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HAS SILICA INCREASED IN LAKE SUPERIOR WATERS?¹

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With 3 figures in the text

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Lake Superior, the largest ($82,000 \text{ km}^2$ and $12,000 \text{ km}^3$) and deepest (405 m) of the Laurentian Great Lakes, has the longest residence time (138 yr) and has been affected relatively little by anthropogenic activities in the watershed (IJC 1977). In contrast to the other Laurentian Great Lakes, there is no direct evidence for changes in concentration of major ions or nutrients other than a recent $3 \mu\text{g N}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$ increase in nitrate (Weiler 1978, 1981). However, Munawar and Munawar (1978) reported that phytoplankton populations in the western end of the lake showed effects of nutrient enrichment, and Stoermer et al. (1985) concluded from analysis of siliceous microfossils in a core from the eastern part of the lake that Lake Superior had become more eutrophic in the last 80 years.

Stoermer et al. (1985) also showed that biogenic silica (BSi) concentrations increased in their core in a pattern consistent with a theoretical model of phosphorus enrichment in these phosphorus-limited waters. The model predicts that diatom production and diatom sedimentation increases with phosphorus enrichment and that as a result silica (Si) concentrations in the water mass will decrease (Schelske et al. 1983). In contrast to this theory, Si concentration in the water has not decreased but in fact may either have increased slightly in the last 30 years (Weiler 1978) or increased from 2.2 to $2.6 \text{ mg SiO}_2\cdot\text{L}^{-1}$ in the last 15 years (Schelske 1985). An increased rate of diatom and BSi sedimentation, and a concomitant increase in Si concentration, can be explained only by postulating that the lake is not at steady state and that Si inputs to the lake have increased (Schelske 1985).

This paper provides additional evidence that BSi sedimentation and soluble Si concentration have increased in Lake Superior. We also attempt here to assess whether disposal of taconite tailings in Silver Bay or increased

weathering of silicate minerals by acid rain in the drainage basin can account for the increased Si loading that must be invoked if the Si mass balance has changed.

In the following equation

$$\Delta M = (TI + AI + UAS) - (OL + PS) \quad (1)$$

the change in Si mass (ΔM) represents the change in Si concentration over time. Source terms are tributary and atmospheric inputs (TI and AI) and previously unaccounted anthropogenic sources (UAS). Loss terms are outflow loss (OL) and permanent sedimentation (PS). Changes in the mass balance of Si are important to document because, if present, they have resulted from relatively recent (within three decades) perturbations of this large system and thus have important implication for long-range management of the Lake Superior ecosystem. Here we attempt to evaluate this relationship insofar as possible with the limited data presently at hand.

METHODS

Sediment cores were collected with a box corer at four stations in Lake Superior (Fig. 1) as part of the HISED project (J. A. Robbins, Great Lakes Environmental Research Laboratory, NOAA, Ann Arbor, MI, pers. comm.). Core H56A was sectioned at 0.5-cm intervals to 10 cm and 1-cm intervals to 20 cm and the other three cores were sectioned at 2-cm intervals. Longer cores were not available from the box core subsamples. Biogenic (amorphous) silica was measured on dry sediment samples using a Na_2CO_3 extraction at 85°C (Stoermer et al. 1985, Schelske et al. 1983). The method employs a correction for mineral silicates (Krausse et al. 1983).

Silica in filtered water samples and BSi collected on either Millipore or Nuclepore filters was determined using the heteropoly blue method (Krausse et al. 1983). Similar methods were also used for data on Si concentrations obtained from the literature. Water samples for 1983 were collected in deep water off the Keweenaw Peninsula (Robert. Keen, Michigan Technological University, Houghton, MI) and for 1986 were collected 6.8 km from Rock Harbor lighthouse, Isle Royale, to depths of 60 m in approximately 130 m of water (Janis Meldrum, National Park Service, Houghton, MI) (Fig. 1).

All data for Si and BSi in water and sediment samples are reported in units of SiO_2 . Samples analyzed in our laboratory were calibrated with a Si standard (16.64 mM - 0.2%), J. T. Baker Chemical Co.

