

# Sedimentary geochemical record of human-induced environmental changes in the Lake Brunnsviken watershed, Sweden

Joyanto Routh<sup>1</sup>

Department of Geology and Geochemistry, Stockholm University, S 10691 Stockholm, Sweden

Philip A. Meyers

Department of Geological Sciences, University of Michigan, Ann Arbor, Michigan 48109-1063

Örjan Gustafsson

Institute of Applied Environmental Research, Stockholm University, S 10691 Stockholm, Sweden

Mark Baskaran

Department of Geology, Wayne State University, Detroit, Michigan 48202

Rolf Hallberg and Anna Schöldström

Department of Geology and Geochemistry, Stockholm University, S 10691 Stockholm, Sweden

## Abstract

Environmental changes in Lake Brunnsviken, its watershed, and the greater Stockholm region since the middle of the nineteenth century have left interpretable geochemical imprints in the bottom sediments. These human-induced perturbations within the lake's watershed included agriculture, urbanization, sewage and industrial disposal, and water column aeration. Smaller  $\delta^{15}\text{N}_{\text{total}}$  values, high organic carbon mass accumulation rates, low C:N ratios, and larger  $\delta^{13}\text{C}_{\text{org}}$  values identify periods of increased nutrient delivery and elevated primary productivity in the lake. C:S ratios that change from high to low trace the transition from an oxic hypolimnion to an anoxic one during the periods of high productivity. Accumulations of redox-sensitive trace elements increase during the anoxic period and are further magnified during a time of industrial waste discharge into the lake. A recent decrease in black carbon concentrations in sediments reflects the conversion from wood and coal to cleaner forms of energy.

The composition of lake sediments generally reflects the environmental conditions in and around a water body that existed at the time of their accumulation. Organic matter is a small yet important component of sediments because of its associations with biota, nutrient cycles, and geochemical processes. Photosynthetic plants and microbes that inhabit the lake and its surroundings produce organic matter, and organisms that dwell in the lake depths and sediments consume it. Metabolism and oxidation of organic carbon remove dissolved oxygen from the lake waters and sediments, increase their alkalinity, and lead to  $\text{CaCO}_3$  dissolution. Lowered oxygen levels drive redox reactions that simultaneously redistribute trace elements and nutrients. Environmental changes in and around a lake affect how much and what kind of organic matter is delivered to the aquatic system and

initiate a series of geochemical processes that can leave a decipherable record in the sediments.

Different environmental conditions leave geochemical signals in sediment records that can be used to interpret paleoecological and paleoenvironmental histories (e.g., Schelske and Hodell 1991; Bernasconi et al. 1997; Kaushal and Binford 1999; Sternbeck and Hallberg 2000; Meyers and Teranes 2001; Meyers 2003). Notably, periods of high sedimentation rates and greater lacustrine primary productivity can preserve evidence of these short-term processes that affect organic matter delivery and burial in sediments. Here, we report the results of a multiparameter study of the effects of a succession of environmental changes over the last 150 yr on the geochemical properties of the sediments from Lake Brunnsviken, Stockholm, Sweden. The study demonstrates the utility of these bulk geochemical variables in exploring the historical changes and environmental perturbations in the Lake Brunnsviken ecosystem. Many aspects of this study can be extended to other lacustrine systems that have experienced analogous changes in organic matter delivery and its characteristics.

## Methods

*Site description*—The setting of Lake Brunnsviken makes it an interesting subject for geochemical study. It is a slightly

<sup>1</sup> Corresponding author (joyanto.routh@geo.su.se).

## Acknowledgments

We thank Tomas Hjorth, who helped us on numerous occasions with the fieldwork; Lars Erik Bågander, who provided data for trace metals and pore-water chemistry; and Birgitta Boström, who translated some of the Swedish history for the area. Stefano Bernasconi helped us make the Suess-effect corrections. Thoughtful reviews by Mark Brenner and an anonymous reviewer are greatly appreciated. Funding for this study was provided through grants from Kungliga Vetenskapsakademien and J. Rickert stiftelsen to J.R.

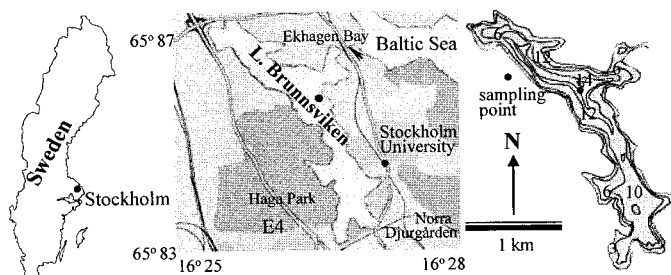


Fig. 1. Position of Lake Brunnsviken near the Baltic Sea and within the northern part of Stockholm. The 14-m deep sampling location is shown in the bathymetric map of the lake. Depths are given in meters below the lake surface (modified from Vattenprogram 2000).

brackish lake (2.8–4.6‰), with a maximum depth of 14 m, and is situated 3 km north of central Stockholm (Fig. 1). The lake has a total surface area of 1.56 km<sup>2</sup> and a drainage area of 14 km<sup>2</sup> (Vattenprogram 2000). Brackish water from the Baltic Sea (salinity of 6–8‰ in surface water) enters through a narrow passage between the lake and Ekshagen Bay (Fig. 1) and causes strong density stratification.

More than 40% of the lake catchment area is urbanized with major highways and heavy traffic that are a source of trace metals. Not surprisingly, Lake Brunnsviken sediments have the highest levels of Cd, Cu, Cr, Hg, and Pb compared with other lakes near Stockholm (Vattenprogram 2000). In spring, siliceous algae predominate in the lake, whereas in summer cyanobacteria (*Planktothrix*, *Aphanizomenon* spp., *Anabaena*, and *Oscillatoria*) become dominant (Vattenprogram 2000). Phosphorus and nitrogen levels are both high and promote intense annual spring and summer algal blooms. These algal blooms cause depletion of dissolved oxygen and development of seasonal anoxia in the hypolimnion (Vattenprogram 2000).

Dramatic environmental changes in and around the lake over the past two centuries make it an ideal candidate for study of the effects of environmental shifts on lake sediment geochemistry. First-growth forests were cleared for agriculture around 1816. Initially, most of the cleared land around the lake was used for housing the royal stables and farms and for an agriculture and horticulture experimental station (Lantsbrukakademiens in 1816) under the directives of King Karl XIII (Kungliga Vetenskapsakademien 2002). Shortly after this period, around the mid-1800s, the earliest algal blooms in the lake were reported (Norberg 1997). Farming waned in the early 1900s, and second-growth oak and pine forests replaced the farms. The land adjoining the lake was used to establish the Veterinary School, which opened in 1912, followed by the Royal Swedish Academy in 1915, the Forest School in 1917, and the Royal School of Technology in 1918. The E4 national highway that passes close by the lake was completed in the late 1950s, and the Stockholm University new campus was opened in the early 1960s. Construction of major roads and housing accompanied establishment of these institutions and led the way to rapid population growth and development. Urbanization around the lake expanded rapidly, and direct disposal of sewage and industrial wastes into the lake started in the 1940s. Sewage disposal

into the lake, however, gradually diminished and was completely stopped in 1969. A wood impregnation factory north of the lake discharged creosote-containing wastes into the lake during the middle part of the twentieth century (Norberg 1997).

In an effort to improve water quality, oxygen was pumped into the hypolimnion between 1973 and 1981. More recently, bottom water has been routinely pumped out into the Baltic Sea to enhance inflow of fresh surface water into the lake (Norberg 1997). Water quality monitoring that started in 1974 indicates a trend toward greater water clarity and substantially diminished P, N, and chlorophyll concentrations (Vattenprogram 2000). The change in nutrient status shifted the trophic status of the lake from eutrophic (1970–1980) to oligomesotrophic (present day) conditions. However, odors of H<sub>2</sub>S and petroleum and high trace element levels in sediments persist (Vattenprogram 2000; Stockholm University unpubl. data), and the Swedish Environmental Protection Agency continues to rank the lake in a state of high nutrient alert.

