

Decadal diagenetic effects on $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ studied in varved lake sediment

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Abstract

To assess the long-term (27 yr) effects of sediment aging on stable carbon and nitrogen isotope values ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$), we used a collection of eight freeze cores of annually laminated (varved) lake sediment collected from 1979 to 2007 in Nylandssjön (northern Sweden). Previous research has shown that 20–23% of carbon and 35% of nitrogen is lost in 27 yr. Material from specific years was compared in the cores, e.g., $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of the surface varve of the 1979 core was followed in cores retrieved in 1980, 1989, 1993, 2002, 2004, and 2006. $\delta^{13}\text{C}$ increased by 0.4–1.5‰ during the first 5 yr. After this initial increase, only minor fluctuations were recorded. There is a good correlation between the magnitude in $\delta^{13}\text{C}$ changes and the initial carbon and nitrogen concentrations, indicating that the initial sediment composition is important for the ^{13}C fractionation. $\delta^{15}\text{N}$ gradually decreased by 0.3–0.7‰ over the entire 27-yr period. The lack of correlation with the initial sediment composition and the gradual decrease in $\delta^{15}\text{N}$ indicates a microbial control on $\delta^{15}\text{N}$ change. The diagenetic changes in the stable isotope values that occur in Nylandssjön are small, but of the same magnitude as the down-core variation in the varves deposited 1950–2006. Diagenetic effects should be considered when $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ are used to study organic matter sources or paleoproductivity, especially when dealing with recent trends or small changes. Based on our findings, diagenetic effects for $\delta^{13}\text{C}$ are observed during the first 5–10 yr, whereas no delimitation can be recommended for $\delta^{15}\text{N}$.

In paleolimnology, stable carbon (C) and nitrogen (N) isotope values ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) are used to derive information on C and N sources and pathways. In combination with other sedimentary proxies (e.g., total C, C:N ratio), $\delta^{13}\text{C}$ can also reveal information about long-term changes in nutrient availability and lake productivity (Meyers and Lallier-Vergès 1999; Meyers and Teranes 2001; Meyers 2003). Shifts in $\delta^{15}\text{N}$ may also indicate influences from anthropogenic N sources, such as fertilizers or sewage.

The source of $\delta^{13}\text{C}$ in sediment organic matter is either allochthonous or autochthonous, and the relative proportion of these two different components influences the isotopic composition of the sediment organic matter. To which degree a certain lake relies on allochthonous or autochthonous C sources is highly variable. Whereas the autochthonous C sources prevail in many lakes, the respiration of allochthonous C can exceed the gross photosynthetic C fixation in unproductive lakes (Duarte and Prairie 2005; Karlsson et al. 2007).

Allochthonous material originates from different sources, and the vegetation type in the catchment has a strong influence on the isotopic composition. For example, C_4 plants have considerably higher $\delta^{13}\text{C}$ values ($\delta^{13}\text{C} = -10\text{‰}$ to -15‰) compared to C_3 plants ($\delta^{13}\text{C} = -23\text{‰}$ to -31‰ ; Meyers and Teranes 2001). Thereafter, the isotopic composition of allochthonous material might be affected by degradation in soils and streams before entering a lake.

The isotopic composition of autochthonous material is also influenced by a large number of in-lake processes, and hence algal material has a very variable $\delta^{13}\text{C}$, both over time and between different lakes. One important factor for

this is C limitation, which is a result of the slow exchange of carbon dioxide (CO_2) over the water–atmosphere interface, and the fact that algae discriminate against ^{13}C in their photosynthesis. Thus, an increasing algal productivity results in an increase in $\delta^{13}\text{C}$ in the bioavailable C pool, which consequently also raises the $\delta^{13}\text{C}$ of the algae. High productivity can also distort $\delta^{13}\text{C}$ values if algae start to assimilate C through dissolved HCO_3^- ($\delta^{13}\text{C} = 1\text{‰}$) instead of dissolved atmospheric CO_2 ($\delta^{13}\text{C} = -7\text{‰}$) (Keeley and Sandquist 1992). In lake systems where C cycling is mainly controlled by primary production, the response can be observed seasonally as well as during periods with long-term eutrophication (Brenner et al. 1999; Lehmann et al. 2004a). As a result of the above-described processes, increases in organic matter accumulation together with increased $\delta^{13}\text{C}$ values in the sediment (organic matter) are usually interpreted as an increase in trophic level (Teranes and Bernasconi 2005). However, in eutrophic lakes with anoxic basins, microbially mediated C cycling processes can alter the C isotope value by adding organic matter with a low $\delta^{13}\text{C}$ value (Spooner et al. 1994).

