SIZE STRUCTURE OF PARTICULATE BIOGENIC SILICA IN LAKE MICHIGAN[1]

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ABSTRACT. Recent data suggest that chemical estimates of biogenic silica in the Laurentian Great Lakes include large fractions of non-living fragmented diatoms. Therefore, measurements of particulate biogenic silica (BSi) in different size classes (0.2-0.4 μm, 0.4-10 μm, 10-20 μm, and >20 μm) were made from April through July 1987 in southeastern Lake Michigan to assess the importance of diatom fragments to chemical estimates of BSi. During the spring diatom bloom, the period of maximum BSi concentrations, the greatest percentage of BSi (86%) was found in the microplankton size fraction (>10 μm) associated with living diatoms. By contrast, following thermal stratification, when dissolved silica was depleted from epilimnetic waters, particles <10 μm in size dominated and averaged 52% of total BSi. This fraction contained mostly fragmented diatom frustules. Our estimate of non-living diatoms is consistent with previous studies showing that, following the spring diatom bloom, 40% to 60% of total diatom abundance is non-living. Seasonal decreases in epilimnetic BSi, declining from 11.3 μmol L^{-1} in late April to an average of 1.96 μmol L^{-1} during the stratified period, were due primarily to loss of the largest size fraction (>20 μm) which decreased from 76% of total BSi in April to 36% in July. BSi <10 μm varied by less than a factor of two throughout the study period, averaging 3.23 ± 2.79 μmol L^{-1}. Particles 0.2-0.4 μm averaged 0.277 ± 0.178 μmol L^{-1}. These particles are probably produced through frustule dissolution, settle slowly, and may lead to enhanced BSi recycling rates.
INDEX WORDS: Silica, diatoms, particle size, Lake Michigan.

INTRODUCTION

The annual cycle of dissolved silica (DSi) in Lake Michigan has been described in detail in several studies (Rousar 1973, Conway *et al.* 1977) and the historical data have been summarized by Schelske (1988). However, few studies have elucidated the dynamics of biogenic silica (BSi), i.e., that particulate silica attributed to diatoms (Conway *et al.* 1977, Glover 1982, Conley 1983, Schelske *et al.* 1983, Laird *et al.* 1988). Recent data suggest that chemical estimates of BSi measured in the Great Lakes may include a large fraction of non-living

fragmented diatoms. A previous analysis of water column phytoplankton populations in Grand Traverse Bay, Lake Michigan, (Glover 1982) indicated that fragmented and whole dead diatom cells accounted for as much as 40% to 60% of total diatom abundance. Similarly, Laird *et al.* (1988) calculated the non-living portion of BSi settling from the epilimnion during the early portion of summer stratification to be ca. 43% of the diatom silica estimated from sedimentation traps. Numerous siliceous fragmented particles also have been reported in the nepheloid layer of Lake Ontario (Sandilands and Mudroch 1983).

However, there is no information available regarding the size structure of BSi in waters of the Great Lakes. The importance of particles in mediating the removal of contaminants from the water column is well established (e.g., Eadie and Robbins 1987). In addition, the size structure of the particle pool influences both settling rates (Bien-

fang 1985) and regeneration rates of biogenic silica (Hurd and Birdwhistell 1983). We report here size-fractionated measurements of BSi from southeastern Lake Michigan in order to assess the importance of diatom fragments to chemical estimates of BSi and their implications for the biogeochemical cycling of silica.

METHODS

Water samples were collected in 5-L opaque Niskin bottles aboard the R/V *Shenehon* between April and July 1987 at a 100-m station, 26 km west of Grand Haven, Michigan (43° 1' 11" N × 86° 36' 48" W). Samples were taken from the surface layer only during the winter mixed period and at three depths after thermal stratification.