**Sampling**—Sediment and lake waters were collected from the deepest part of the lake during 2000–2001 (Fig. 1). A gravity corer was used to obtain four relatively undisturbed sediment cores (35–40-cm long × 55-mm diameter) located close to each other.

**Dissolved organic carbon in pore waters**—One core was sliced into 2-cm layers inside a N<sub>2</sub>-filled box. These samples were centrifuged at 10,000 rpm (3023 × g) for 30 min to isolate pore waters. The pore water and surface water samples were filtered through 0.45-μm Millipore filters. Dissolved organic carbon (DOC) concentration was measured with a Shimadzu TOC 5000 analyzer using the TOC-IC mode. Reproducibility of duplicate runs was ±10%. All DOC analyses were finished within 48 h of sampling.

**Elemental, stable isotope, and black carbon analyses**—A second core was sliced at 1-cm intervals in the laboratory and freeze-dried in preparation for elemental carbon, nitrogen, and sulfur, stable C and N isotopic, and black carbon analyses. Total carbon, nitrogen, and sulfur contents were measured using a Carlo Erba 2500 elemental analyzer. To test for the possible presence of CaCO<sub>3</sub> in the sediments, randomly chosen samples were treated with HCl to remove carbonates and then analyzed for residual carbon, total nitrogen, and total sulfur. The carbon contents of the intact and acid-treated samples agreed within 5% (relative standard deviation) and reveal (1) virtually no CaCO<sub>3</sub> is present in the lake sediments, and (2) absence of a systematic isotopic difference between the different samples. Thus, total carbon measurements reflect the total organic carbon (TOC) content in the sediments. The C<sub>organic</sub> and N<sub>total</sub> isotopic compositions of the acid-treated samples were analyzed using a continuous flow system consisting of a Carlo Erba elemental analyzer coupled to a Finnigan MAT Delta S mass spectrometer. Data are reported in conventional delta (δ) notation, which is the per mil (‰) deviation from the Vienna PeeDee Belemnite limestone standard (VPDB) for C and the atmospheric N<sub>2</sub> standard for total N. Reproducibility of duplicate analyses

was  $\pm 0.1\%$ . Black carbon was analyzed by the modified selective chemothermal oxidation method after carbonates and amorphous organic matter were removed by roasting acid-treated samples at  $375^\circ\text{C}$  in air for 24 h (Gustafsson et al. 2001).

**Radiometric dates**—A third core was sliced at 1-cm intervals and freeze-dried. Dry sediment samples were pulverized, and known amounts of the powdered samples were sealed in vials to allow for the ingrowth of daughter products of  $^{222}\text{Rn}$ . Activities of  $^{210}\text{Pb}$ ,  $^{137}\text{Cs}$ , and  $^{226}\text{Ra}$  were determined using a high purity Ge-well detector coupled to InSpector (Canberra Inc.). Total  $^{210}\text{Pb}$  activity was directly determined by measuring the 46.5-keV gamma peak. Parent-supported levels of  $^{210}\text{Pb}$  were determined by measuring the activity of  $^{214}\text{Pb}$  (352 keV) and  $^{214}\text{Bi}$  (609 keV). Self-absorption corrections were not applied as the standards used to calibrate the counting system and the samples had similar densities.  $^{137}\text{Cs}$  activities were determined by measuring 661.6-keV peak. The chronology was established using the down core variations of excess  $^{210}\text{Pb}$  activities (22.3 yr half-life) using a constant initial concentration model and by assigning a date of 1986 to the  $^{137}\text{Cs}$  impulse peak. Details of the dating calculations used are given in Baskaran and Naidu (1995).

**Trace elements**—Additional gravity cores (30–35-cm long) were obtained in 2000, 2001, and 2002 from approximately the same location for measurement of sediment trace element compositions and pore-water sulfate and  $\text{H}_2\text{S}$ . These cores were sliced at 2-cm intervals, and pore waters were isolated by centrifuging the samples at 10,000 rpm for 30 min. Pore waters were filtered and analyzed using a Hitachi U-1100 spectrophotometer for sulfate.  $\text{H}_2\text{S}$  was measured by the colorimetric method. The dewatered sediments were digested in  $7\text{ mol L}^{-1}\text{ HNO}_3$  and analyzed for Cd, Cu, Ni, Pb, and Zn by flame atomic absorption spectrophotometry. The colorimetric procedure and the  $\text{HNO}_3$  digestion are standard Swedish methods (SIS 1993a,b). We report the results of these analyses as composites of the three core profiles.

## Results

**Linear sedimentation and mass accumulation rates**—Linear sedimentation rates (in millimeters per year) and mass accumulation rates (MARs; in milligrams per square centimeter per year) were calculated from measurements of  $^{210}\text{Pb}$ ,  $^{137}\text{Cs}$ , and water contents of sediment samples. Water content decreases from 96% to 82% with depth in the 44-cm long core. The  $^{210}\text{Pb}$  method of dating assumes a constant rate of supply of excess  $^{210}\text{Pb}$ , and negligible postdepositional sediment disturbance (Robbins 1978). The excess  $^{210}\text{Pb}$  was calculated from the total  $^{210}\text{Pb}$  and  $^{226}\text{Ra}$  concentrations for each layer. The mean sediment MAR based on excess  $^{210}\text{Pb}$  over the  $^{210}\text{Pb}$ -datable portion of the core is  $36.1\text{ mg cm}^{-2}\text{ yr}^{-1}$  (Fig. 2). The mass accumulation rate was extrapolated to horizons beyond  $^{210}\text{Pb}$ -datable age range ( $^{210}\text{Pb}$  was measured to 31 cm, corresponding to 1905, and the ages were extrapolated to 44 cm, corresponding to 1847; Figs. 3 and 4). A prominent  $^{137}\text{Cs}$  peak at 7 cm is thought to be from the 1986 Chernobyl accident (Fig. 3) and yields a linear

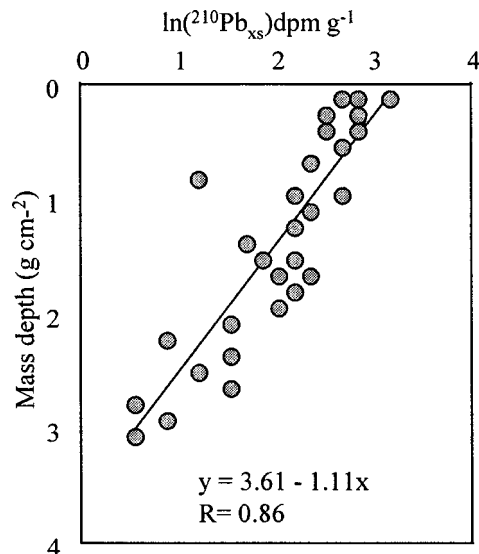


Fig. 2.  $^{210}\text{Pb}$  accumulation rate in Lake Brunnsviken sediments.

sedimentation rate of  $5.0\text{ mm yr}^{-1}$  and a MAR of  $34.2\text{ mg cm}^{-2}\text{ yr}^{-1}$  for the upper sediments. Although the  $^{137}\text{Cs}$ -based MAR agrees well with the  $^{210}\text{Pb}$ -based MAR,  $^{137}\text{Cs}$  undergoes postdepositional migration that affects the calculated ages and MARs (e.g., Comans et al. 1989). We therefore applied the ages and MARs based on the  $^{210}\text{Pb}$ -dating model to the Lake Brunnsviken sediment record.