As is the case for $\delta^{13}\text{C}$, there are a number of factors influencing the $\delta^{15}\text{N}$ composition of the bioavailable N pool in a lake, and consequently also the sediment. N-fixing cyanobacteria can decrease the isotopic value through atmospheric N_2 fixation (Brenner et al. 1999). Changes in the phytoplankton community or input from heterotrophic sources also affect the isotopic signal (Lehmann et al. 2004b). Denitrification in anoxic bottom waters and runoff from farms and human sewage can be manifested as an increase in the isotopic signal (Hodell and Schelske 1998; Lehmann et al. 2004b). In eutrophic Baldeggersee and Lake Lugano, Teranes and Bernasconi (2000) and Lehmann et al. (2004a), respectively, found that the $\delta^{15}\text{N}$ signal

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responded to fluxes of dissolved N from external sources rather than reflecting any occurring N transformation reactions.

In addition to the ambiguity about the isotope signatures of the source material and all the factors that influence the $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ isotopes in the water mass, the effects of diagenesis at the sediment–water interface and in the sediment might also change the isotope record of the organic matter ultimately preserved in the sediment. Most previous studies of diagenetic effects on isotopic composition either have looked at processes that occur over shorter time periods (Spooner et al. 1994; Bernasconi et al. 1997) or have been carried out on non-varved sediments, where there are some uncertainties associated with sediment mixing and dating (Hodell and Schelske 1998; Ostrom et al. 1998). In Lake Ontario, core-top isotope values of surface sediment reflected the $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ in sediment trap material (collected biweekly to monthly over 3 yr; Hodell and Schelske 1998). Results from the same study also indicated that there was no alteration of organic matter $\delta^{13}\text{C}$ in the sediment when comparing two cores from Lake Ontario sampled 6 yr apart at the same location. A few studies exist from varved lake sediments (Teranes and Bernasconi 2000, 2005; Neunlist et al. 2002). In eutrophic Baldeggersee (with artificially aerated lake bottom waters), the $\delta^{15}\text{N}$ of sediment trap material (collected approximately every 3 weeks over 2 yr) reflected core-top values (Teranes and Bernasconi 2000). Lehmann et al. (2002) came to a different conclusion in the eutrophic and anoxic Lake Lugano. When they compared sediment trap material to corresponding varves in a sediment core, they found an average depletion of 1.5‰ in $\delta^{13}\text{C}$ and 1.2‰ in $\delta^{15}\text{N}$ over 4–15 yr. These results also agree with an anoxic incubation experiment on lacustrine biomass from the same lake, in which $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ decreased 1.6‰ and 3‰, respectively, in 111 d. However, it is worth noting that the comparison of sediment trap material from different years with corresponding varves indicated that the $\delta^{15}\text{N}$ change was very variable, with both negative and positive changes.

This illustrates that many factors and processes may affect the $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ signals in lake sediments. Previous studies assessing diagenetic effects on isotopes in lake sediments typically cover only processes that occur within the first few years after deposition. In this study, we address the effects of diagenetic processes on $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ isotopes in lake sediments over nearly three decades. For this purpose we use a series of varved sediment cores retrieved from Nylandssjön since the 1970s to track the isotopic signal changes spanning an age from 0.5 up to 27 yr. The varved sediment provides a good time control and allows us to follow the sediment from individual years through time. Based on the unique Nylandssjön core series, we have shown in a previous study that 23% of C and 35% of N is lost within 27 yr (Gälman et al. 2008); based on those results we have now extended our analyses in this study to include stable isotopes.

Methods

Study site—Nylandssjön (62°57'N, 18°17'E) is a small (0.28 km²) dimictic boreal-forest lake, located at the coast

of the Gulf of Bothnia in northern Sweden. The lake is a circum-neutral, soft-water lake (calcium concentration in the water is 0.1 mmol L⁻¹; no calcium carbonate precipitation). The phosphorus concentration is about 20 $\mu\text{g L}^{-1}$, and regular oxygen depletion occurs in the hypolimnion in summer and in winter (Gälman et al. in press), which is a prerequisite for varve formation. In the 17.5-m-deep basin, varves have formed since the beginning of the 20th century because of cultural eutrophication (Renberg 1986). The lake has both autochthonous and allochthonous organic matter sources. Three years of sediment trap studies show a minimum for the C:N ratio of 8, a maximum of 15, and an average of 11 (Gälman unpubl.). Because C:N ratios of terrestrial organic matter range from 20 to 100 (Jasper and Gagosian 1989) and plankton and bacteria usually have C:N ratios in the range from 5 to 8 (Meyers 1994), on the order of 70% of the organic matter in Nylandssjön sediment is suggested to be of autochthonous origin.