RESULTS

Data for three sediment cores in addition to core H56A that was studied by Stoermer et al. (1985) were used to determine if BSi concentration increased recently in cores from other areas of the lake (Fig. 2). Only one core (LS-KB-83) does not fit the theoretical pattern that would be expected in response to phosphorus enrichment (Schelske et al. 1983). The other three cores show the increase in BSi in the upper 5-10 cm of sediments that would be expected from recent phosphorus enrichment of the water mass. Available data thus support the conclusion that permanent sedimentation of BSi has increased in Lake Superior.

A plot of Si concentrations in water shows an increase in concentration for seasonal data collected from 1973 and 1986 (Fig. 3a). How much concentrations have increased depends on the interpretation of the data collected in the early 1970s. The CCIW data for 1968-73 which originally had

been reported as values of approximately $2.2 \text{ mg}\cdot\text{L}^{-1}$ were systematically increased by $0.15 \text{ mg}\cdot\text{L}^{-1}$ to correct for a presumed error that resulted from storage of intermediate analytical standards in glass containers (see Weiler 1978). However, data collected by GLRD in 1969, 1970, and 1971 (Schelske and Roth 1973) also indicated that Si concentrations were approximately $2.2 \text{ mg}\cdot\text{L}^{-1}$ or not as large as the corrected CCIW value of $2.4 \text{ mg}\cdot\text{L}^{-1}$. The highest mean for 1970 for samples collected in the cold water mass (4°C or less) at deep stations between Michipicoten Island and the Keweenaw Peninsula (Schelske and Roth 1973) was $2.32 \pm 0.04 \text{ mg}\cdot\text{L}^{-1}$. This mean, even though data were collected in July, should reflect high values for the seasonal cycle and thus indicates that the Si concentration in 1970 may have been $0.30 \text{ mg}\cdot\text{L}^{-1}$ less than in the same area of the lake where data were collected in 1983 and 1986. Available data thus support the conclusion that an increase in Si concentration of at least $0.20 \text{ mg}\cdot\text{L}^{-1}$ and possibly $0.30 \text{ mg}\cdot\text{L}^{-1}$ occurred between the early 1970s and 1986 in Lake Superior.

Biogenic silica in water was measured to determine whether standing crops of diatoms could account for the increase in Si concentrations in water samples. Concentrations of BSi measured in our laboratory ranged from a mean of $0.014 \text{ mg}\cdot\text{L}^{-1}$ in February 1980 to $0.24 \text{ mg}\cdot\text{L}^{-1}$ in August 1986. Except for August, concentrations were $<0.1 \text{ mg}\cdot\text{L}^{-1}$, or much smaller than the postulated increase of 0.2 to $0.3 \text{ mg}\cdot\text{L}^{-1}$. A seasonal change in BSi concentrations would be expected to reflect seasonal changes in standing crops of diatoms. However, these seasonal data, in particular low values that occur before the lake is stratified thermally, indicate that changes in diatom standing crop would not account for the observed increase in Si concentration.

DISCUSSION

We conclude that increases in Si loading and Si concentration have occurred in Lake Superior. Available data can not be used for a precise estimate of the absolute magnitude of either change on the mass balance of Si. The problem is complicated because we also conclude that the sediment loss of BSi has increased. Therefore, in the mass balance the increase in loading has been greater than that indicated by the increase in Si concentration, i.e. the loading increase must be equal to the sum of the increases in Si concentration and permanent sedimentation of BSi (see Eq. 1).

Whether an increase in Si concentration had occurred after 1969 was considered in mass balance calculations of Si in Lake Superior (Schelske 1985). Although the data base is limited, it appears that an increase in Si concentration has occurred since 1969 (Fig. 3). The magnitude of this change must be established from more extensive spatial sampling and probably from volume-weighted averages of data. In addition, it is obvious that data must be collected over periods of years and possibly decades and that the accuracy of values obtained must be verified at the time of collection if small changes in concentration are to be determined.