**Changes in organic matter concentrations and mass accumulation rates**—TOC concentration is around 9% by weight toward the base of the core before it increases to 14% between 39–40 cm (Fig. 4). Between 25–38 cm, TOC concentrations remain between 8% to 10%. TOC starts to increase above 38 cm, peaks at nearly 20% at 19 cm (corresponding to 1951), and then starts to drop. During 1977–1981, TOC concentrations are around 7% in sediments at 9–10 cm. The top 5 cm in the core indicates a TOC concentration of about 10%.

TOC MAR values remain between 3 and  $4\text{ mg C cm}^{-2}\text{ yr}^{-1}$  from 1847 to 1944 except for an interlude of somewhat elevated values of  $4.1\text{--}5.1\text{ mg C cm}^{-2}\text{ yr}^{-1}$  (Fig. 3). The TOC MAR increases to reach a maximum of  $7.1\text{ mg C cm}^{-2}\text{ yr}^{-1}$  in 1951 before it starts to decrease, and reaches around  $2.6\text{ mg C cm}^{-2}\text{ yr}^{-1}$  between 1977–1981. In recent years, TOC MAR again shows an increase and ranges between  $3.1$  and  $3.9\text{ mg C cm}^{-2}\text{ yr}^{-1}$ .

**C:N ratios**—Well-defined differences in atomic  $\text{C}_{\text{organic}}:\text{N}_{\text{total}}$  values correspond to four zones of differing organic matter accumulation in Lake Brunnsviken sediments (Fig. 3). Sediments deposited between 1847 and 1874 indicate  $\text{C}_{\text{organic}}:\text{N}_{\text{total}}$  values of 10, typical of lakes in which the organic matter is from in-lake algal production (Meyers and Ishiwatari 1993). This is succeeded by higher  $\text{C}_{\text{organic}}:\text{N}_{\text{total}}$  ratios indicative of a significant contribution from organic matter of vascular land plants between 1878 and 1928. From 1932 to 1981, organic matter changes back to a predominantly algal source characterized by the  $\text{C}_{\text{organic}}:\text{N}_{\text{total}}$  ratio of



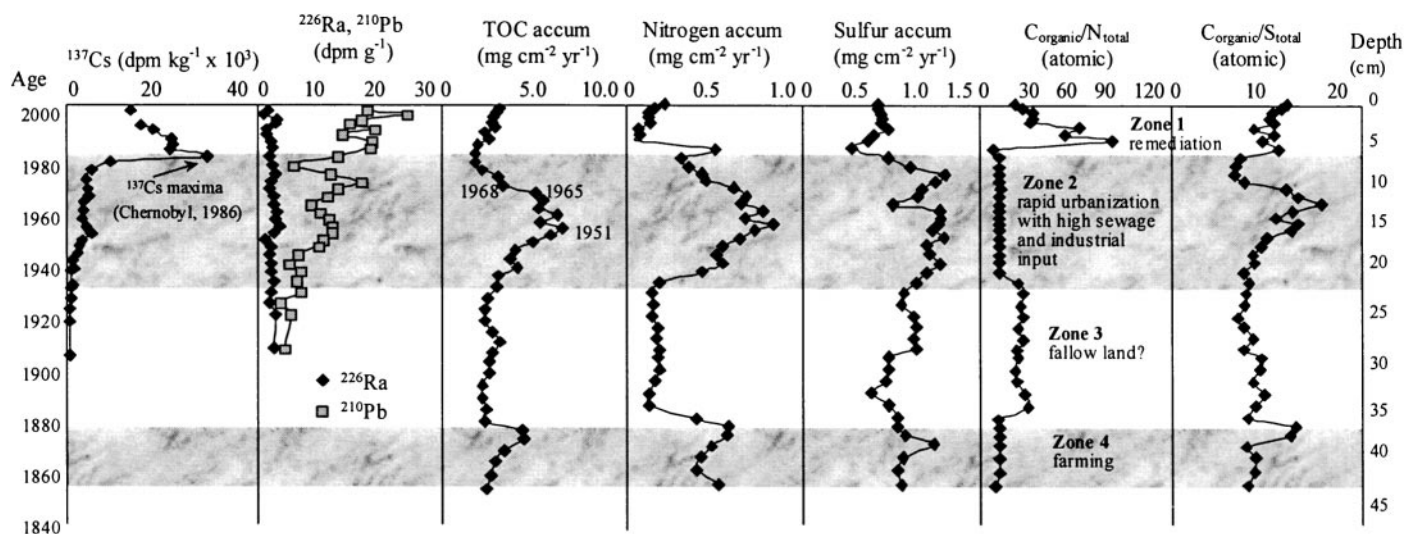


Fig. 3.  $^{137}\text{Cs}$ ,  $^{226}\text{Ra}$ , and  $^{210}\text{Pb}$  activities, total organic carbon (TOC), total nitrogen (TN), and total sulfur (TS) mass accumulation rates, atomic  $\text{C}_{\text{organic}}:\text{N}_{\text{total}}$ , and atomic  $\text{C}_{\text{organic}}:\text{S}_{\text{total}}$  in sediments deposited in Lake Brunnsviken since 1840. Ages of sediment are based on  $^{210}\text{Pb}$  dating. Dates prior to 1900 were assigned based on extrapolating of the mean mass sedimentation rate from 1900 to present.

10.  $\text{C}_{\text{organic}}:\text{N}_{\text{total}}$  ratios in sediments deposited between 1984 and 1999 fluctuate between 22 and 102, which implies a predominant imprint of terrestrial organic matter.

**C : S ratios**—The atomic  $\text{C}_{\text{organic}}:\text{S}_{\text{total}}$  ratios in Lake Brunnsviken sediments vary between 8.8 and 19.9 (Fig. 3). The values in the pre-1928 sediments range narrowly between 9 and 12, except for elevated values of  $\sim 16$  between 1867 and 1870. In contrast, the values in the 1932–1981 sediment zone fluctuate widely from 9 to 20.  $\text{C}_{\text{organic}}:\text{S}_{\text{total}}$  values at the 1984 sediment horizon are  $\sim 12$  before they increase to  $\sim 15$  at the sediment surface.

**Carbon and nitrogen isotopic composition of organic matter**—Measured  $\delta^{13}\text{C}_{\text{organic}}$  values range from  $-28.5\text{‰}$  to  $-26.2\text{‰}$ , with the least negative values appearing in the zones 2 and 4 having low C:N values and elevated TOC MARs (Figs. 3 and 4). Total  $\delta^{15}\text{N}$  values range from 4.3‰

to 8.0‰. The low  $\delta^{15}\text{N}$  values of 4‰ to 5‰ coincide with less negative  $\delta^{13}\text{C}_{\text{organic}}$  values and elevated TOC MARs (Figs. 3 and 4).

**Accumulation of black carbon**—The accumulation rates of black carbon (BC) in Brunnsviken sediments range from 0.1 to 0.2  $\text{mg cm}^{-2} \text{yr}^{-1}$ . Accumulation of BC increases from the bottom of the core to reach its highest value in sediments deposited between 1932 and 1954, and then it decreases, starting in the early 1960s, until stabilizing in the 1970s around 0.1  $\text{mg cm}^{-2} \text{yr}^{-1}$  (Fig. 4).