The varves in Nylandssjön are thick and distinct. The most distinctive feature of a varve from Nylandssjön is the thin dark winter layer, which consists in large part of organic matter, but also of iron sulfide (FeS), which gives the blackish color (Shchukarev et al. 2008). Other seasonal layers are also discernable by the naked eye. Formation processes of this type of sediment were outlined by Renberg (1981a). The thickness of surface varves is ~1 cm, but thickness decreases to 2–3 mm in 50-yr-old sediment. Varve thickness decreases with age by compaction and remineralization, but the internal structure and color of the varves are not changed with time, and it is easy to identify the individual varves and to match cores taken in different years (Renberg 1986; Gälman et al. 2006, in press). For further details about the lake and sediment properties see Gälman et al. (2006, 2008).

Sediment sampling and subsampling—Sediment cores were taken using a freeze corer (Renberg 1981b) in late winter (usually March–April) from the lake ice surface. The cores used in this study were taken in 1979, 1980, 1989, 1993, 2002, 2004, 2006, and 2007. The uppermost varve in these cores represents sediment deposited during the previous year, i.e., in the 2007 core the surface varve is the sediment deposited in 2006 (most sediment is deposited between May and November). The cores were stored frozen until subsampling.

Subsampling followed Renberg (1981b) and was done in 2004–2007. Each frozen core was cleaned with a woodworker's hand plane. After cleaning, digital photographs were taken for documentation and then individual varves were cut and scraped off with a steel scalpel. For further details about sediment sampling and subsampling see Gälman et al. (2008).

Isotope analyses—The isotope analyses were done at the Department of Geology and Geochemistry, Stockholm University, Sweden, in November 2007. Freeze-dried samples were combusted with a Carlo Erba NC2500 analyzer connected to a Finnigan MAT Delta Plus mass spectrometer via a split interface to reduce the gas volume. The analyzer was calibrated against certified reference

Table 1. A list of the different certified reference materials (SRMs) used to calibrate the $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ analyses.

Certified SRM	$\delta^{13}\text{C}$ vs. VPDB* (‰)	Certified SRM	$\delta^{15}\text{N}$ vs. air (‰)
IAEA-CO-1	2.48	IAEA-N-1	0.43
IAEA-CO-8	-5.75	IAEA-NO-3	4.72
NBS18	-5.01	USGS25	-30.41
NBS19	1.95	—	—

* VPDB, Vienna Pee Dee belemnite.

materials (Table 1). All $\delta^{13}\text{C}$ is referenced to Vienna Pee Dee belemnite, and $\delta^{15}\text{N}$ is referenced to air (regarded as 0‰). Analytical quality was controlled using internal standards (peptone) and the precision of the analyses, calculated as one standard deviation ($n = 24$), was $\pm 0.2\text{‰}$ for $\delta^{13}\text{C}$ and $\pm 0.1\text{‰}$ for $\delta^{15}\text{N}$. To test the homogeneity of our samples, we also included a replicate sample for each 10th sample, giving a total of 13 replicates. All values for the replicate samples were within $\pm 0.2\text{‰}$ for $\delta^{13}\text{C}$ and $\pm 0.1\text{‰}$ for $\delta^{15}\text{N}$.

The approach for the assessment of diagenetic changes—To assess diagenetic effects, i.e., whether $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ change in the varves as the sediment ages in the lake bottom, isotopes were analyzed in years for which we have surface varves in the core series (i.e., varves deposited in 1978, 1979, 1988, 1992, 2001, 2003, 2005, and 2006) and we tracked how δ values changed over time. For example, the isotopic signal of the material deposited in 1978 (the surface varve in the core that was sampled in April 1979) was compared to the 1978 varve in the core taken in 1980 (after 1 yr in the lake bottom), in the 1989 core (after 10 yr), in the 1993 core (after 14 yr), and so on until the 2006 core (after 27 yr). In three of the cores, from 1979, 2004, and 2007, isotopes were also measured varve by varve from the surface varve and down-core, to assess between-core variability but also to facilitate the interpretation of diagenesis on the varve tracking series. In order to determine whether the diagenetic effects on the isotope values are related to properties of the initial sediment material or to the changes in C and N concentrations, data on total C, N, and C:N ratio (atomic ratio) previously published in Gälman et al. (2008) have also been used.

