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Carbon budget of a mid-latitude, groundwater-controlled lake: Isotopic evidence for the importance of dissolved inorganic carbon recycling

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Abstract—The carbon cycle of the groundwater-controlled Lake Gościąż, Poland, was investigated. The study covered a period of intensive primary production from April to November 1993. Physiochemical and isotope characteristics of the lake system (depth profiles of temperature, pH, alkalinity, concentrations of Ca^{2+}, dissolved inorganic carbon (DIC), and $\delta^{13}C$ of DIC) were monitored on a monthly basis. Carbon isotope compositions of calcite samples collected in the sediment traps were determined.

The carbon cycle of the lake was simulated using a numerical model which accounts for all basic processes controlling concentration and carbon isotope composition of DIC. The model allowed researchers to quantify the relative importance of sources and sinks of carbon influencing the $\delta^{13}C_{DIC}$ in the epilimnion and, consequently, of the authigenic calcite deposited in the sediments. Inorganic carbon dissolved in groundwaters feeding the lake appeared to be insufficient to maintain the concentration and $\delta^{13}C$ of DIC in the epilimnion in the observed range. DIC originating from decomposition of organic matter is a crucial element of the carbon budget of the lake. For the entire studied period, it accounted for about two-thirds of the total DIC supplied to the epilimnion; its average $\delta^{13}C$ was −25.5‰. Decomposition of organic matter within the lake appeared to be at least one-third higher than its production. Of the external sources of carbon, groundwater inflow contributes 50%, terrestial biomass, 30%, and atmospheric CO_2, 20% of the total carbon input to the lake. Evasion of CO_2 and CH_4 drives the average $\delta^{13}C_{DIC}$ in the epilimnion to the values which are considerably higher than $\delta^{13}C$ of the external sources of carbon. *Copyright © 1997 Elsevier Science Ltd*

1. INTRODUCTION

Groundwater-controlled lakes are among the most sensitive systems responding to environmental changes now taking place on the continents. Whereas water balance of such a lake is a sensitive function of precipitation regime and the land-use practices, their aquatic chemistry and biology respond quickly to fluctuations of climate and to man-induced changes in the catchment area. Lacustrine sediments preserve valuable records of paleoenvironmental conditions, with the time resolution approaching, in the case of laminated sediments, the resolution of paleoclimatic records preserved in ice cores (Goslar et al., 1995).

Over the past three decades, the isotopes of carbon and oxygen were used in lake studies to decipher paleoenvironmental conditions from the sedimentary records. The ^{18}O content of authigenic lacustrine carbonates preserved in sediments may be a paleothermometer and/or indicator of changes in the water balance of a lake (e.g., Stuiver, 1970; Lister, 1988; Talbot, 1990; Gasse and Van Campo, 1994). The isotopic composition of lake water is used to derive components of the water balance, in particular for lakes with significant groundwater inflow and outflow rates (e.g., Zimmermann, 1978; Zuber, 1983; Gonfiantini, 1986; Krabbenhoft et al., 1990). The carbon isotope ratio ($^{13}C/^{12}C$) of authigenic calcite has been considered an indirect indicator of climatic conditions (Stuiver, 1970). The equilibrium isotopic enrichment between dissolved inorganic carbon (DIC) and calcite changes only by few hundreths of permil for 1°C while the isotopic composition of DIC is influenced by various physiochemical and biological processes occurring in the lake. Thus, the quantitative interpretation of the $\delta^{13}C$ record preserved in lacustrine calcite is commonly problematical.

The $\delta^{13}C$ records preserved in lacustrine calcite are often interpreted in terms of variations in the photosynthesis-respiration cycle within the lake and/or as indication of varying intensity of CO_2 exchange between the lake and the atmosphere (McKenzie 1982, 1985; Turner et al., 1983; Fritz, 1984; Quay et al., 1986; Herczeg and Fairbanks, 1987; Andrews et al., 1993). Photosynthetic removal of CO_2 from the surface waters promotes precipitation of calcite and leads to enrichment of the remaining DIC in ^{13}C. During subsequent decomposition of organic matter, isotopically light inorganic carbon is released back into the lake waters. The exchange of CO_2 between the lake and the atmosphere usually leads to enrichment of DIC in ^{13}C. Numerous factors influencing $\delta^{13}C_{DIC}$ are interrelated; therefore, qualitative interpretations of $\delta^{13}C$ records in authigenic calcite may lead to equivocal conclusions concerning mechanisms of carbon cycling in the studied lake system. For example, high productivity causes increased burial of organic matter, which results in increase in ^{13}C content in authigenic carbonate records (Scholle and Arthur, 1980; Dean and Stuiver, 1993). McKenzie (1982, 1985) showed that increased productivity may cause both increase and decrease in $\delta^{13}C$ of calcite, depending on circulation patterns within the lake. Schelske and Hodell (1991) found that the relationship between primary productivity and $\delta^{13}C$ of calcite is influenced by seasonal progression of calcite precipitation.