**Geochemical patterns in sediment pore waters**—DOC concentrations in sediment pore waters increase from 1,783  $\mu\text{mol L}^{-1}$  at 33 cm to peak at 3,900  $\mu\text{mol L}^{-1}$  at 25 cm. DOC concentrations continue to steadily decline until the core top is reached. The pore waters indicate a general pat-

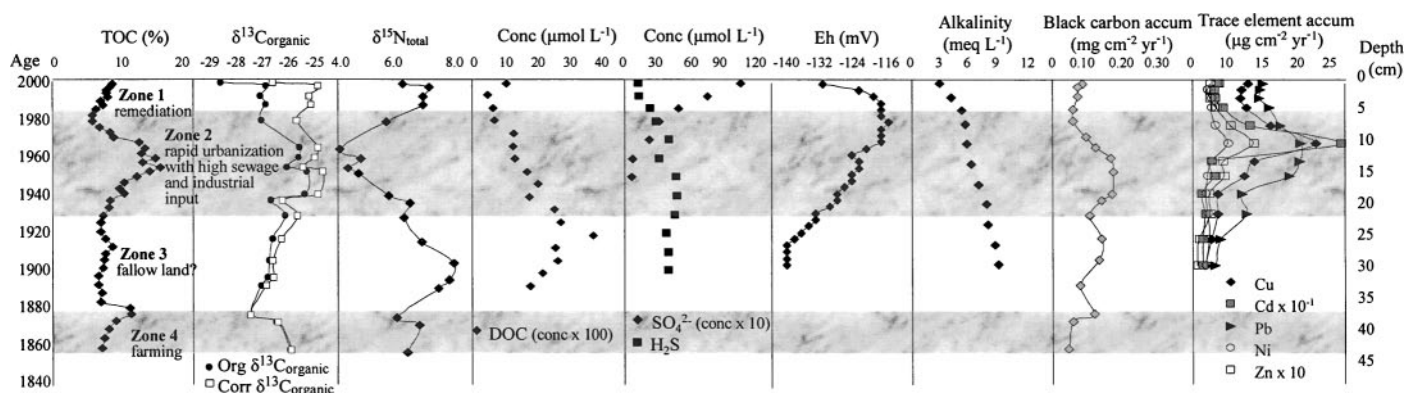


Fig. 4. Organic carbon concentrations (TOC),  $\delta^{13}\text{C}_{\text{organic}}$ ,  $\delta^{15}\text{N}_{\text{total}}$ , interstitial dissolved organic carbon (DOC), interstitial  $\text{H}_2\text{S}$  and  $\text{SO}_4$ , Eh, alkalinity, black carbon, and trace metal accumulation rate in sediments deposited in Lake Brunnsviken. Both measured  $\delta^{13}\text{C}_{\text{organic}}$  values and values adjusted for the Suess effect are shown. Ages of sediment are based on  $^{210}\text{Pb}$  dating. Dates prior to 1900 were assigned based on extrapolating of the mean mass sedimentation rate from 1900 to present.

tern of higher sulfate and Eh values and lower H<sub>2</sub>S and alkalinity levels toward the top of the core (Fig. 4).

*Trace elements*—We assessed the accumulation rates of Cu, Cd, Ni, Pb, and Zn. The mass accumulation rates of these elements start to increase around 1940 and peak at 1965 (Fig. 4). However, in recent years trace element accumulation has decreased substantially.

## Discussion

*Paleolimnological proxies*—Despite the early diagenetic alterations in lacustrine sediments, sedimentary organic matter retains specific information, which one can comprehend using different paleolimnological proxies. These geochemical proxies retain important information about the different sources of organic matter, their delivery, and the abundance of biota that produced it.

Total organic carbon represents the organic matter that escaped remineralization during sedimentation and reflects the different origins of organic matter, delivery routes, depositional processes, and preservation. TOC concentrations are expressed as weight:weight ratios and, therefore, are influenced by other sediment components. For example, variation in grain size affects TOC and, consequently, TOC concentrations can become higher in the deeper parts of the lake where fine-grained sediments predominate. Therefore, TOC MARS are preferred over bulk TOC concentrations as a paleolimnologic proxy because they compensate for changes in bulk sedimentation rates and compaction (Meyers and Lallier-Vergès 1999). A good control on the sediment dating is, however, necessary to calculate reliable TOC MARS to measure the delivery and preservation of organic matter.

Carbon:nitrogen ratios help to identify the origins of sedimentary organic matter. Atomic C:N ratios >20 indicate vascular plant material, whereas lower C:N ratios indicate a mixture of algal or marine organic matter sources (Meyers and Ishiwatari 1993). Organic matter in algae, phytoplankton, and zooplankton is characterized by high protein content, and hence low C:N ratios, whereas terrestrial plants are characterized by low protein content, and hence high C:N ratios. This fundamental difference in organic matter serves as a reliable parameter for paleolimnologic reconstructions. Once organic-rich sediments deposit, C:N values appear to experience little further change, and any variation in them supports the idea of change in organic matter input rather than representing a diagenetic artifact (Kaushal and Binford 1999).

The weight:weight C:S ratio of typical marine sediment is 2.8, whereas the average value of lake sediment is 30 (Berner and Raiswell 1984). Because we used atomic ratios instead of weight ratios in our study, these values correspond to 7.5 and 80, respectively. The S<sub>total</sub> content is usually a good indicator of pyrite sulfur (Berner and Raiswell 1984), especially in organic-rich sediments. Thus, the C:S ratio helps in understanding in-lake processes (e.g., sulfate reduction, Fe-S cycling) that affect the delivery and preservation of organic matter. The C:S ratio has been successfully applied as a paleoenvironmental proxy toward interpreting paleosalinity (Sohlenius et al. 1996), bottom-water aeration

(Raiswell et al. 1988), early diagenesis (Chowdhury and Noble 1996), and the trophic state in lakes (Urban et al. 1999).

Carbon isotopes have been most commonly used to differentiate the different organic matter sources in lakes. The  $\delta^{13}\text{C}$  values of algal and C<sub>4</sub>-type material are distinctively different, but there is little difference between algal versus terrestrial C<sub>3</sub>-type material. An option is plotting the  $\delta^{13}\text{C}$  values versus C:N ratios to distinguish the different organic matter sources (e.g., Meyers and Ishiwatari 1993). Carbon isotopes have also been widely used as an indicator of enhanced aquatic productivity in lakes (e.g., Hodell and Schelske 1998; Brenner et al. 1999). Primary producers preferentially remove dissolved <sup>12</sup>CO<sub>2</sub> from water and leave the remaining dissolved inorganic carbon depleted in <sup>12</sup>C (e.g., Bernasconi et al. 1997; Hodell and Schelske 1998; Meyers and Teranes 2001). When productivity is high, the availability of <sup>12</sup>CO<sub>2</sub> gradually diminishes and a progressively greater fraction of the <sup>13</sup>CO<sub>2</sub> is incorporated into organic matter. The consequence is that the  $\delta^{13}\text{C}$  of organic matter produced under conditions of high productivity becomes less negative. Because many factors affect the carbon isotopic signal of sedimented organic matter, separating a organic matter source from in-lake processes based on  $\delta^{13}\text{C}$  values can become complicated. Recent studies indicate that in systems where dissolved atmospheric CO<sub>2</sub> ( $\delta^{13}\text{C} = -7\text{‰}$ ) is limited and algae begin to use dissolved HCO<sub>3</sub><sup>-</sup> ( $\delta^{13}\text{C} = 1\text{‰}$ ) as carbon source, their isotopic composition becomes heavier than C<sub>3</sub>-type land plants (up to  $-9\text{‰}$ ; Hollander and MacKenzie 1991; Bernasconi et al. 1997). In contrast, large input of isotopically light soil dissolved inorganic carbon ( $\delta^{13}\text{C} = -12\text{‰}$ ) can lead to in-lake production of isotopically light algal organic matter ( $\delta^{13}\text{C} = -32\text{‰}$ ; Meyers 2003).