Results

The $\delta^{13}\text{C}$ down-core values show an increasing trend, from approximately -31.5‰ in 2006 to approximately -28.5‰ in the 1950s, whereas the $\delta^{15}\text{N}$ values for the same period decrease from approximately 3.1‰ to approximately 2.7‰ . The agreement between the 2007 core and the 2004 core is generally good for both $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ (Fig. 1a,b). When the overlapping section of the 2004 core and the 1979 core is compared, there are visible differences. Throughout the 13-yr-long overlapping period, the 1979 core has lower $\delta^{13}\text{C}$ values (-0.1‰ to -1.1‰) and higher $\delta^{15}\text{N}$ values (0.1‰ to 0.7‰) than the 2004 core, and the difference decreases with increasing age of the sediment (Fig. 1a,b). This result is completely in agreement with the results of our diagenetic comparison, in which surface varves are

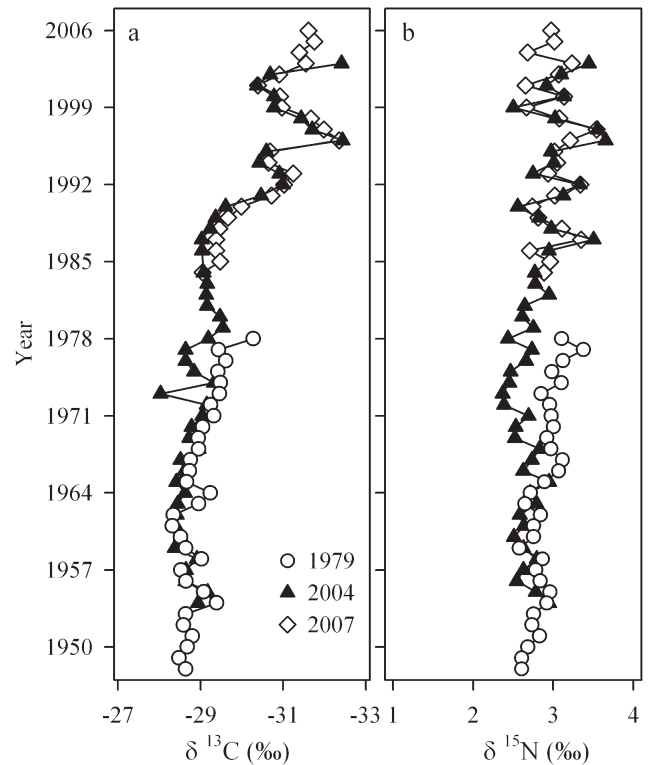


Fig. 1. (a) $\delta^{13}\text{C}$ and (b) $\delta^{15}\text{N}$ of the individual varves of the 1979, 2004, and 2007 cores plotted against calendar years.

tracked in cores taken in subsequent years (Fig. 2a,b). The analyses of this varve series show that $\delta^{13}\text{C}$ increases by $0.4\text{--}1.5\text{‰}$ during the first 5 yr and thereafter fluctuates without any obvious trend, whereas $\delta^{15}\text{N}$ shows a decrease of $0.3\text{--}0.7\text{‰}$ that continues throughout the 27-yr-long data series.

To visualize how fractionation of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ is related to changes in total C and N loss and changes in C:N ratio, we have plotted $\delta^{13}\text{C}$ change vs. relative total C loss (Fig. 3a), $\delta^{13}\text{C}$ change vs. C:N ratio change (Fig. 3b), $\delta^{15}\text{N}$ change vs. relative total N loss (Fig. 3c), and $\delta^{15}\text{N}$ change vs. C:N ratio change (Fig. 3d). All changes are calculated against the values of the initial material (i.e., surface varve). Neither the relative total C loss (Fig. 3a) nor the C:N ratio change (Fig. 3b) appears to have any effect on the magnitude of the $\delta^{13}\text{C}$ change; the slope of the different years varies substantially. For the $\delta^{15}\text{N}$ change the pattern is similar to $\delta^{13}\text{C}$ (i.e., no correlation) during the first part of the plots, which corresponds to the early change in C:N ratio and N concentration. When looking at the latter part of the plots, representing the time period from about 10 yr after sedimentation, the $\delta^{15}\text{N}$ change appears to have a much better correlation to both changes in total N concentration (Fig. 3c) and C:N ratio (Fig. 3d).