There are numerous examples of mathematical models describing evolution of DIC in groundwater systems which were developed mainly for the purpose of ^{14}C dating (e.g., Mook 1976, 1980; Wigley, 1975; Reardon and Fritz, 1978; Salomons and Mook, 1986). Similar models were applied to other natural water systems such as speleothems (Hendy, 1971; Duliński and Różański, 1990), calcite depositing streams (Usdowski et al., 1979; Dandurand et al., 1982), and soil calcite (Cerling, 1984; Salomons and Mook, 1986; Dörr and Münnich, 1987). Wigley et al. (1978) presented a general theoretical framework for such models. This approach combines mass balance calculations with a Rayleigh distillation scheme to predict both chemical and isotopic evolution of a system. We do not have a comprehensive model describing isotopic evolution of DIC in lakes. The majority of the existing studies address selected aspects of the problem such as the effects of chemically enhanced absorption of CO_2 from the atmosphere on $\delta^{13}C_{DIC}$ in a soft-water lake (Herczeg and Fairbanks, 1987) or the diagenetic decomposition of organic matter and subsequent diffusion of DIC affecting the porewater $\delta^{13}C_{DIC}$ profiles from lake sediments (Herczeg, 1988). Quay et al. (1986) used chemical and isotopic data to build a carbon balance model with CO_2 invasion and net organic carbon production rates. McConnaughy et al. (1994) tracked patterns of carbon cycling within a lake using a chemical budget approach.

Our study was undertaken with the goal of quantifying parameters that control the isotope composition of calcite precipitating in Lake Gościąż, Poland. Annually laminated sediments of this lake cover the last thirteen thousand years and represent a unique record of paleoenvironmental changes in central Europe during the Late Glacial and Holocene (Różański et al., 1991; Goslar et al., 1995). The paper presents the results of chemical and isotopic investigations of the carbon cycle in Lake Gościąż carried out from April to November 1993. The carbon cycle of the lake was then simulated, using a numerical model which accounts for basic processes controlling carbon fluxes in the lake as well as carbon isotope composition of DIC and the precipitated calcite. Measurements and modelling of $\delta^{18}O$ for the lake waters and calcite will be discussed in detail in a forthcoming paper.

2. STUDY SITE AND METHODS

Lake Gościąż (surface 0.45 km^2, volume $2.1 \cdot 10^6$ m^3, max. depth 22 m, mean depth 4.5 m) is located in central Poland in the Gostynin lake district (Fig. 1). Lake Gościąż is the largest of four lakes drained by a small stream, Ruda. The catchment of the lake is at present entirely forested and free of direct anthropogenic influences. The basin cuts through Quaternary sands and gravels of glacial origin and reaches Tertiary rocks (Madeyska, 1991). The lake is fed mainly by numerous springs discharging along the 1 km long southern shore, below a 4 m high escarpment (some springs may also discharge underwater). Preliminary studies aimed at establishing the water balance of the lake suggest that groundwater constitutes more than 90% of the total inflow (Gierszewski, 1993). Lake Gościąż is connected by a shallow, wide channel, (Fig. 1) with Lake Mielec, the latter drained by the Ruda stream. The shallow groundwater aquifer feeding the lake is composed mainly of glacial sands and gravels containing ground carbonate minerals derived from mechanical erosion by an ice sheet.

The characteristic morphological feature of the Lake Gościąż basin is two relatively small, well-defined regions of deep water: 22 m in the center of the lake and <12 m in the western part. This configuration leads to sediment focusing and high sedimentation rates (over 1 cm per year; Goslar, 1993) in the deeper parts of lake. The bottom sediments consist mainly of authigenic calcite (up to 80%) and organic matter (Wicik, 1993).