$\delta^{15}\text{N}$  values have been used to identify organic matter sources and to reconstruct paleoproductivity histories (e.g., Herczeg et al. 2001; Talbot and Johannessen 1992), but their use has been limited. The  $\delta^{15}\text{N}$  signature of organic matter from algae using dissolved inorganic nitrogen (DIN) is ca. 8.5‰ versus C<sub>3</sub>-type plants using atmospheric N<sub>2</sub> with values of ca. 0.5‰ (Peterson and Howarth 1987). Drawdown of the DIN reservoir yields larger  $\delta^{15}\text{N}$  values in algal organic matter. However, interpreting the  $\delta^{15}\text{N}$  values is not always straightforward. For example, denitrification or anthropogenic input from farm runoff and sewage can result in larger  $\delta^{15}\text{N}$  values (Teranes and Bernasconi 2000), whereas an abundance of cyanobacteria, which directly fix atmospheric N<sub>2</sub>, leads to lower  $\delta^{15}\text{N}$  values (Fogel and Cifuentes 1993). Moreover, shifts in phytoplankton assemblages may influence the  $\delta^{15}\text{N}$  values, adding to the complexity (Peterson and Fry 1987).

*Present study*—Results of our study reveal that delivery of organic matter to the Lake Brunnsviken sediments has varied since the early nineteenth century. These variations affected pore-water geochemistry and in-lake processes. Moreover, unreactive black carbon and trace metals were added to the lake from outside sources. We infer these environmental changes in and around Lake Brunnsviken based on multiple lines of geochemical evidence in the sediment

and porewaters, and in light of historical data on human activities in the watershed.

*Changes in organic matter concentrations and mass accumulation rates*—There are distinct changes in the amount and composition of organic matter buried over the past 150 years in Lake Brunnsviken. These variations reflect the sequence of different environmental changes on organic matter delivery and degradation in the recent history of this lake. Degradation of organic matter is typically limited to the uppermost layers of lake sediments, where it can diminish TOC concentrations by as much as 20% in well-oxygenated systems (Hodell and Schelske 1998). In contrast, organic matter concentration does not change significantly in deeper sediment layers after burial. In fact, the amount of natural post-burial loss of organic carbon is likely to be less in Lake Brunnsviken because of its strong stratification and oxygen-depleted hypolimnion. Thus, variations in sediment TOC concentrations in Lake Brunnsviken mostly reflect changes in rates of delivery and type of organic matter deposited. The lower TOC concentrations in the 9–11-cm interval are an important exception that probably resulted from an enhanced period of organic matter degradation caused by artificial aeration in the 1970s.

The high accumulation rates of TOC and N (and S to some extent) identify past episodes of increased primary productivity in Lake Brunnsviken. The modest increases in all three parameters from 1863 to 1870 correspond to the historical reports of algal blooms in the mid-1800s (Norberg 1997). The more dramatic increases from 1942 to 1962 correspond to disposal of sewage and industrial wastes directly into the lake beginning around 1940. These environmental impacts may have been compounded by the rapid urbanization of the local area that started in the late 1940s. MARs declined starting in 1968 and have remained relatively low, probably in response to the combined effects of diversion of sewage and industrial waste away from the lake, remedial pumping of oxygenated waters to the hypolimnion, and flushing of the bottom waters into the Baltic Sea.

*C:N ratios*—Both zones in which  $C_{\text{organic}}:N_{\text{total}}$  values are  $\sim 10$  correspond to parts of the sediment record in which TOC MARs are elevated, and the lower C:N values confirm the increased algal productivity that the higher MARs imply. Values of  $\sim 25$  that appear in the sediment record from 1878 to 1928 may reflect the period between the end of nineteenth century agriculture and the onset of twentieth century urbanization in the Brunnsviken watershed. Evidently, algal productivity was low, and forest litter was the major source of organic matter delivery to the lake. The exceptionally high  $C_{\text{organic}}:N_{\text{total}}$  ratios in sediments deposited from 1984 to 1989 indicate presence of woody land plant debris, probably as tiny bits of twigs and sawdust mixed into the sediment layers. The particles must be fine-grained because we did not observe them during slicing or grinding of the dry sediments. Their postulated presence implies a period of near-lake forest clearance during the urban development of the local area.

*C:S ratios*—The C:S ratios in Lake Brunnsviken sediments (8.8–19.9) are elevated relative to marine sediments (7.5) because the lake waters receive small amounts of dissolved sulfate from the Baltic Sea. However, the atomic ratios are significantly lower than average lake sediment (80; Berner and Raiswell 1984). Strong density stratification that exists in Lake Brunnsviken probably affects the C:S ratios by causing seasonal hypolimnetic anoxia and incorporation of sulfur, as sulfide, into sediments. Occurrence of sulfate reduction as evidenced by Eh,  $H_2S$ , and alkalinity measurements (*see below*) probably plays a role in affecting S enrichment. In addition, high dissolved and sedimentary Fe content in the lake (Lars-Eric Bågander unpubl. data) can also react with  $H_2S$  to form pyrite. Additional input of S into the lake may also occur from rain, snow, and dry deposition (Mylona 1996).  $S_{\text{total}}$  accumulation in Brunnsviken sediments remains more or less the same around  $0.80\text{--}0.95\text{ mg cm}^{-2}\text{ yr}^{-1}$  until it starts to increase around 25 cm ( $1.02\text{ mg cm}^{-2}\text{ yr}^{-1}$  corresponding to 1932) and peak at 12 cm ( $1.16\text{ mg cm}^{-2}\text{ yr}^{-1}$  corresponding to 1971). This trend is similar to the S deposition models for Sweden, which indicate the S maximum during the 1970s (Mylona 1996). The models relate the S maximum to increased input from atmosphere, which has decreased in recent years due to stricter environmental regulations.

The interval of notably low  $C_{\text{organic}}:S_{\text{total}}$  ratios present in sediments from 1968–1977 corresponds closely to the 1973–1981 period of hypolimnetic aeration and low TOC MARs. The low ratios evidently represent loss of organic carbon available for burial in sediments because of aeration. In a study on accumulation of S in Swiss lake systems, Urban et al. (1999) described the effects of aeration. The authors indicated a sudden drop in C:S ratio following aeration and poor correlation between C:S and sulfate (similar to Lake Brunnsviken). They suggest that aeration can destroy organic S compounds resulting in high redox potential not conducive to chemical reactions of  $H_2S$  with organic matter or even prevent the arrival of reactive organic matter into anaerobic sediment depths.

The two episodes of elevated  $C_{\text{organic}}:S_{\text{total}}$  values during periods of higher productivity have two possible and opposite explanations. They may record times of oxygenated bottom conditions that prevented formation of the sulfide required for pyrite precipitation and for incorporation of sulfur into sedimentary organic matter (e.g., Eville 1960; Hofmann et al. 2000). Alternatively, they may record times of increased organic matter delivery to the lake bottom. Because elevated  $C_{\text{organic}}:S_{\text{total}}$  values correspond to periods of high algal productivity and because the period of hypolimnetic aeration depressed C:S ratios, we conclude that high  $C_{\text{organic}}:S_{\text{total}}$  ratios are a consequence of high organic matter sedimentation.