Discussion

Before the isotope results are assessed, a few points concerning the field sampling must be considered. First, the

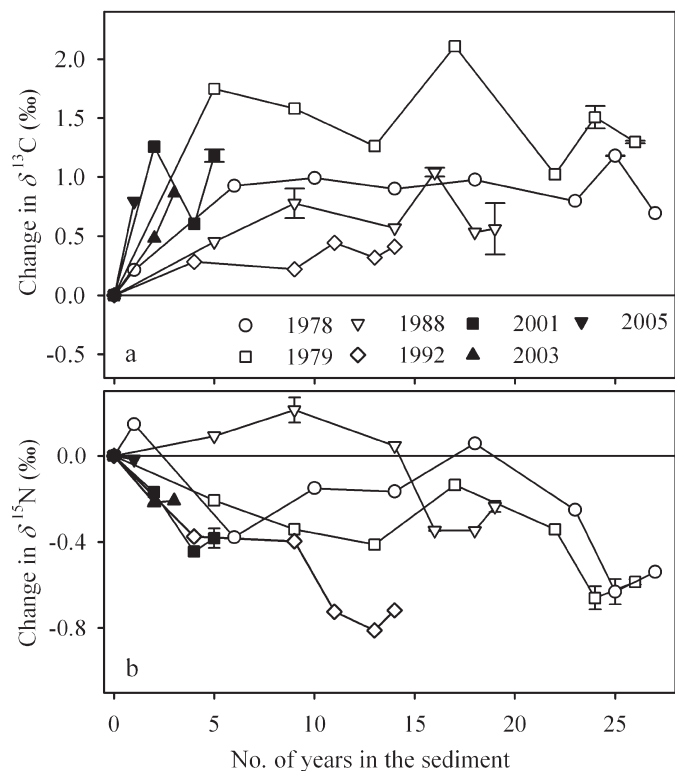


Fig. 2. Changes of (a) $\delta^{13}\text{C}$ and (b) $\delta^{15}\text{N}$ over time. The surface varve from each of the cores (sampled in 1979, 1980, 1989, 1992, 2002, 2004, and 2006) is tracked and analyzed in cores taken in subsequent years, and the deviation in $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ compared to the value of the surface varve (here set to zero) is plotted on the y axis. The x axis represents the number of years the surface varve has been in the sediment. Error bars indicate the variability between replicate samples.

sampling was performed during late winter and, when sampled, the sediment organic matter in the surface varve was therefore already up to 1 yr old. Consequently, it is not possible to compare our results to those from studies based on analyses of fresh algal material or material from sediment traps. Whereas such studies deal with the effects of early degradation (months and up to a year), our study looks at intermediate to long-term effects (years to decades) of degradation. Second, two sediment cores cannot be retrieved from exactly the same spot, and consequently the material composition might differ slightly between cores. Third, small differences between samples can also be introduced during subsampling, handling, and analyses. Nevertheless, previous studies have shown very good reproducibility for total C and N concentrations between cores (Gälman et al. 2006). This is in agreement with recorded trends in Fig. 1, where we find a good consistency between cores (e.g., peaks in 1954 and 1996 for $\delta^{13}\text{C}$ and peaks in 1987 and 1996–1997 for $\delta^{15}\text{N}$). The varve-tracking series (Fig. 2) also displays a consistent pattern for $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ change, even if the magnitude differs between years (especially for $\delta^{13}\text{C}$). $\delta^{13}\text{C}$ values increase during about the first 5 yr in the sediment and thereafter fluctuate without any obvious trend (Fig. 2a). In contrast to $\delta^{13}\text{C}$,

$\delta^{15}\text{N}$ seems to have a decreasing trend through out the entire 27-yr period encompassed by the dataset (Fig. 2b).

The conclusion that $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ change over time is further strengthened by the divergence between the profiles of the 1979 and 2004 cores (Fig. 1). After the 1979 core was retrieved and subsequently stored frozen, the diagenetic changes of the varves were stopped, “frozen in time,” whereas these changes proceeded in the lake bottom. Therefore, the $\delta^{15}\text{N}$ values of the overlapping sequence (1978–1954) are lower in the 2004 core than in the 1979 core, with a larger disagreement at the top and a smaller disagreement at the bottom, even though the difference still persists after more than 20 yr. For $\delta^{13}\text{C}$, the clear difference between the two cores lasts only for about 5 yr (maximum 10 yr), which is consistent with the results presented in Fig. 2. The relatively small difference between the 2004 core and the 2007 core (except for $\delta^{13}\text{C}$ in the top varve) may seem to contradict our conclusions. The 3 yr separating these two cores can explain the small differences in $\delta^{15}\text{N}$, but for $\delta^{13}\text{C}$, where the largest change occurs in the first 5 yr (Fig. 2a), one would expect to see a difference even in this short time period. However, as we have shown, some varve years show a relatively small overall change in $\delta^{13}\text{C}$ (e.g., 1992). The combination of the short time period separating the 2004 and 2007 cores and the fact that there can be small differences in the initial sediment composition between the two cores because of different sampling locations provide a reasonable explanation as to why we do not see a larger difference in $\delta^{13}\text{C}$ between the 2004 core and the 2007 core.