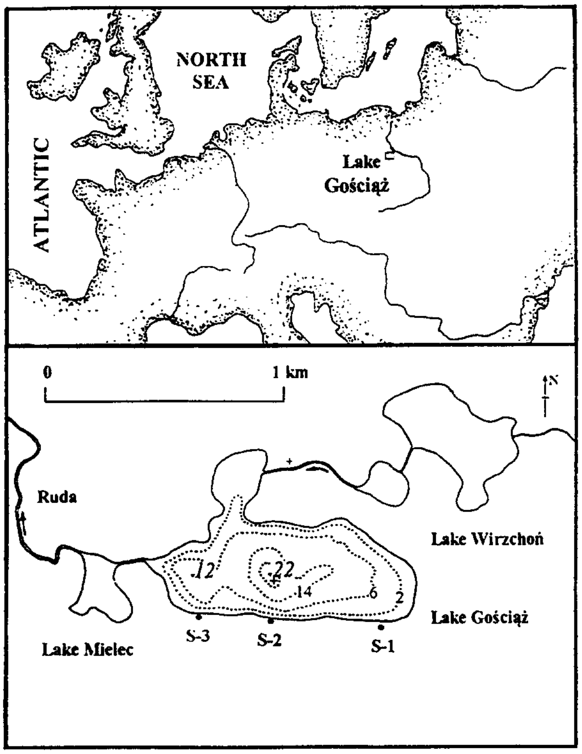

Fig. 1. (a) Location of Lake Gościąż in central Europe. (b) Schematic map of the lake with sampling points indicated by crosses (lake and stream Ruda) and filled circles (monitored springs).

Samples of water and settling material were collected at approximately monthly intervals between 2 April and 16 November 1993. Sampling covered the period of the most intensive primary production. The lake water samples for isotope and chemical analyses were collected at several depths (usually 1, 3, 5, 8, 13, and 18 m) in the deepest part of the lake. Additional sampling was done between 5 and 9 July 1994 to study short-term changes of the chemical parameters. Three major springs located along the southern shore (Fig. 1) were also sampled. Waters of the Ruda stream were monitored upstream from the lake. *In situ* temperatures were determined, and $HgCl_2$ was added to water samples to prevent biological activity.

Selected analyses (pH, alkalinity, $[Ca^{2+}]$) were performed in the field laboratory within a few hours of sampling, using ion selective electrodes (ORION). Analyses repeated the next day on the samples stored in a refrigerator showed no significant changes. A glass pH electrode was also used for alkalinity measurements, following manufacturer's protocol. Analytical reproducibilities (1 σ) for the above-mentioned analyses were better than 0.03%, 4%, and 1%, respectively. The equilibrium equations for the carbonate system were used to calculate the concentrations of CO_2, HCO_3^-, and CO_3^{2-} in the lake waters and the Saturation Index for calcite. These parameters were then recalculated for the *in situ* temperatures of the water samples. Only pH and SI were significantly affected by the water temperature differences between sampling and measurement; maximum change for both parameters was 0.15. For most of the epilimnetic samples, this change was much smaller. The ion selective electrode used for $[Ca^{2+}]$ determination is sensitive only to this form of calcium. Total dissolved calcium content was determined for a few samples after filtration through 0.45 μm filter by use of the ICP-AES method. These results were 10–15% higher than those obtained with the ion selective electrode. This difference is due to presence of ion pairs and colloidal forms of calcium.

Fluxes of organic matter and precipitated calcite were determined with the aid of sediment traps deployed in the deepest part of the lake (Giziński et al.,). The traps were located at a depth of 10 m, below the thermocline. The two types of traps used were cone-shaped traps with a diameter of 0.7 m to collect settling matter during one-day periods and pipe traps with a diameter of 0.1 m, replaced every month (Giziński et al.,). The trap data (flux densities of calcite and organic matter) were used to calculate the net photosynthesis and calcite production in the epilimnion. The Redfield stoichiometry was used to convert mass of the organic matter collected in the traps to net photosynthesis expressed in moles of carbon assimilated per unit time. Calcite is practically the only carbonate mineral present in the samples of Lake Gościąż sediments. Only trace amounts of other carbonate minerals (rhodochrosite, siderite) and no dolomite and aragonite were found (Łącka and Starnawska,)

The carbon isotope ratios of DIC were determined on CO_2 liberated from 500 mL of water after acidification. Evacuation of CO_2 to the vacuum line was enhanced by magnetic stirrer; CO_2 was collected in traps cooled with liquid nitrogen. Commonly, extraction was carried out a few days after sampling. Samples stored in a refrigerator up to 2 months did not reveal significant changes in $\delta^{13}C_{DIC}$ (Wachniew, 1995). The overall precision of $\delta^{13}C_{DIC}$ determinations was better than 0.3‰. The carbon isotope ratio in calcite samples from sediment traps was analysed using the standard method based on the reaction with phosphoric acid (McCrea, 1950). The overall precision of $\delta^{13}C$ analyses of calcite samples was around 0.1‰. The carbon isotope ratios of DIC and calcite are expressed relative to V-PDB standard (Coplen, 1994).