*Carbon and nitrogen isotopes*—Elevated lake productivity increases both TOC MARs and  $\delta^{13}C_{\text{organic}}$  values. The amount of organic matter that is buried in lake sediments is diminished by metabolism and remineralization, but the isotopic composition is relatively unaffected by these postphotosynthetic processes (Schelske and Hodell 1995). Although  $\delta^{13}C_{\text{organic}}$  values are reliable recorders of lake paleoproductivity



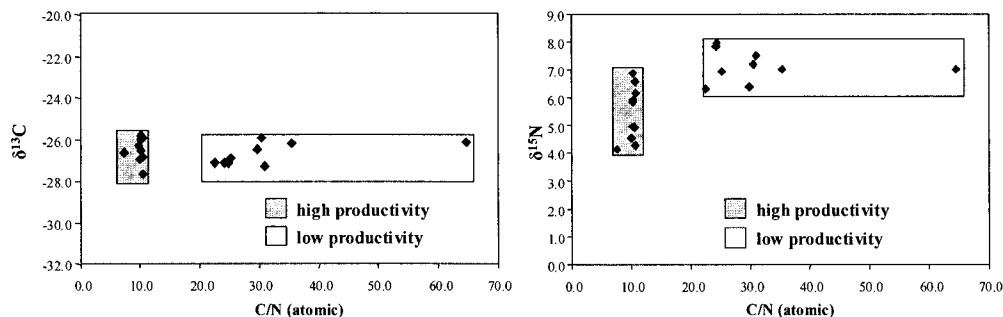


Fig. 5. Comparisons of Suess-effect-adjusted  $\delta^{13}\text{C}_{\text{organic}}$  values,  $\delta^{15}\text{N}_{\text{total}}$  values, and atomic  $\text{C}_{\text{organic}}:\text{N}_{\text{total}}$  values of sediments cored from Lake Brunnsviken, Sweden. C:N values clearly distinguish times of elevated and natural lake productivity and highlight excursions in isotopic compositions associated with elevated productivity.

tivity, they should be corrected for the Suess effect—the shift to more negative  $\delta^{13}\text{C}$  values of atmospheric  $\text{CO}_2$  caused by fossil fuel combustion. This shift was 1.4‰ between 1840 and 1989, with about 1.0‰ of the shift occurring since 1940 (Keeling et al. 1989). Addition of  $^{12}\text{C}$  to the atmosphere has continued since 1989. We subtracted the progressively greater fossil fuel contributions of isotopically light carbon from the measured  $\delta^{13}\text{C}_{\text{organic}}$  values to correct for the Suess effect. The corrections expand the period of less negative values to encompass sediments up to 1997, and they make the most negative value of the topmost sediment similar to the values of sediments deposited in the middle of the nineteenth century (Fig. 4). This correction is significant, inasmuch as it is unreasonable to believe that modern productivity in Lake Brunnsviken is less than the productivity 150 years ago.

General agreement between changes in trophic state and human-induced anthropogenic activities in the lake (Vattenprogram 2000) suggests that changes in  $\delta^{13}\text{C}_{\text{organic}}$  values reflect shifts in paleoproductivity. Fewer negative corrected  $\delta^{13}\text{C}_{\text{organic}}$  values in sediments deposited in 1847 and from 1932 to 1967 indicate that primary production was elevated at these times.  $^{13}\text{C}$  enrichment in organic matter during periods of increased productivity as noted here can occur for several reasons. First, algae preferentially use the lighter ( $^{12}\text{C}$ ) isotope for photosynthesis, thereby depleting it and forcing the cells to use  $^{13}\text{C}$  for carbon fixation. Second, increased primary production may deplete the aqueous  $\text{CO}_2$  levels forcing the usage of  $\text{HCO}_3^-$  as a carbon source (C in  $\text{HCO}_3^-$  is 8‰ heavier than C in aqueous  $\text{CO}_2$ ). Finally, as lakes become eutrophic, deeper waters and sediments experience longer periods of anoxia that leads to methanogenesis, and production of isotopically light  $\text{CH}_4$  and heavy  $\text{CO}_2$  (e.g., Gu and Schelske 1996). Because these periods of isotope-identified elevated productivity differ in their peak expressions from those suggested by elevated TOC MARs, we postulate that preservation of organic matter has been variable in Lake Brunnsviken. The discrepancy between  $\delta^{13}\text{C}$  values and TOC MARs is especially striking in the upper parts of the sediment record that correspond to times of aeration (1971–1983) and more recent flushing of the hypolimnion (Fig. 4). This study indicates that while early diagenetic processes may not affect the  $\delta^{13}\text{C}$  values of sedimenting organic matter (Schelske and Hodell 1995), active human in-

tervention may cause striking discrepancies and should be taken into account.

In shallow lakes where macrophyte biomass can contribute significantly to total lake primary productivity, the  $\delta^{13}\text{C}_{\text{organic}}$  values may be affected by the relative contribution of algae versus higher plants. Macrophytes display a wide range of  $\delta^{13}\text{C}_{\text{organic}}$  values, from about  $-30\text{‰}$  to  $-12\text{‰}$  (Boutton 1991). The  $\delta^{13}\text{C}_{\text{organic}}$  values of organic matter produced by lacustrine algae and  $\text{C}_3$  vascular plants are often indistinguishable because both types of plants use isotopically identical sources of inorganic carbon— $\text{CO}_2$  dissolved either in lake water or present in the atmosphere. Therefore, we cannot assess the possible significance of macrophytes in affecting the  $\delta^{13}\text{C}_{\text{organic}}$  values of its sedimented organic matter in Lake Brunnsviken.

Changes in the corrected  $\delta^{13}\text{C}_{\text{organic}}$  values in response to changes in organic matter delivery are subtle in comparison to those of C:N values (Fig. 5). Given the fact that  $\delta^{13}\text{C}_{\text{organic}}$  values of lacustrine algae and  $\text{C}_3$  plants are mostly similar (Meyers and Ishiwatari 1993), this is not surprising. Large increases in aquatic productivity are needed before the effects of selective removal of dissolved  $^{12}\text{CO}_2$  become evident in sediment records. Indeed, as noted in other studies, changes in nutrient concentration and productivity may not always yield linear shifts in the  $\delta^{13}\text{C}_{\text{organic}}$  values throughout the lake's trophic trajectory (e.g., Brenner et al. 1999).

The  $\delta^{15}\text{N}$  value of sedimenting organic matter is generally related to the supply and use of the DIN pool. When the DIN pool is small, the preferential uptake of the lighter isotope by algae diminishes, and  $\delta^{15}\text{N}$  values become larger. Such values appear where more negative  $\delta^{13}\text{C}_{\text{organic}}$  values indicate the decreased paleoproductivity that would result from limited nitrate availability. In contrast, smaller  $\delta^{15}\text{N}$  values can result from greater availability of DIN for biological use, and this condition typically stimulates primary productivity in lakes (Hodell and Schelske 1998; Meyers and Teranes 2001). Parts of the Lake Brunnsviken sediment record that exhibit smaller  $\delta^{15}\text{N}$  values correspond to low C:N values indicative of algal organic matter and the high-TOC MARs indicative of elevated productivity (Figs. 3 and 4).

Previous studies related similar concurrent shifts to lower  $\delta^{15}\text{N}$  and C:N values with increased primary productivity and/or trophic state in Florida lakes (e.g., Gu et al. 1996;

Brenner et al. 1999). The authors postulated that the isotopic shift might represent greater contributions of  $^{15}\text{N}$ -depleted organic matter produced by  $\text{N}_2$ -fixing cyanobacteria. If so, then the lower  $\delta^{15}\text{N}$  values record the conditions that favor cyanobacteria in which dissolved oxygen is low or absent in the photic zone. Eutrophication in Lake Brunnsviken has indeed been related to intense cyanobacterial blooms in the mid-1900s, and even in recent years cyanobacteria continue to overtake the siliceous algae during summer (Vattenprogram 2000). The  $\text{N}_2$ -fixing cyanobacteria perhaps account for some of the decline in  $\delta^{15}\text{N}$  values, but their role in affecting the primary productivity in Lake Brunnsviken is open to question. The  $\delta^{15}\text{N}$  values only reach 4.3‰, which is outside the range of  $\text{N}_2$ -fixation (−3‰ to 1‰; Fogel and Cifuentes 1993). Teranes and Bernasconi (2000) suggest that incorporation of ammonium during the more anoxic periods that follow the high-productivity cycles could decrease  $\delta^{15}\text{N}$  values in lacustrine sediments. However, with no data on ammonium levels the role of such microbial processes is speculative.

