mesotrophic Lake)
Logger	3	4.9 -5.1	12	24	7.6	Clear 1	8	Headwater Lake
Beaver	3	5.2 -5.3	2	23 -26	5.0	Brown 15	3.8	Acidifying over the last 25 years
Doc Grieg	21	5.6	2	24	7.8	Clear	17	Fish mortality by S. err(1982)
Crozier	19	7.5	119	169	7.1	Pale Brown 6	20	Anaerobic below 1cm (Black sediment)
Crawford	3	7.8	280	480	6.2	Green 4	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 WATERS OF STUDY LAKES IN ONTARIO, CANADA

Lake Name	Mean Water Column Total Bacterial Density ($X10^7$/ml)	Lake Sediment Sulphate Reducers** ($X10^3$/ml)	Lake Sediment Sulphur Oxidizers** ($X10^3$/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	0.021
Crozier	1.9	---	---
Doc Greig	1.7	---	---
Beaver	0.7	0.005	0.069

* 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)

Algoma Area

Lake	Depth m.	pH	$SO_4^{=}$ (mg L^{-1})	$\delta^{34}S\,^0/_{00}$	Bed Rock Type
WW1	5(4)	6.8	24.9	5.31	Siderites & greenstones
WW2	2(4)	6.8	28.2	5.54	Siderites & greenstones
Beaver	(3.8)	5.2	3.9	3.87	Granite
Crozier	20	7.0	8.6	6.5-10.4*	Granite bedrock overlain by pockets
Fenton	17	7.5	8.2	4.5	Carbonate-rich overburden
Doc Greig	17	5.6	5.6	3.42	Granite
Logger	(4)	4.9	6.8	3.50	Granite

*Samples taken at mid depth.
Lake - seasonally stratified.

TABLE 4

SULPHUR CONTENT AND ISOTOPE RATIOS IN LAKE SEDIMENT

DRIVE CORES (WAWA SMELTER AREA) UPWIND*

Lakes	Sample No.	Core Depth (cm)	Sulphate		Pyrite+(Org.$SO_4^=$)		Org.-S (Carbon-Bonded)		Total S	
			[S] ppm	$\delta^{34}S^0/_{00}$	[S] ppm	$\delta^{34}S^0/_{00}$	[S] ppm	$\delta^{34}S^0/_{00}$	[S] ppm	$\delta^{34}S^0/_{00}$
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^0), no significant amounts were found.

**Values calculated.

TABLE 5

SULPHUR CONTENT AND ISOTOPE RATIOS IN LAKE SEDIMENT

DRIVE CORES (WAWA SMELTER AREA) DOWNWIND*

Lakes	Sample No.	Core Depth (cm)	Sulphate		Pyrite+(Org.$SO_4^{=}$)		Org.-S (Carbon-Bonded)		Total S	
			[S] ppm	$\delta^{34}S^{0}/_{00}$	[S] ppm	$\delta^{34}S^{0}/_{00}$	[S] ppm	$\delta^{34}S^{0}/_{00}$	[S] ppm	$\delta^{34}S^{0}/_{00}$
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^0), no significant amounts were found.

**Values calculated.

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ISOTOPIC AND DIATOM EVIDENCE OF BACTERIAL SULPHATE REDUCTION IN SEDIMENTS

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