3. RESULTS AND DISCUSSION

3.1. Water Chemistry

Temporal variations of mean pH, DIC, and $[Ca^{2+}]$ in the epilimnion, the monitored spring waters, and Ruda stream are summarized in Fig. 2a–c. Although the spring waters are not uniform in their chemistry, they reveal considerably lower pH and higher Ca^{2+} concentrations than the epilimnetic waters. With respect to DIC content, spring and epilimnetic waters are less distinguishable. The lowest pH and DIC are from spring S-1, but it is placed in a depression filled with peat where properties of discharging groundwaters can be modified. Two other springs seem to be more representative of the original groundwater input. The waters of Ruda stream, flowing from the upstream lakes, are depleted in DIC and Ca^{2+} in comparison to Lake Gościąż. However, Ruda, supplying only 10% of water inflow, has little influence on water balance and chemistry of the lake waters.

Figure 3 shows the depth profiles of temperature, pH, and SI, as well as of Ca^{2+}, DIC, and CO_2 concentrations, in the Lake Gościąż waters recorded over the whole studied period of 1993. Thermal stratification divides the lake into two parts with contrasting physiochemical conditions. Permanent supersaturation of the surface waters with respect to calcite promotes precipitation of calcite. Concentrations of Ca^{2+} and DIC in the epilimnion decreased over the period of thermal stratification due to their removal with settling organic matter and calcite. Highest pH and SI values, associated with the lowest CO_2 concentrations, were usually observed between 3 and 5 m, pinpointing the zone of the most intense primary production. The maximum supersaturation, 7.5-fold with respect to calcite observed in Lake Gościąż, is typical for mesotrophic lakes (Küchler-Krischun and Kleiner, 1990). Waters in the hypolimnion were undersaturated with respect to calcite over the stratification period. Release of DIC from decomposition of organic matter and dissolution of calcite in the bottom waters and in the sediments should have resulted in constant increase in DIC and $[Ca^{2+}]$ in the hypolimnion. In fact, a reverse trend was observed over some intervals, especially for Ca^{2+}, indicating removal of both species from the hypolimnion. Between 5 July and 7 September, parallel decrease and subsequent increase in DIC and $[Ca^{2+}]$ occurred in the entire water column (Fig. 2d,e). This could not be an analytical artifact because parallel patterns were not observed for DIC and $[Ca^{2+}]$ in groundwaters and Ruda (Fig. 2).

Short-term changes of the physiochemical parameters were observed in the epilimnion daily between 5 and 9 July 1994 (Fig. 4). The pH and SI values were relatively high, as well as primary productivity (Wachniew, 1995). From 5 to 7 July, the weather was stable, with high air temperatures, low wind speed, and high insolation. During this period, algal photosynthesis and concomitant precipitation of calcite