Additional factors may play a role in causing the excursions of up to ~4‰ in  $\delta^{15}\text{N}$  signatures. For example, anthropogenic inputs and denitrification processes could increase the  $\delta^{15}\text{N}$  values (Terranes and Bernasconi 2000). While enhanced anthropogenic inputs from farming (late 1800s) and sewage disposal (1940–1969) have occurred in the past, the  $\delta^{15}\text{N}$  values are surprisingly low (only 4‰ to 6‰) during these periods. Artificial aeration since 1973 should have effectively reduced water column denitrification and its potential influence on the  $\delta^{15}\text{N}$  values. In fact, we do not know whether denitrification has ever been an important process in the past in this lake. It seems that the Brunnsviken sediment record reflects a composite of perhaps several ongoing processes with contrasting effects on the  $\delta^{15}\text{N}$  values, and separating the different in-lake processes from cultural disturbances is complicated.

In the past,  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  signatures have both been successfully used to record changes in the trophic state in lakes (e.g., Hodell and Schelske 1998). However, stratigraphic changes in the  $\delta^{15}\text{N}$  values in this study correspond more closely to C:N values than to corrected  $\delta^{13}\text{C}_{\text{organic}}$  values (Fig. 5). This comparison of the two isotopic proxies versus C:N ratio indicates that  $\delta^{15}\text{N}$  values can be more sensitive than Suess-effect-corrected  $\delta^{13}\text{C}_{\text{organic}}$  values to changes in algal productivity in systems like Lake Brunnsviken. Notably, during periods of higher productivity, the C:N ratio remains constant while both  $\delta^{13}\text{C}_{\text{organic}}$  and  $\delta^{15}\text{N}$  values vary. In contrast, periods of low productivity are characterized by relatively constant isotopic compositions and variable C:N values. This clearly indicates that isotopic values do respond to internal changes in productivity, and they show promise as proxies for interpreting paleolimnological changes.

**Black carbon accumulation pattern**—BC is the highly condensed carbonaceous residue produced from incomplete combustion of biomass and fossil fuels. Accumulation rates of BC differ significantly from the TOC pattern. The highest BC levels in sediments were deposited between 1932 and 1954, and then they decrease starting in the early 1960s until stabilizing in the 1970s. Gustafsson et al. (1997) reported a

similar trend in BC deposition in Mystic Lake, Massachusetts, in suburban Boston. This pattern is attributed to change from burning of wood and coal to combustion of petroleum and natural gas with the advent of rapid industrialization in the western world (Gustafsson et al. 1997; Schmidt and Noack 2000). Consistent with this hypothesis, Sweden's greater dependence on oil, hydro-electric, and nuclear energy over wood and coal since the mid-1960s (IEA 2000) resulted in an overall decrease in BC accumulation.

**Geochemical patterns in lake and sediment pore waters**—Organic matter, measured as TOC, is abundant (7–20%) in the Lake Brunnsviken sediments (Fig. 4). The increase in pore-water DOC concentration implies continued in situ microbial breakdown of organic matter with depth, and the decrease in deeper sediments reflects the diminished availability of biodegradable organic matter in these sediments implied by their lower TOC concentrations. The pore-water data substantiate the degradation of organic matter and occurrence of sulfate reduction in Lake Brunnsviken. Because the lake is connected to the Baltic Sea through Ekhagen Bay, diluted seawater with sulfate levels of ca. 1.2 mmol  $\text{L}^{-1}$  routinely enters the lake. Although the net input of sulfate varies seasonally, it provides the electron acceptors required for anoxic organic matter degradation. The reducing conditions indicated by low dissolved oxygen concentrations and negative Eh values favor fermentation and sulfate reduction in the sediments. In the upper part of the core, it is likely that production of secondary organic matter from degradation of primary organic matter (fermentation) overrides the net effect of microbial consumption (sulfate reduction). With increase in depth, the sulfate-reducing activity probably increases within the core. The probability of these processes is supported by decreases in pore-water sulfate and DOC levels and increases in  $\text{H}_2\text{S}$  and alkalinity levels (Fig. 4).

**Changes in accumulation of trace elements**—We assessed the mass accumulations of Cu, Cd, Ni, Pb, and Zn, which typically result from increased urban development, industrial wastes, and traffic. Accumulation rates of these trace elements start to increase around the 1940s and peak at 1965 (Fig. 4). These maxima coincide with input of industrial waste and sewage into Lake Brunnsviken. In recent years, accumulation of all these trace elements has decreased substantially, similar to what has been reported at other sampling locations in central Stockholm (e.g., Sternbeck and Östlund 2000; Vattenprogram 2000). We conclude that a change in delivery of these trace elements over time is the principal factor in their variation with depth in the Brunnsviken sediments.

Geochemical properties of the sediments in Lake Brunnsviken reflect the effects of human-induced environmental modifications. Greater accumulation of TOC after the mid-1800s resulted from enhanced primary productivity that reflects changes in the agriculture and associated soil disturbance that started in the catchment area around 1816, but waned around the early 1900s. During this period when land was increasingly left fallow, mostly terrestrial organic matter drained into the lake from surficial runoff, as evidenced by high C:N values. A later increase in primary productivity



in the lake can be related directly to the addition of sewage and industrial waste. The 1950s recorded some of the highest TOC and N accumulation rates in sediments. After direct input of sewage and industrial waste into the lake was stopped and steps were taken to improve the water quality, a sharp fall in the TOC accumulation rate occurred.

Bulk organic matter variables analyzed in this study indicate the presence of different environmental conditions and organic matter sources during the deposition of sediments. The sediment core records periods of elevated primary productivity in the lake that are highlighted by high-TOC MARs, low C:N ratios, and larger  $\delta^{13}\text{C}$  values. Because  $\delta^{15}\text{N}$  values decrease during these periods, increased delivery of bioavailable nitrogen probably was important to the productivity enhancement. Contrasting geochemical conditions occur during the lower productivity periods that are indicated by relatively lower TOC MARs, higher C:N ratios, larger  $\delta^{15}\text{N}$  values, and smaller  $\delta^{13}\text{C}$  values.