The different surface varves tracked in the varve series (Fig. 2a,b) show rather different magnitudes of change in $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ over time. To evaluate these differences, we correlated $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ change with different parameters of the initial material (total C and N concentrations, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$, and C : N ratio; Table 2). In this analysis we use only varves for which the varve-tracking series covers more than 4 yr (i.e., 1978, 1979, 1988, 1992, and 2001). For $\delta^{13}\text{C}$ the change was calculated as the mean change for samples older than 4 yr (i.e., for which the $\delta^{13}\text{C}$ change has more or less stopped), and for $\delta^{15}\text{N}$ the change was calculated as the mean of the two oldest samples. We find a good correlation between $\delta^{13}\text{C}$ change and the initial total C and N concentrations ($R^2 = 0.76$ and 0.72 , respectively). There is also a weak correlation between $\delta^{13}\text{C}$ change and the initial C : N ratio ($R^2 = 0.53$), whereas there seems to be no correlation between $\delta^{13}\text{C}$ change with either the initial $\delta^{13}\text{C}$ or the initial $\delta^{15}\text{N}$. For $\delta^{15}\text{N}$ change there is only a weak correlation with the initial $\delta^{15}\text{N}$ ($R^2 = 0.52$); all other parameters are uncorrelated to the $\delta^{15}\text{N}$ change. These analyses indicate that the $\delta^{13}\text{C}$ change is controlled by the composition of the source material, whereas the $\delta^{15}\text{N}$ change seems to be rather independent of the composition of the initial sediment material. These correlations, however, are done on a rather small number of samples, especially for the shorter time series (i.e., 2001).

The sediment consists of a mixture of organic matter from various sources with different $\delta^{13}\text{C}$ values and different behavior during degradation, which can explain the diagenetic ^{13}C fractionation. Proteins and carbohy-