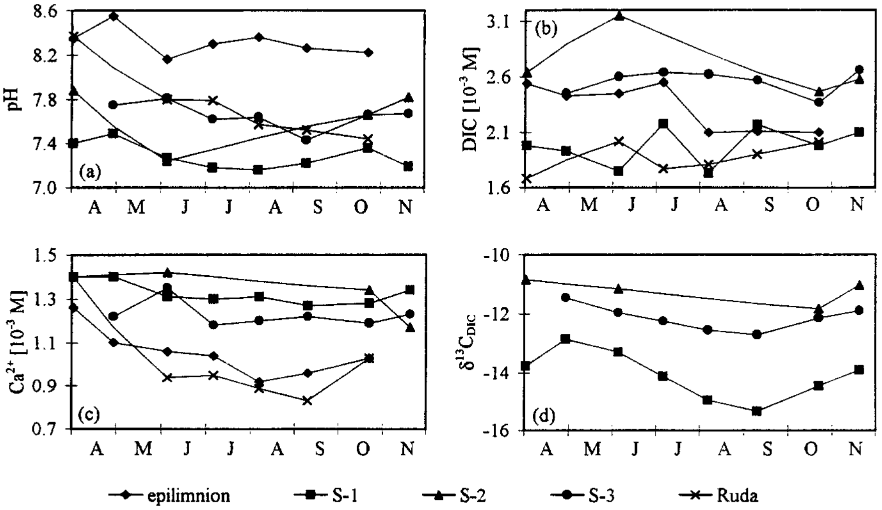

Fig. 2. A comparison of pH, DIC and Ca^{2+} concentrations, and $\delta^{13}C_{DIC}$ determined in 1993 in the epilimnion of Lake Gościąż (mean values), the monitored springs, and stream Ruda.

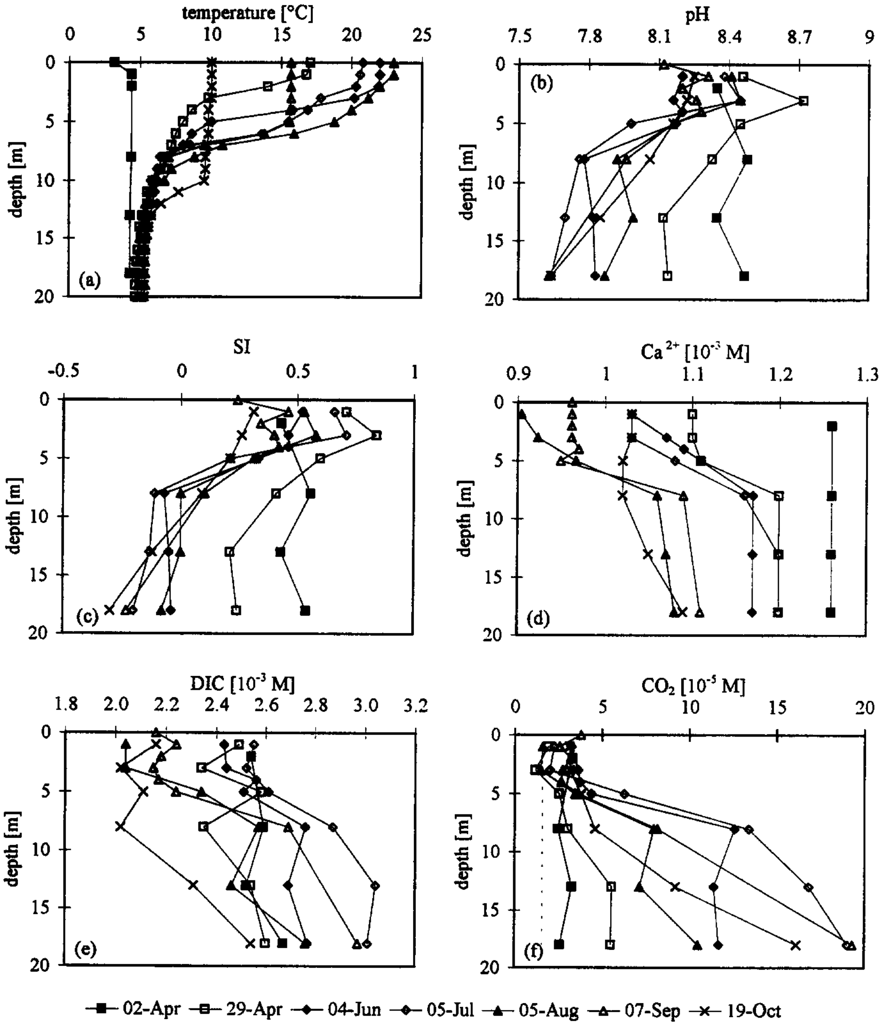

Fig. 3. Depth profiles of the physiochemical parameters monitored in Lake Gościąż from 2 April to 19 October 1993. Dashed line represents CO_2 concentration in equilibrium with the atmosphere.

caused a significant decrease in DIC and [Ca^{2+}]. On 8 July, the air temperature dropped by almost 10°C, wind speed increased, and intensive rain started. These drastic weather changes significantly decreased the vertical gradients of temperature and concentrations of dissolved species. We explain this as due to partial exchange of waters between the epi- and hypolimnion and/or release of DIC and Ca^{2+} from the sediments in shallow parts of the lake. Wind-induced turbulences and thermal convection caused by cooling of water surface result in mixing of water column. Whole variety of mixing processes control mass fluxes within the epilimion but also across the thermocline and water-sediment interface. These processes may affect concentrations of DIC and Ca^{2+} in the whole lake (Imboden and Wüest, 1995).