Data from only three of four cores support our hypothesis that sedimentation of BSi has increased because of increased diatom production resulting from phosphorus enrichment. It is not unusual that all cores do not show the expected theoretical pattern because we have obtained similar results from an analysis of more than 50 cores from Lake Michigan (Schelske et al. 1986, unpublished data). Independent evidence for our nutrient enrichment hypothesis was obtained from the diatom stratigraphy of core H56A (Stoermer et al. 1985). Similar changes in BSi concentration and diatom populations also

have been found in Lake Huron which has undergone slightly more phosphorus enrichment (unpublished data). We, therefore, believe that this evidence for an increase in permanent sedimentation is conclusive and that it demonstrates the sensitivity of the paleolimnological approach in determining effects of nutrient enrichment in this pristine lake.

To account for the observed increases in Si concentration in water and BSi in sediments requires an increase in external loads of Si. We believe that the two most likely sources are increased rates of mineralization of silicate minerals as the result of recent increases in acidity of precipitation and the disposal of taconite tailings by Reserve Mining Co. at Silver Bay, Minnesota.

That acidic precipitation could increase chemical weathering of Si, calcium, magnesium, and bicarbonate in the Lake Superior basin has been suggested by Thompson (1978). She concluded that the natural carbonic acid weathering cycle has been accelerated by acid precipitation and that 10 to 20 years would be required before the resulting increases in loading would be analytically measurable in the lake. Her analysis indicates that silicate weathering has been increased 30% by acid precipitation. Although the effect of acid precipitation on silicate weathering has been considered theoretically (Johnson 1984), the resulting increase in Si loading apparently has not been measured in most studies on effects of acid precipitation.

Disposal of taconite tailings could affect loadings either directly by the introduction of soluble Si with the tailings slurry at the time of disposal or by subsequent leaching of tailings in the lake. Disposal totaled more than 400 million metric tons (Lind and Glass 1980). If 0.1% of the tailings were immediately soluble Si, 400 thousand metric tons of soluble Si would

have been added to the lake which in itself is equivalent to an increase in Si concentration of $0.033 \text{ mg} \cdot \text{L}^{-1}$ if none was lost via sedimentation or outflow. A soluble Si loading of 8,800 metric tons per year was reported by IJC (1977). Because dumping occurred mainly after 1965 (Lind and Glass 1980), actual in-lake changes in concentration would not have been affected measurably by outflow from this lake with a 138-yr residence time.

Leaching of Si from the tailings deposited on the bottom also must increase loading to the lake. That such an increase must occur is obvious from pore water data presented by Nriagu (1978). His results show a very high pore water concentration of Si ($44 \text{ mg} \cdot \text{L}^{-1}$ in the 0-2-cm interval) of a core in the tailings disposal area. Predicted fluxes using Fick's first law of diffusion and Nriagu's data indicate that Si flux from this core was as much as $500 \text{ g} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$ or as much as a 100-fold greater flux than the average predicted from other cores (Johnson and Eisenreich 1979). If this Si flux occurred over the 130 km^2 area of obvious taconite tailings at least 0.25 cm deep (We did not attempt to measure enhanced fluxes from the area of measurable tailing deposits which were found over an area of at least $3,000 \text{ km}^2$, IJC 1977.), it would represent an annual loading of 65,000 metric tons per year, a nearly 150% increase in present estimated external loadings of 45,000 metric tons, or an $0.0054 \text{ mg} \cdot \text{L}^{-1} \cdot \text{yr}^{-1}$ increase in Si concentration if none is lost to permanent sedimentation.

Estimates of increased direct Si loading and increased Si flux from taconite tailings may not be conservative. However, combined estimates for all previously unaccounted sources in loading could account for a $0.30 \text{ mg} \cdot \text{L}^{-1}$ increase in Si concentration over a 20-year period as shown.

	<u>Million Metric Tons</u>	<u>mg.L⁻¹</u>
Acid precipitation	2.8	0.23
Taconite tailings		
Direct dumping	0.40	0.033
Sediment leaching	1.3	0.11

By contrast, the present loss resulting from permanent sedimentation over 20 years is estimated to be 2.4 million metric tons provided 5% of the annual diatom production is sedimented. This estimate could vary by factors of two or more depending on assumptions used (Schelske 1985), but it indicates permanent sedimentation may be comparable in magnitude to previously unaccounted sources.