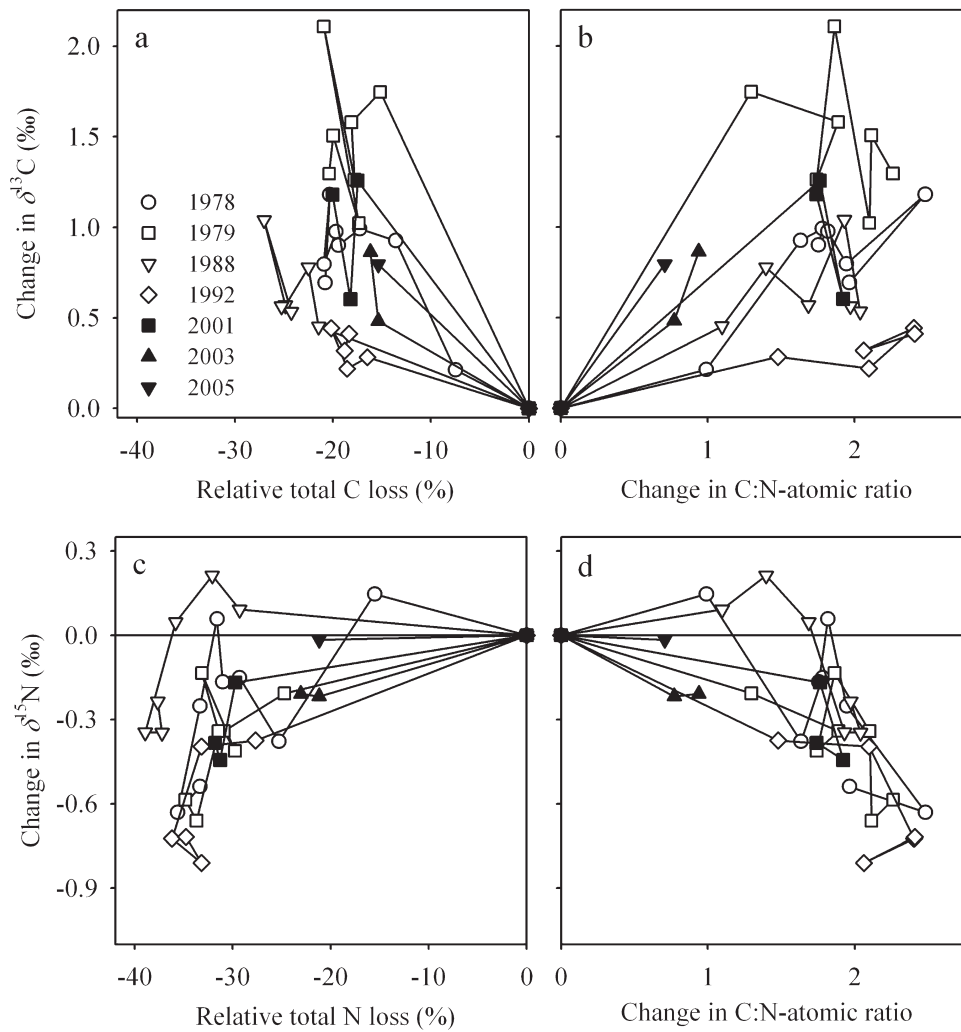


Fig. 3. (a) $\delta^{13}\text{C}$ change vs. relative total C loss, (b) $\delta^{13}\text{C}$ change vs. C:N atomic ratio change, (c) $\delta^{15}\text{N}$ change vs. relative total N loss, and (d) $\delta^{15}\text{N}$ change vs. C:N atomic ratio change. All changes are related to the initial material (i.e., surface varve) for that specific year. Data on C and N concentrations and C:N atomic ratio are from Gälman et al. 2008.

drates, which are easily degradable, are generally enriched in ^{13}C compared to total plant tissue, whereas resilient substances like lipids are depleted (Degens 1969; Deines 1980). A selective loss of proteins and carbohydrates caused by microbial degradation would lead to a decrease in $\delta^{13}\text{C}$ (Harvey et al. 1995). However, in Nylandssjön $\delta^{13}\text{C}$ increases during diagenesis (Fig. 2a), which might have a number of explanations. The up-to-1-yr-old sediment that comprises our starting material is already degraded when

the diagenetic study starts. Because of the degradation of proteins and carbohydrates, these surface varve samples can therefore already be depleted in ^{13}C (compared to fresh sediment) when they are sampled as surface varves. When degradation continues, more of the less susceptible (and isotopically depleted) material is degraded and the residual sediment material is enriched. It has also been shown that hydrolysis of proteins (Bada et al. 1989; Silber et al. 1992) and bacterial biosynthesis (Macko and Estep 1984) might

Table 2. R^2 values for the correlation for the observed changes in $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ compared to different organic matter quality parameters of the initial material (i.e., the surface varve). Only years in which the varve tracking covers more than 4 yr (i.e., 1978, 1979, 1988, 1992, and 2001) have been used. The change in $\delta^{13}\text{C}$ is calculated as the mean change for samples older than 4 yr. The change in $\delta^{15}\text{N}$ is calculated as the mean of the two oldest samples. Data on C and N concentrations and C:N ratio are from Gälman et al. 2008.

	Initial [C]	Initial [N]	Initial $\delta^{13}\text{C}$	Initial $\delta^{15}\text{N}$	Initial C:N ratio
Change in $\delta^{13}\text{C}$	0.76	0.72	0.00	0.17	0.53
Change in $\delta^{15}\text{N}$	0.10	0.10	0.13	0.52	0.07

lead to ^{13}C enrichment of the residual material. Plotting the $\delta^{13}\text{C}$ change against the C concentration loss (Fig. 3a) shows that as the total C concentration decreases the $\delta^{13}\text{C}$ increases. When the total C concentration becomes stable after 5–10 yr, the change in $\delta^{13}\text{C}$ almost stops. Taking these findings together with the results from the correlation analysis, we suggest that the $\delta^{13}\text{C}$ change is caused by a higher proportion of isotopically lighter (^{12}C) material in easily degradable fractions of the organic matter in the sediment, and when the C loss stops, the change in $\delta^{13}\text{C}$ therefore also stops. There seems to be no correlation between the magnitude of the $\delta^{13}\text{C}$ change and the change in C:N ratio (Fig. 3b; please note that in Fig. 3b,d we use the C:N ratio change, whereas in Table 2 we use the C:N ratio of the initial material). However, there is a tendency for the change in C:N ratio during the first year to be accompanied by a change in $\delta^{13}\text{C}$, whereas the later change in C:N ratio does not give rise to any change in $\delta^{13}\text{C}$. This probably can be explained by the fact that the N loss, and consequently also the C:N ratio change, continues for a longer time than the C loss (Gälman et al. 2008).