Biogenic silica (BSi) was determined on four size classes of particles: 0.2–0.4 μm, 0.4–10 μm, 10–20 μm, and >20 μm. Analysis of BSi was done in triplicate on material retained on 10 μm and 0.4 μm Nuclepore polycarbonate filters, on material retained on 0.2 μm Nuclepore polycarbonate filters after filtration through the 0.4 μm filters, and on material retained by a 20 μm Nitex net. Total BSi was calculated by summing BSi concentrations from the 0.2–0.4 μm and >0.4 μm size fractions. In all filtrations 250 mL of lake water and 47 mm diameter filters were used. The >20 μm and >10 μm fractions were completed under gravity filtration, and the >0.4 μm and the 0.2–0.4 μm fractions were filtered at vacuum pressures less than 200 mm Hg. A wet alkaline extraction (0.1 N NaOH) was used to extract BSi from the particulate matter. This was followed by analysis of the extract for dissolved silica (DSi) on a Technicon AutoAnalyzer II (Krausse *et al.* 1983). DSi also was determined on the 0.4 μm Nuclepore filtrate.

Samples from the different size fractions were preserved with acid Lugol's solution, filtered, and permanent slides prepared in Permount. Slides were examined at 1250X with a Leitz Ortholux microscope.

BSi and DSi depletion rates were calculated from linear regression analysis of surface mixed layer concentrations on time. Regression analysis was completed using PROC GLM with PC SAS on untransformed data.

Although numerous classification schemes and terminologies have been used to categorize phytoplankton cell sizes (Sieburth *et al.* 1978, Malone 1980, Sicko-Goad and Stoermer 1984), for purposes of this discussion we will classify BSi >10

μm as being derived from microplankton (Sicko-Goad and Stoermer 1984). Size fractionation techniques provide a rapid way of partitioning suspended matter into various size categories (Runge and Ohman 1982). However, it is recognized that such fractionation schemes are imprecise and rely on the ability of filters to retain particles within the respective size classes. Nuclepore polycarbonate filters similar to those used in this study retain on average 94% of the material filtered (Stockner *et al.* 1990).

RESULTS

From April through early May, the lake was isothermal with temperatures ca. 3–4°C. Weak thermal stratification began by the mid-May sampling (Fig. 1); surface temperatures increased thereafter. Vertical DSi profiles (Fig. 2a) and BSi profiles (Fig. 2b) followed typical seasonal trends (Conway *et al.* 1977) with concentrations decreasing in the epilimnion throughout the stratified period and concentrations generally increasing deeper in the water column.

Biological utilization of DSi, with its conversion into BSi, was well underway by the time sampling was begun in early April 1987 (Fig. 3). DSi concentrations decreased in surface waters both before thermal stratification (7 April to 15 May 1987) and after the onset of permanent stratification (28 May to 21 July 1987), at a rate of 0.249 μmol L^{-1} d^{-1} (S.E. = 0.0267, r^2 = 0.98, p < 0.02) and 0.0242 μmol L^{-1} d^{-1} (S.E. = 0.00453, r^2 = 0.91, p < 0.02), respectively. BSi loss rates from surface waters before thermal stratification (excluding the first sampling) were 0.259 μmol L^{-1} d^{-1} (S.E. = 0.0744, r^2 = 0.92, N.S. at p < 0.05) and 0.0470 μmol L^{-1} d^{-1} (S.E. = 0.0086, r^2 = 0.91, p < 0.02) after stratification. Total silica depletion (TSi = DSi + BSi) rates before and after the onset of stratification were 0.303 μmol L^{-1} d^{-1} (S.E. = 0.0809, r^2 = 0.88, p < 0.02) and 0.0714 μmol L^{-1} d^{-1} (S.E. = 0.00763, r^2 = 0.97, p < 0.02), respectively.