3.2. Carbon Isotopes

$\delta^{13}C_{DIC}$ values of spring waters varied seasonally, becoming most negative in summer (Fig. 2d). This seasonality, which is also seen in pH data, likely derives from seasonal changes in the biological activity in soils. During the summer months, the infiltrating waters are exposed to higher partial pressure of biogenic CO_2. Carbonates in these soils have been leached to a depth of about 3 m (Wicik and Więckowski, 1991). Consequently, dissolution takes place in a closed system, where half of DIC derives from the biogenic CO_2 (Salomons and Mook, 1986). These conditions are reflected in $\delta^{13}C_{DIC}$ values of the spring waters (−15‰ ÷ −11‰) which are intermediate between typical $\delta^{13}C$ values for carbonates of marine origin (0‰) and for organic matter (−28‰). Water from spring S-1, discharging through peat, seems to contain more biogenic DIC.

Figure 5 shows the depth profiles of $\delta^{13}C_{DIC}$ in the lake obtained between April and October 1993. The observed patterns of temporal and spatial distribution of $\delta^{13}C_{DIC}$ are similar to other mid-latitude lakes (Killey and Fritz, 1979; McKenzie, 1982, 1985; Quay et al., 1986; Herczeg and Fairbanks, 1987; Hollander and McKenzie, 1991). During spring overturn (profile obtained on 2 April), the lake was homogeneous with respect to $\delta^{13}C_{DIC}$. Later, $\delta^{13}C_{DIC}$ gradually increased in the epilimnion and decreased in the hypolimnetic waters. The maximum difference within the $\delta^{13}C_{DIC}$ profiles

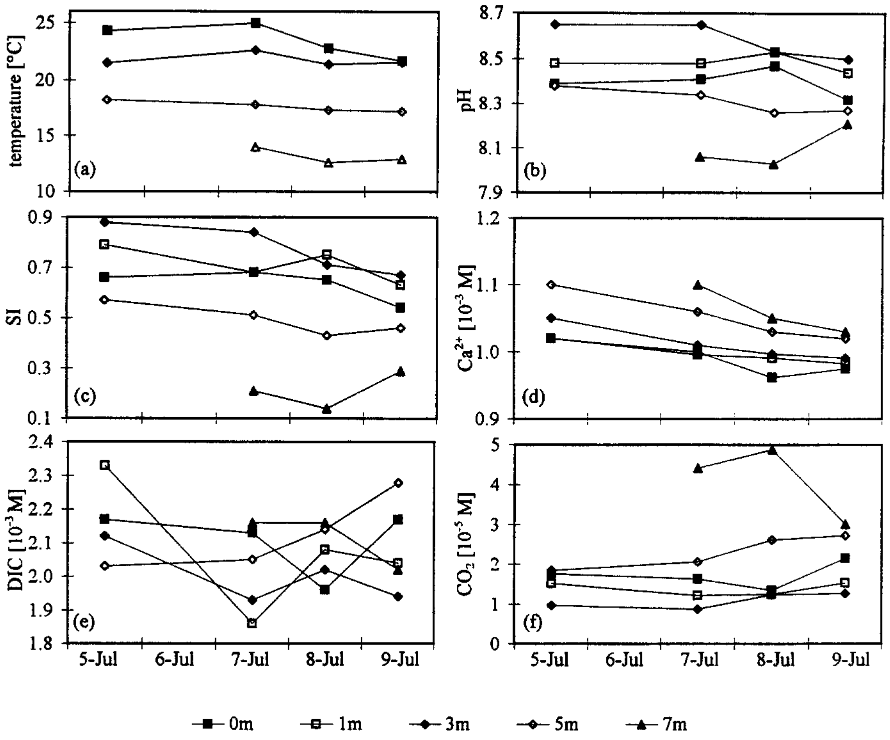

Fig. 4. Short-term variability of the physiochemical parameters in the epilimnion of Lake Gościąż monitored from 5 to 9 July 1994.

in the epilimnion and hypolimnion occurred in September; the October profile revealed partial mixing of the lake.