There are a large number of isotopic fractionation factors that are involved in the inorganic and biochemical cycling of N at the sediment–water interface and in the sediment (see table 1 in Talbot 2001). During diagenetic loss of N in lacustrine systems, kinetic fractionation is suggested to increase $\delta^{15}\text{N}$, i.e., the remaining N is enriched in ^{15}N (Talbot 2001). This is not the case in Nylandssjön, where the remaining N is depleted of ^{15}N and consequently $\delta^{15}\text{N}$ decreases in the varves over time (Fig. 2b). However, isotopic depletion of bacterial N can be caused by excretion of ^{15}N ammonia during bacterial biosynthesis (Macko and Estep 1984). Diagenetically caused isotopic depletion of ^{15}N in residual material in anoxic environments has also been reported in a few other studies in marine (Libes and Deuser 1988; Altabet et al. 1991) and freshwater conditions (Lehmann et al. 2002). When looking at the $\delta^{15}\text{N}$ change in Nylandssjön in relation to total N loss over time (Fig. 3c), this change behaves differently compared with the $\delta^{13}\text{C}$ change. During the initial phase with a large loss of N from the sediment, $\delta^{15}\text{N}$ does not change to any large extent. The main shift in $\delta^{15}\text{N}$ occurs when the N loss has more or less stopped. This decoupling between the total N loss rate and the $\delta^{15}\text{N}$ change leads us to believe that a microbial process is responsible for the fractionation of N isotopes, in which the microbes continue to repeatedly reuse the N in the sediment even when total N loss has more or less stopped. This would explain both the relatively linear appearance of the $\delta^{15}\text{N}$ change (Fig. 2b) and the continued $\delta^{15}\text{N}$ decrease even when total N loss has subsided (Fig. 3c). It would also explain the weak correlation of the quality of the initial material and the magnitude of the $\delta^{15}\text{N}$ change (Table 2) and why there is some correlation between $\delta^{15}\text{N}$ change and the latter part of the change in C:N ratio (Fig. 3d), which seems to be controlled by the small N loss ongoing even after 20 yr.

Here we present the first study on long-term diagenetic effects on stable C and N isotopes in lake sediments based on the analysis of varves, well controlled in time and space. Because almost all previous studies encompass only the

effects of early diagenesis, or are not well controlled in time, there are only a limited number of studies to compare our results with. Contradictory to our result, the results from studies of early diagenesis in Baldeggersee (with artificially aerated hypolimnion; Teranes and Bernasconi 2000) and Lake Ontario (with oxic hypolimnion; Hodell and Schelske 1998) suggest that the $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values of sediment organic matter record the primary signal despite a significant organic matter loss. Furthermore, Hodell and Schelske (1998) compared two cores collected in 1993 and 1994, and suggested that a difference in mean down-core $\delta^{15}\text{N}$ of 2‰ reflected the differential loss of ^{14}N between the two core sites, because one core site had a lower sedimentation rate and was presumed to have a higher organic matter degradation rate. However, Lehmann et al. (2002) compared sediment trap data with a varved sediment core in anoxic Lake Lugano and found an isotopic depletion of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ during sedimentary diagenesis (2–14 yr). The average $\delta^{15}\text{N}$ change of -1.2 ‰ units was larger in Lake Lugano than in Nylandssjön, and in contrast to the results of this study, they found a $\delta^{13}\text{C}$ decrease over time. The explanation is probably the different starting points, because the sediment trap organic matter from Lake Lugano was only 2–3 weeks old, whereas our youngest samples (the surface varves) were already up to 1 yr in age when they were compared to the aged sediment.

The limited number of well-controlled studies of long-term changes of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ in sediments does not give a conclusive picture of the diagenetic effects on stable isotope values. The reported results include a decrease, no alteration, and an increase of the isotopic values. These large differences, together with our results, i.e., that the $\delta^{13}\text{C}$ change is controlled by the quality of the initial material whereas the $\delta^{15}\text{N}$ change seems to be microbially controlled, indicate that there might be no uniform pattern in the diagenetic effects on isotopic composition between lakes. Differences between lakes in the initial sediment material composition, e.g., allochthonous vs. autochthonous ratio, and in conditions in the sediment, e.g., oxic or anoxic, which control the microbial communities, might make the direction and magnitude in $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ changes specific to individual lakes or lake types.

Although the changes that occur in the stable isotope values as the sediment ages may seem relatively small in Nylandssjön, diagenesis is a factor to consider when interpreting paleolimnological data, especially when interpreting small changes and changes in recent sediments. This is underlined by the fact that the diagenetic change with time in Nylandssjön is of the same magnitude as the variation in the varves during the period 1950–2006. When interpreting $\delta^{13}\text{C}$ trends in lacustrine sediments, changes within the first 5–10 yr in the top sediment should not be uncritically interpreted as being caused by changes in limnological conditions, because this study shows that they can be caused by diagenesis. When it comes to $\delta^{15}\text{N}$, it is more difficult to give valid recommendations, because the diagenetic change encompasses the whole surveyed period of 27 yr, and it cannot be ruled out that $\delta^{15}\text{N}$ change continues even after this period.

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