During the spring diatom bloom, the period of maximum surface BSi concentrations, highest BSi concentrations were in the larger size fractions (Fig. 4). The percentage of total BSi in the >20 μm size fraction dramatically decreased throughout the sampling period from 76% in April to 36% of total BSi in late July (Fig. 5). The percentage of BSi in the microplankton (>10 μm) size fraction averaged 86% of total BSi prior to thermal stratification and decreased to 52% of total BSi during
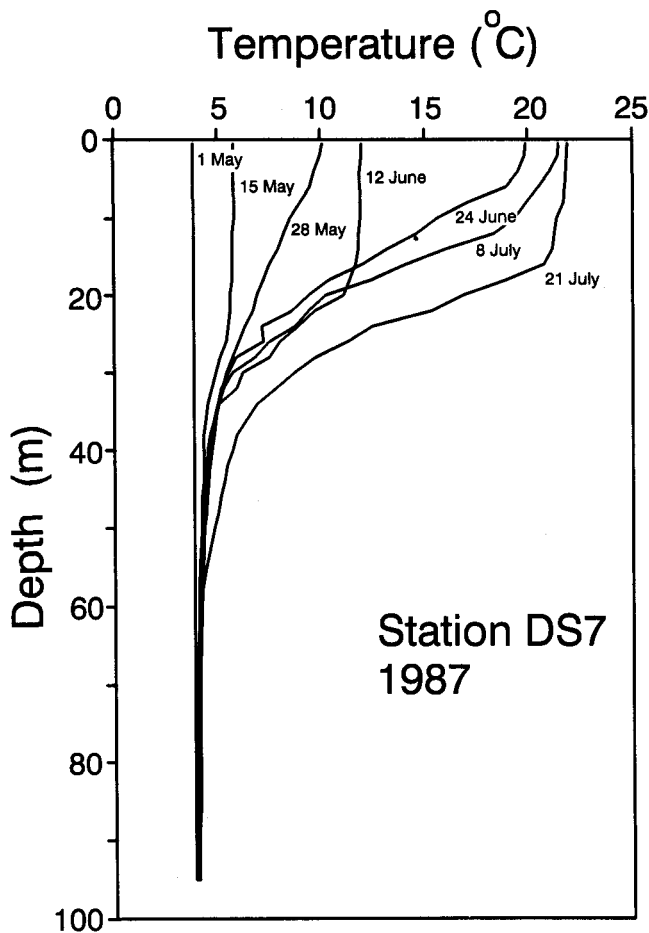
Temperature (°C)

FIG. 1.   *Vertical profiles of temperature from 1 May 1987 to 28 July 1987. Temperature profiles for 7 April 1987, 23 April 1987 and 1 May 1987 all show an isothermal water column with temperature ranging from 3.2-4.1°C.*

summer stratification. BSi concentrations in the < 10 μm size fraction varied by less than a factor of two throughout the study period, averaging 3.23 ± 2.79 μmol L^{-1} (N = 9) for all samples and 4.05 ± 3.91 μmol L^{-1} (N = 9) for summer epilimnetic samples only. BSi in the 0.2-0.4 μm size fraction in surface waters increased gradually throughout at a rate of 0.0053 μmol L^{-1} d^{-1} (S.E. = 0.0015, r^2 = 0.66, p < 0.02), averaging 0.309 ± 0.224 μmol L^{-1} (N = 9) for epilimnetic samples and 0.277 ± 0.178 μmol L^{-1} (N = 19) for all samples. The percentage of BSi in the smallest size fraction also gradually increased over time (Fig. 5). However, because mean epilimnetic BSi concentrations were very low during the summer stratified period (1.96 μmol

L^{-1}), the 0.2-0.4 μm size fraction averaged 24% of total BSi.

Numerous unidentifiable small particles, similar to those pictured in Sandilands and Mudroch (1983) were observed under microscopic examination of the 0.2-0.4 μm size fraction. The <10 μm size fraction contained mostly fragmented diatoms, although a few small viable diatoms were observed. During the period of spring isothermal mixing (April and early May) the >20 μm size fraction contained typical spring bloom diatoms (Fahnenstiel and Scavia 1987; G. L. Fahnenstiel, Great Lakes Environmental Research Laboratory, National Oceanic and Atmospheric Administration, Ann Arbor, MI; personal communication).