Epilimnetic $\delta^{13}C_{DIC}$ values shift only 1.5‰ positive due to preferential assimilation of ^{12}C-enriched CO_2 by algae during photosynthesis; the hypolimnetic values become 3.5‰ more negative due to the release of ^{12}C-enriched CO_2 by organic matter decay in the water column and in the sediments. This relatively small increase in $\delta^{13}C_{DIC}$ in the epilimnion can be explained only by continuous addition of substantial amounts of isotopically light carbon. The potential reasons for the replenishment of light carbon to the eplimnion are (1) inorganic carbon released during decomposition of organic matter in the sediments and in the waters, (2) DIC contained in the groundwaters feeding the lake ($\delta^{13}C_{DIC}$ between −15‰ and −11‰), and (3) invasion of CO_2 from the atmosphere, especially chemically enhanced invasion when $\delta^{13}C$ of invaded CO_2 can be as low as −20‰ (Herczeg and Fairbanks, 1987). However, the extremely low pCO_2 and high pH values, favouring chemically enhanced invasion of CO_2, were not observed in the surface waters.

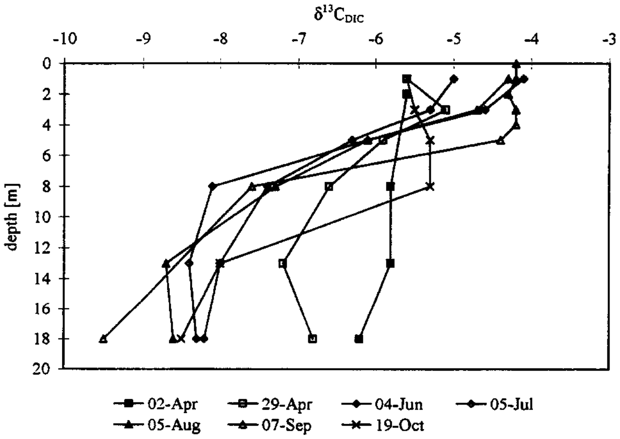

Fig. 5. Depth profiles of $\delta^{13}C_{DIC}$ determined in 1993 in Lake Gościąż.

Although no measurements were made during the winter months, the available data indicate that between the autumn and spring overturns, the lake waters were replenished with DIC and Ca^{2+} (Fig. 2), apparently with little impact on $\delta^{13}C_{DIC}$. Data from Lake Greifen, Switzerland (McKenzie, 1982; Hollander and McKenzie, 1991) also document small changes of $\delta^{13}C_{DIC}$ between December and May. A complete mixing of Lake Gościąż with the patterns of DIC and $\delta^{13}C_{DIC}$ from 7 September should produce the uniform $\delta^{13}C_{DIC}$ value of −5.3‰, which is close to the values of 2 April, before the onset of summer stratification. Outside the period of intensive primary production, isotopically light DIC is still supplied with groundwater and recycled from the sediments, leading to elevated concentrations of CO_2 in the lake. Evasion of excess CO_2 to the atmosphere enriches DIC in ^{13}C. This negative feedback may help maintain $\delta^{13}C_{DIC}$ on a relatively stable level between the overturns.

Relatively small variability of $\delta^{13}C_{DIC}$ in the epilimnion resulted in even smaller ranges of $\delta^{13}C$ for calcite precipitated during the studied period (Fig. 6). The apparent isotopic enrichments of the calcite samples collected in the sediment traps, when compared with $\delta^{13}C_{DIC}$ of the water samples collected in the epilimnion, ranged from 1.9‰ to 4.1‰,