In conclusion, the available limited data base does support the conclusion that Si concentration in Lake Superior has increased in the last 15 years. Detection of this change is complicated because it is in the order of 0.01 to 0.02 mg·L⁻¹·yr⁻¹, so small that routine surveys must be conducted over one or two decades to measure changes. Estimating changes in permanent sedimentation would require analysis of a large number of dated sediment cores and is complicated because of the complexity of depositional areas in the lake (Schelske 1985). However, data presented here indicate that permanent sedimentation of BSi may have increased two- or three-fold in recent sediments. If permanent sedimentation of BSi also has increased, previously unaccounted loadings of Si to the lake must have increased in an amount equal to increased permanent sedimentation and increased mass in the water column.

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LIST OF FIGURE LEGENDS

Fig. 1. Map of Lake Superior showing sampling stations and complex pattern of depositional basins.

Fig. 2. Profiles of biogenic silica concentration in sediment cores from Lake Superior.

Fig. 3. Plots of historical data on soluble silica concentration ($\text{mg SiO}_2 \cdot \text{L}^{-1}$) in Lake Superior waters with mean $\pm$ one standard deviation if data were available. A. Comparison of seasonal data collected in 1973 from Zone 13 (IJC 1977, also Weiler 1978) with data collected in 1986. Open symbols designate epilimnetic data and solid symbols designate deep water or hypolimnetic data. Comparisons between years are complicated because samples for 1986 were not collected below 60 m. Therefore, because of seasonal depletion, the most valid comparisons are for the months of May and June. B. Lake-wide annual or cruise mean concentrations.