DISCUSSION

Different size classes of biogenic silica (BSi) exhibited varying patterns of abundance throughout the study period. Decreases in epilimnetic BSi were due primarily to loss of microplankton diatoms, represented by the >10 μm size fraction (Fig. 4). The transition from the winter-spring diatom bloom in Lake Michigan to the summer stratified period is dominated by losses of intact and viable diatoms through settling (Scavia and Fahnenstiel 1987) and larger particles (>20 μm) often account for most of the settling losses from the water column (Bienfang 1985). By the end of the July sampling, significant losses of suspended BSi were observed from all size classes in epilimnetic waters and may be due to grazing (Scavia and Fahnenstiel 1987).

During the spring diatom bloom the greatest percentage of BSi was found in the microplankton size fraction (>10 μm). By contrast, only after thermal stratification, when DSi concentrations were depleted from surface waters and were at their annual minimum (Fig. 3; Schelske 1988), did the particles <10 μm constitute a significant fraction of total BSi (52% of total BSi in epilimnetic waters). Our estimate is consistent with previous studies showing that during the peak of diatom blooms up to 20% of BSi can be in the form of non-living material (Paasche and Østergren 1980) and that 40% to 60% of total diatom abundance in Lake Michigan during the summer stratified period is in diatom debris (Glover 1982, Laird et al. 1988).

The rate of DSi utilization and BSi loss from surface waters were similar to those previously obtained in southeastern Lake Michigan during
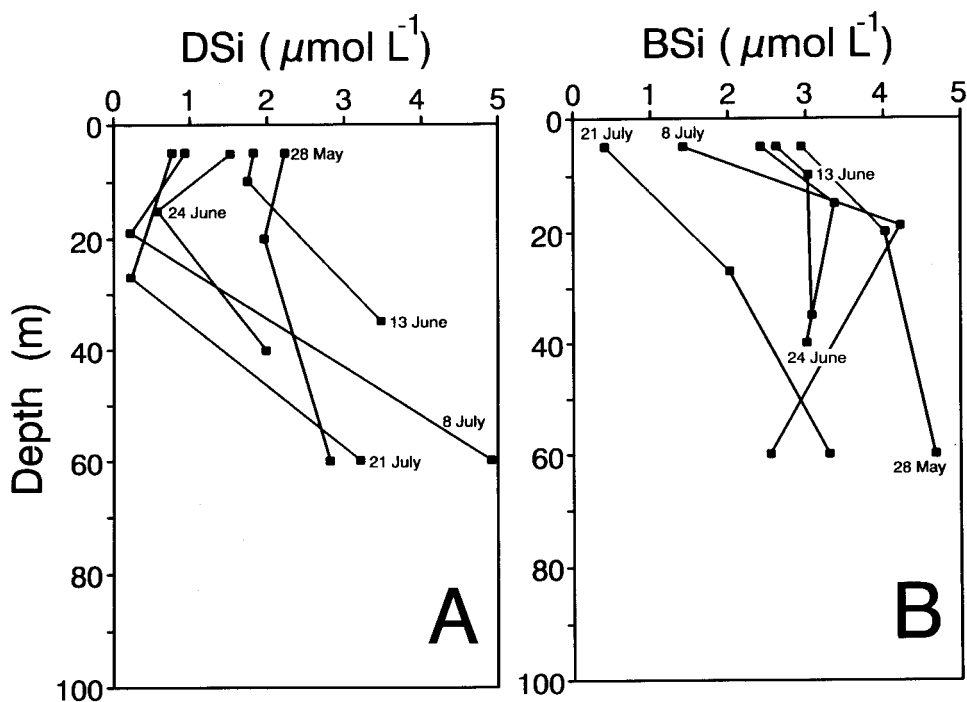
DSi (μmol L^{-1})

BSi (μmol L^{-1})