## References

- BASKARAN, M., AND A. S. NAIDU. 1995.  $^{210}\text{Pb}$ -derived chronology, and the fluxes of  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  isotopes into continental shelf sediments, East Chukchi Sea, Alaskan Arctic. *Geochim. Cosmochim. Acta* **59**: 4435–4448.
- BERNASCONI, S. M., A. BARBIERI, AND M. SIMONA. 1997. Carbon and nitrogen isotope variations in sedimenting organic matter in Lake Lugano. *Limnol. Oceanogr.* **42**: 1755–1765.
- BERNER, R. A., AND R. RAISWELL. 1984. C:S method for distinguishing freshwater from marine sedimentary rocks. *Geology* **12**: 365–368.
- BOUTTON, T. W. 1991. Stable carbon isotope ratios of natural materials: II. Atmospheric, terrestrial, marine, and freshwater environments, p. 173–185. *In* D. C. Coleman and B. Fry [eds.], *Carbon isotope techniques*. Academic.
- BRENNER, M., T. J. WHITMORE, J. H. CURTIS, D. A. HODELL, AND C. L. SCHELSKE. 1999. Stable isotope ( $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ ) signatures of sedimented organic matter as indicators of historic lake trophic state. *J. Paleolimnol.* **22**: 205–221.
- CHOWDHURY, A. H., AND J. P. A. NOBLE. 1996. Organic carbon and pyrite sulphur relationships as evidences of bottom water conditions of sedimentation, Albert Formation fine-grained lacustrine sediments, New Brunswick, Canada. *Mar. Petrol. Geol.* **13**: 79–90.
- COMANS, R. N. J., J. J. MIDDELBURG, J. ZONDERHUIS, J. R. W. WOITTEZ, G. J. DE LANGE, H. A. DAS, AND C. H. VAN DER WEIJDEN. 1989. Mobilization of radiocesium in pore water of lake sediments. *Nature* **339**: 367–369.
- EVILLE, G. 1960. The relation between sulfur and carbon in sediments from the English lakes. *J. Sediment. Petrol.* **30**: 466–470.
- FOGEL, M. L., AND L. A. CIFUENTES. 1993. Isotope fractionation during primary production, p. 73–94. *In* M. H. Engel and S. A. Macko [eds.], *Organic geochemistry principles and applications*. Plenum.
- GU, B., AND C. L. SCHELSKE. 1996. Temporal and spatial variations in phytoplankton carbon isotopes in a polymictic subtropical lake. *J. Plankton Res.* **18**: 2081–2092.
- , ———, AND M. BRENNER. 1996. Relationships between sediment and plankton isotope ratios ( $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ ) and primary productivity in Florida lakes. *Can. J. Fish. Aquat. Sci.* **53**: 875–883.
- GUSTAFSSON, Ö. M., F. HAGHSETA, C. CHAN, J. MACFARLANE, AND P. M. GSCHWEND. 1997. Quantification of the dilute sedimentary soot phase: Implications for PAH speciation and bioavailability. *Environ. Sci. Technol.* **31**: 203–209.
- , AND OTHERS. 2001. Evaluation of a protocol for the quantification of black carbon in sediments. *Glob. Biogeochem. Cycles* **15**: 881–890.
- HERCZEG, A. L., A. K. SMITH, AND J. C. DIGHTON. 2001. A 120 year record of changes in nitrogen and carbon cycling in Lake Alexandrina, South Australia: C:N,  $\delta^{15}\text{N}$ , and  $\delta^{13}\text{C}$  in sediments. *Appl. Geochem.* **16**: 73–84.
- HODELL, D. A., AND C. L. SCHELSKE. 1998. Production, sedimentation, and isotopic composition of organic matter in Lake Ontario. *Limnol. Oceanogr.* **43**: 200–214.
- HOFMANN, P., W. RICKEN, L. SCHWARK, AND D. LEYTHAEUSER. 2000. Carbon-sulfur-iron relationships and  $^{13}\text{C}$  of organic matter for late Albian sedimentary rocks from the North Atlantic Ocean: Paleooceanographic implications. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **163**: 97–113.
- HOLLANDER, D. J., AND J. A. MACKENZIE. 1991.  $\text{CO}_2$  control on carbon-isotope fractionation during aqueous photosynthesis: A paleo- $\text{pCO}_2$  barometer. *Geology* **19**: 929–932.
- IEA. 2000. Sweden key energy indicators (<http://www.iea.org/stats/files/selstats/keyindic/country/sweden.htm>).
- KAUSHAL, S., AND M. W. BINFORD. 1999. Relationship between C:N ratios of lake sediments, organic matter sources, and historical deforestation of Lake Pleasant, Massachusetts, USA. *J. Paleolimnol.* **22**: 439–442.
- KEELING, C. D., AND OTHERS. 1989. A three-dimensional model of atmospheric  $\text{CO}_2$  transport based on observed winds: 1. Analysis of observational data, p. 165–236. *In* D. H. Peterson [ed.], *Aspects of climate variability in the Pacific and Western Americas*. Geophysical Monograph 55, Am. Geophys. Union.
- KUNGLIGA VETENSKAPSAKADEMIEN. 2002. Nationalstadsparken—en symbios mellan stadens kultur och natur. Document 74. p 47 (in Swedish).
- MEYERS, P. A. 2003. Applications of organic geochemistry to paleolimnological reconstructions: A summary of examples from the Laurentian Great Lakes. *Org. Geochem.* **34**: 261–289.
- , AND R. ISHIWATARI. 1993. Lacustrine organic geochemistry—an overview of indicators of organic matter sources and diagenesis in lake sediments. *Org. Geochem.* **20**: 867–900.
- , AND E. LALLIER-VERGÈS. 1999. Lacustrine sedimentary organic matter records of late Quaternary paleoclimates. *J. Paleolimnol.* **21**: 345–372.
- , AND J. L. TERANES. 2001. Sediment organic matter, p. 239–269. *In* W. M. Last and J. L. Smol [eds.], *Tracking environmental changes using lake sediments. V. 2: Physical and geochemical methods*. Kluwer.
- MYLONA, S. 1996. Sulphur dioxide emissions in Europe 1880–1991 and their affect on sulphur concentrations and depositions. *Tellus B, Chem. Phys. Meteorol.* **48**: 662–689.
- NORBERG, B. 1997. Vattenundersökningar i Brunnsvikens 1987–1996. M.S. thesis, Stockholm Univ. (in Swedish).
- PETERSON, B. J., AND B. FRY. 1987. Stable isotopes in ecosystem studies. *Annu. Rev. Ecol. Syst.* **18**: 293–320.
- , AND R. W. HOWARTH. 1987. Sulfur, carbon, and nitrogen isotopes used to trace organic matter flow in the salt-marsh estuaries of Sapelo Island, Georgia. *Limnol. Oceanogr.* **32**: 1195–1213.
- RAISWELL, R., F. BUCKLEY, R. A. BERNER, AND T. F. ANDERSON. 1988. Degree of pyritization of iron as a paleoenvironmental indicator of bottom-water aeration. *J. Sediment. Petrol.* **58**: 812–819.
- ROBBINS, J. A. 1978. Geochemical and geophysical applications of radioactive lead, p. 285–293. *In* J. O. Nriagu [ed.], *Biogeochemistry of lead in the environment. Part A*. Elsevier.
- SCHELSKE, C. L., AND D. A. HODELL. 1991. Recent changes in

- productivity and climate of Lake Ontario detected by isotopic analysis of sediments. *Limnol. Oceanogr.* **36**: 961–975.
- , AND ———. 1995. Using carbon isotopes of bulk sedimentary organic matter to reconstruct the history of nutrient loading and eutrophication of Lake Erie. *Limnol. Oceanogr.* **40**: 918–929.
- SCHMIDT, M. W. I., AND A. G. NOACK. 2000. Black carbon in soils and sediments: Analysis, distribution, implications and current challenges. *Glob. Biogeochem. Cycles* **14**: 777–793.
- SWEDISH STANDARDS INSTITUTE (SIS). 1993a. Measuring H<sub>2</sub>S concentration in water: Method SIS028115.
- . 1993b. Measuring trace metal concentration in sediment: Method SIS028150.
- SOHLENIUS, G. J., STERNBECK, E. ANDREN, AND P. WESTMAN. 1996. Holocene history of the Baltic Sea as recorded in a sediment core from the Gotland Deep. *Mar. Geol.* **134**: 183–201.
- STERNBECK, J., AND R. O. HALLBERG. 2000. Sedimentary trace elements as proxies to depositional changes induced by a Holocene fresh-brackish water transition. *Aquat. Geochem.* **6**: 325–345.
- , AND P. ÖSTLUND. 2000. Metals in sediments from the Stockholm region: Geographical pollution patterns and time trends. *Water Air Soil Pollut.* **1**: 151–165.
- TALBOT, M. R., AND T. JOHANNESSEN. 1992. A high resolution paleoclimatic record for the last 27000 years in tropical West Africa from the carbon and nitrogen isotopic composition of lacustrine organic matter. *Earth Planet. Sci. Lett.* **110**: 23–37.
- TERANES, J. L., AND S. M. BERNASCONI. 2000. The record of nitrate utilization and productivity limitation provided by values in lake organic matter—a study of sediment trap and core sediments from Baldeggersee, Switzerland. *Limnol. Oceanogr.* **45**: 801–813.
- URBAN, N. R., K. ERNST, AND S. BERNASCONI. 1999. Addition of sulfur to organic matter during early diagenesis of lake sediments. *Geochim. Cosmochim. Acta* **63**: 837–853.
- VATTENPROGRAM. 2000. Vattenprogram för Stockholm—sjöar och vattendrag, Programperioden 1995–1999. Stockholm Vatten AB (Technical report in Swedish for 1995–99).

*Received: 21 September 2003*

*Accepted: 28 April 2004*

*Amended: 18 May 2004*