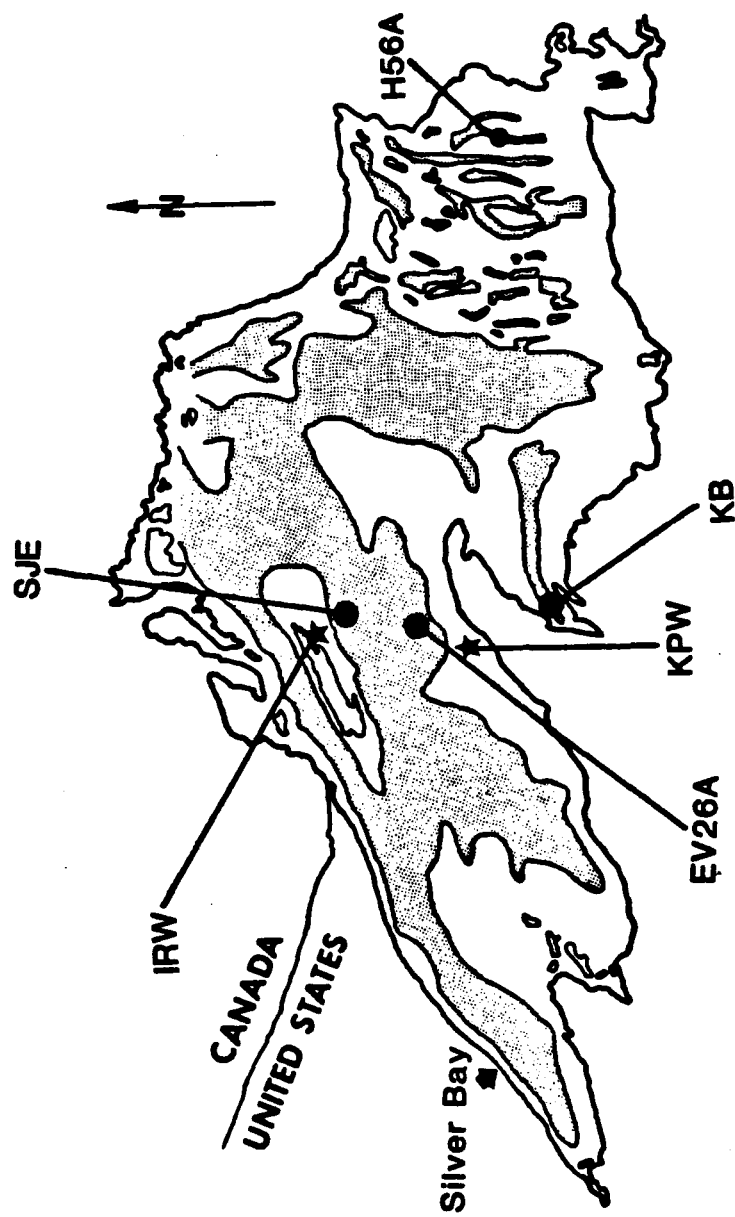


Fig 1

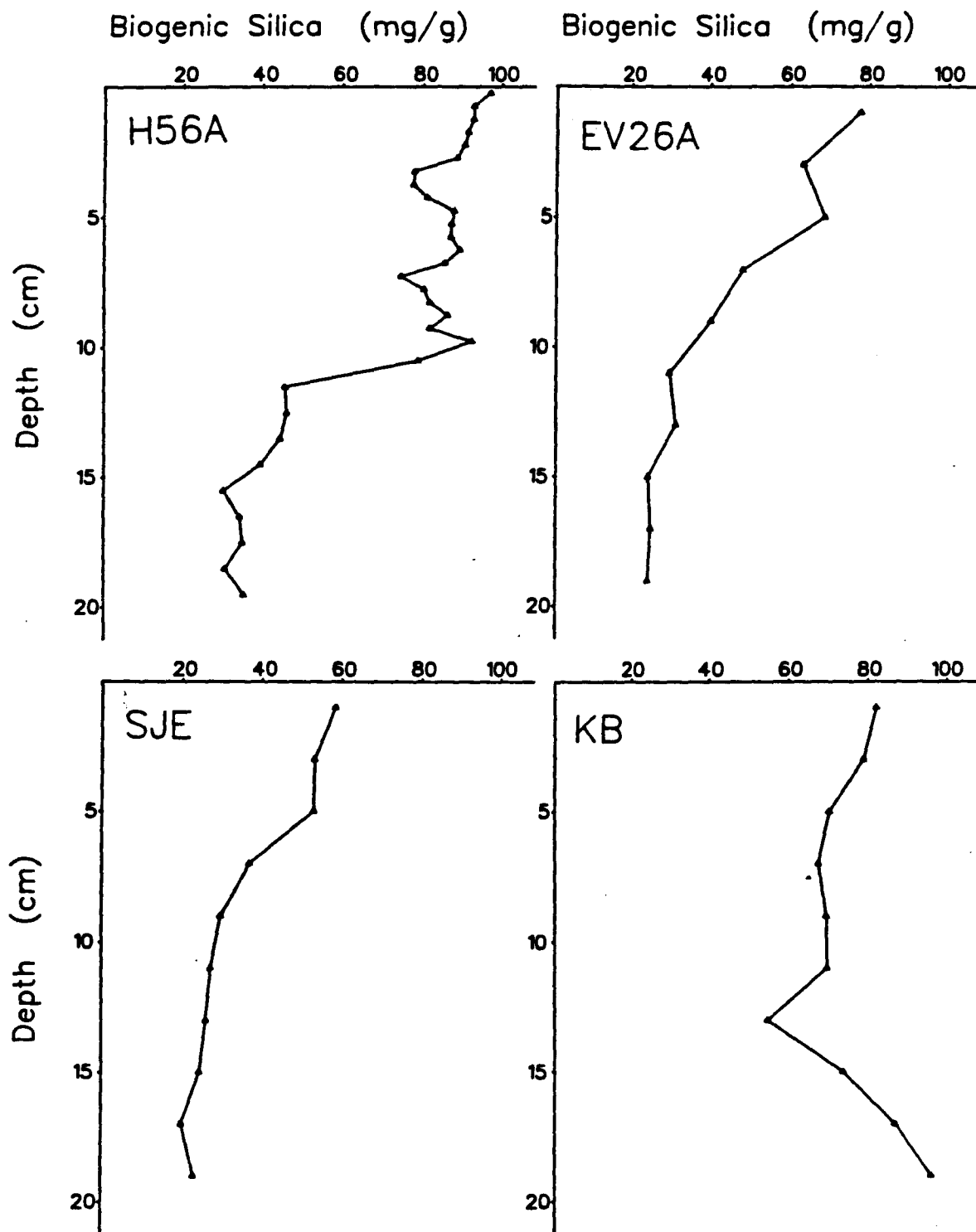


Fig. 2

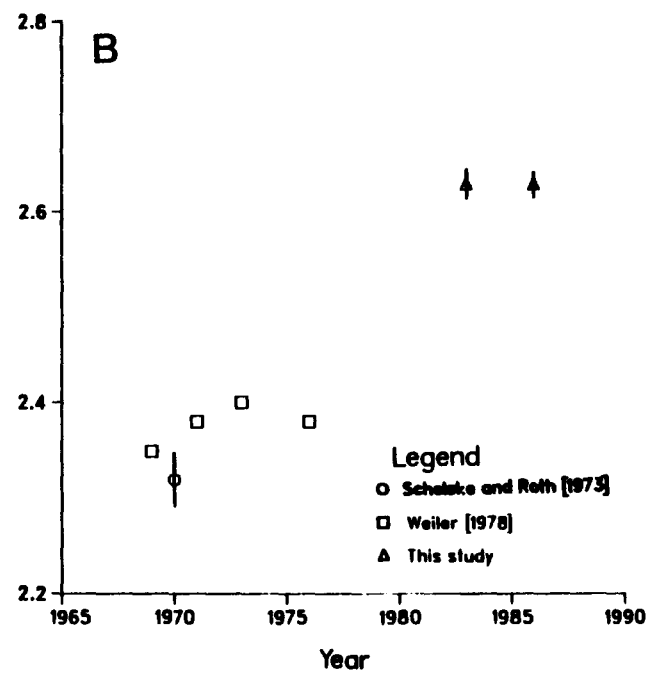
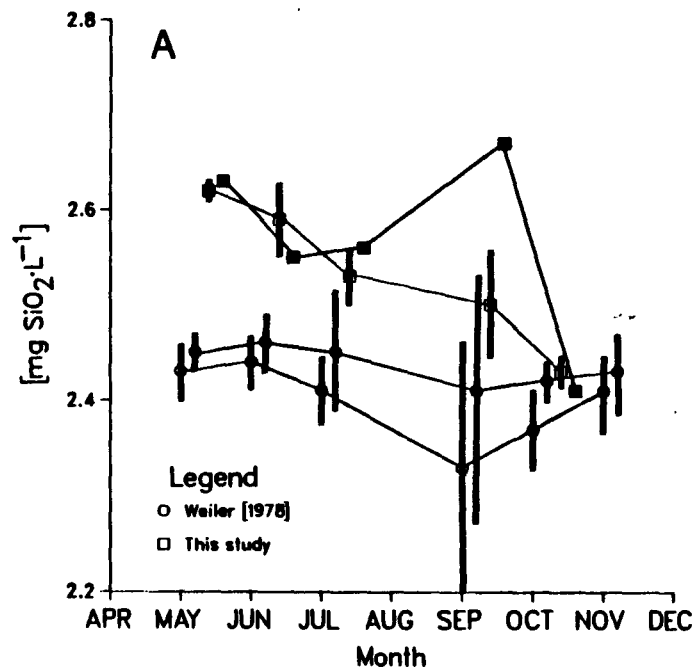


Fig 3

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March 20, 1987

Ms. Janis Meldrum
Apostle Isle National Lakeshore
Route 1 Box 4
Bayfield, WI 54814

Dear Janis:

Thank you for sending the information about the sampling program in the Apostle Islands this summer. I will check around here to find out if a student might be interested in this study to the extent of analyzing the samples and preparing some kind of a report on them. If there is some interest of this type, I think it would be a good project.

The paper that was presented in New Zealand at the SIL meetings is enclosed. It will be published in the proceedings of the meeting (Verh. Internat. Verein. Limnol. 23), probably early in 1988. I will keep you informed about its status. In addition, we are very grateful to you for providing the water samples (as acknowledged in the paper). All of the data could not be published in the Proceedings because there was a page limit with a penalty of \$100 per page for extra pages.

Sincerely,

Claire L. Schelske

Claire L. Schelske
Research Limnologist

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