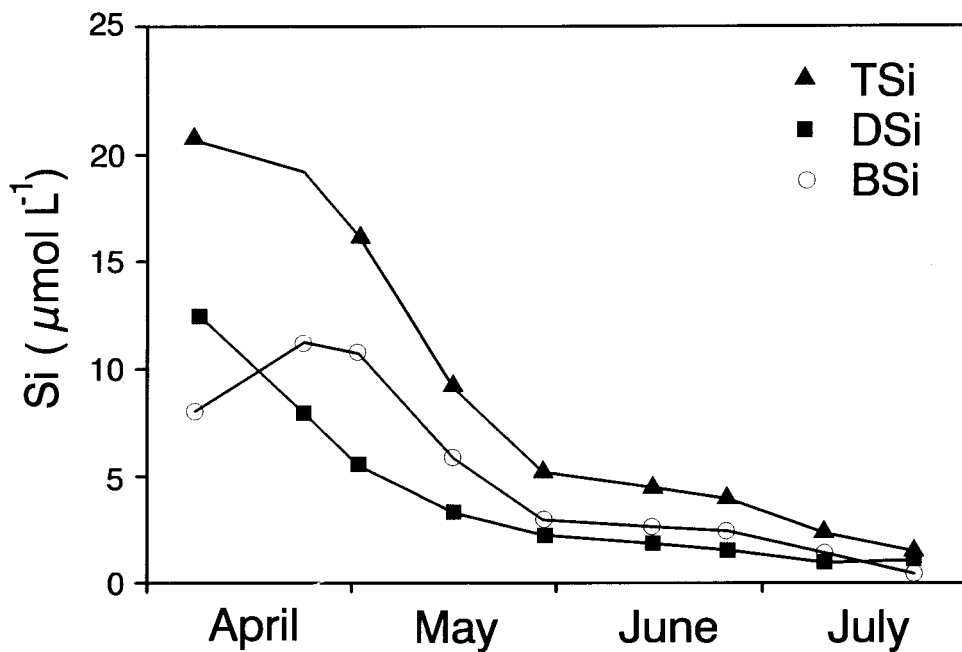*FIG. 2. Vertical profiles of dissolved silica (a) and biogenic silica (b).*

FIG. 3. Epilimnetic dissolved silica (Si), biogenic silica (BSi), and total silica (TSi = DSi + BSi) vs. time.
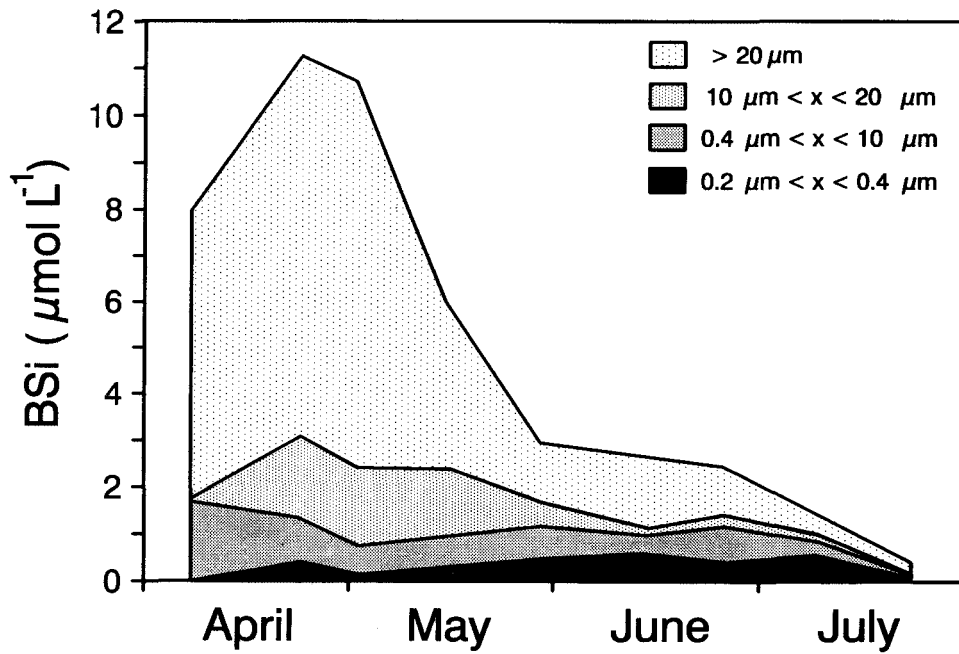
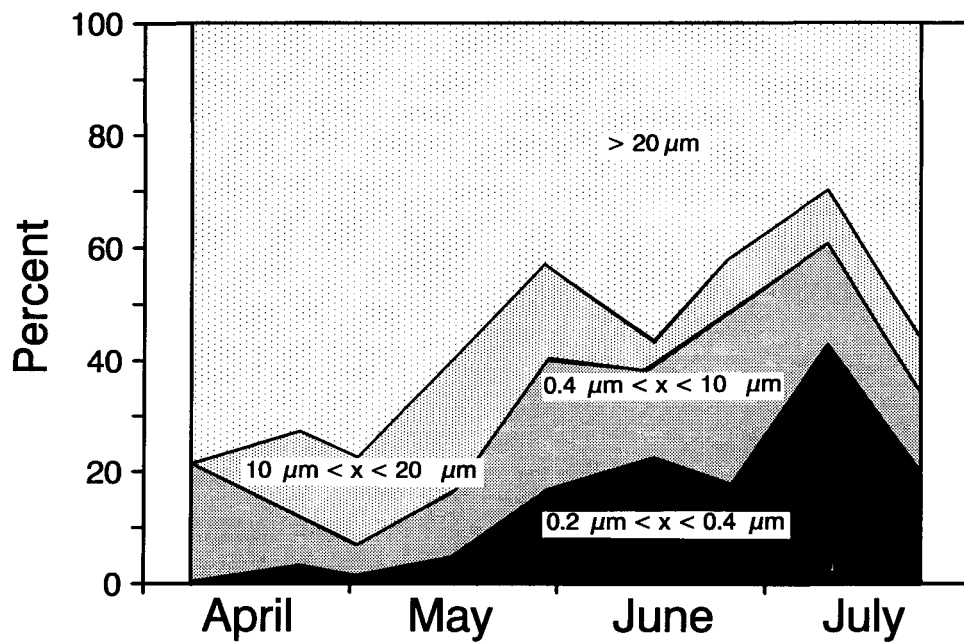FIG. 4. *Size fractionated biogenic silica concentrations vs. time.*

FIG. 5. *Percent of different size fractions of total biogenic silica vs. time.*

spring (Laird *et al.* 1988), but were an order of magnitude less than those observed after stratification. In 1987 both DSi and BSi were essentially lost from surface waters prior to summer stratification, while in most years these losses, which are associated with the spring diatom bloom, occur after thermal stratification (Scavia and Fahnenstiel 1987). Initiation of the spring diatom bloom occurred earlier in 1987 compared to most previous years (Schelske 1988).

A small concentration of 0.2–0.4 μm particles (averaging 0.293 $\pm$ 0.178 μmol L^{-1}) was observed throughout the year. Although a low concentration, because of very low BSi concentrations in epilimnetic waters during summer stratification (1.96 μmol L^{-1}), these small fragments averaged 24% of total BSi. Particles of this size could pass through the pores of filters routinely used in limnological research (ca. 0.45 μm) and therefore would not be assessed as particulate matter (Schelske 1984). In addition, these small particles have the potential of dissolving during storage of samples and increasing DSi concentrations. Numerous 0.2–0.4 μm siliceous particles have also been observed in the nepheloid layer of Lake Ontario (Sandilands and Mudroch 1983). The origin of these particles is most likely material spalled off of siliceous fragments during dissolution (Hurd and Birdwhistell 1983). Our analysis confirms the presence of these particles within the water column of Lake Michigan.

The predominance of smaller size fractions of BSi has implications for the biogeochemical recycling of BSi in Lake Michigan. Settling velocities calculated from Stokes Equation, assuming that the particles are spherical and have a density of 2.0 g cm^{-3} (Hurd 1983), are 1.88 m day^{-1} for 20 μm BSi particles, 0.47 m day^{-1} for 10 μm BSi particles, and negligible (0.0002–0.0008 m day^{-1}) for 0.2–0.4 μm BSi particles. The predominance of diatom fragments in the smaller size fractions that settle slowly and high surface areas available for dissolution (Hurd and Birdwhistell 1983) may lead to enhanced BSi recycling in the water column.

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