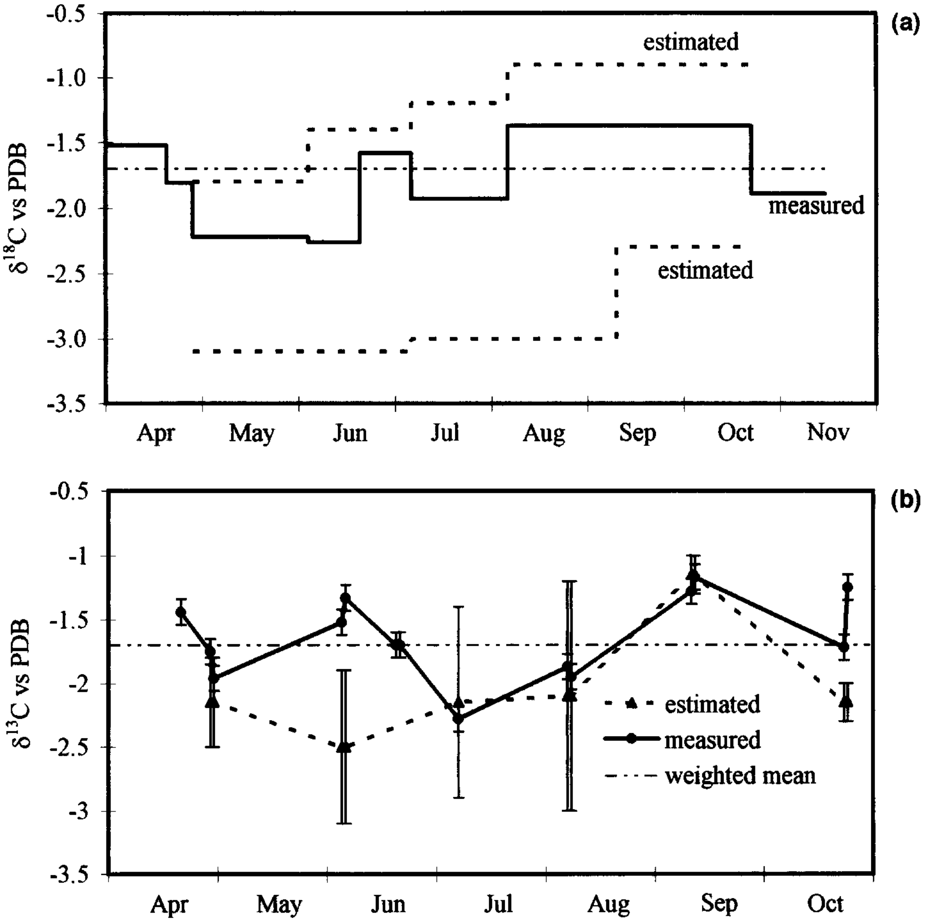

Fig. 6. A comparison of measured and estimated δ^{13}C of calcite for samples collected in sediment traps over (b) one day and (a) longer periods. Wide ranges of estimated values result from variability of $\delta^{13}C_{DIC}$ and water temperatures in the epilimnion. Fractionation factors used for estimation were taken from Bottinga (1968) for fractionation between gaseous CO_2 and calcite and from Zhang et al. (1995) for fractionation between HCO_3^- and gaseous CO_2.

in agreement with the values obtained in other studies (Turner, 1982; Hollander and McKenzie, 1991). However, it should be noted that the sediment traps located 10 m below the water surface integrate the flux of calcite precipitated in the overlying water column over the period of approximately one month, whereas the water samples for analyses of $\delta^{13}C_{DIC}$ were collected only when the traps were replaced. Therefore, this apparent enrichment cannot be regarded as the actual isotopic enrichment associated with precipitation of the particular portion of calcite. Moreover, the physiochemical parameters close to the surface of phytoplankton organisms may be considerably different from the analysed bulk solution even if biological processes are not directly involved in calcification. Consequently, even though calcite precipitates in equilibrium conditions, the overall enrichment between DIC and calcite may vary in a wide range due to the above-mentioned factors. Figure 6 compares the measured and estimated equilibrium δ^{13}C values of calcite. The expected values vary in wide ranges due to the large variability of $\delta^{13}C_{DIC}$ and the temperature of water within the epilimnion. The measured values generally fall into the expected range, with the exception of a few samples collected over a one day period. However, sediment trap experiments cannot unequivocally answer the question of whether isotopic equilibrium is preserved during precipitation of calcite.

4. CARBON BUDGET OF THE LAKE

4.1. Description of the Model

In order to better understand the mechanisms controlling the carbon budget of Lake Gościąż, an attempt was made to model the evolution of DIC and its δ^{13}C in the epilimnion of this lake. Figure 7 shows the major sources and sinks of DIC for the epilimnion of the lake included in the model. DIC is supplied and removed from the lake by inflowing (I) and outflowing (O) waters. Phytoplankton (N) and calcite (K) are produced in the epilimnion and settle removing carbon from the epilimnion. CO_2 is assimilated by phytoplankton during photosynthesis (P) and released during dark respiration (D). Microbial decay of organic matter and dissolution of calcite in the waters and the sediments produce DIC which replenishes the epilimnion (R). The lake was supersaturated with CO_2 (Fig 3f); therefore, the net flux of CO_2 is to the atmosphere (A).

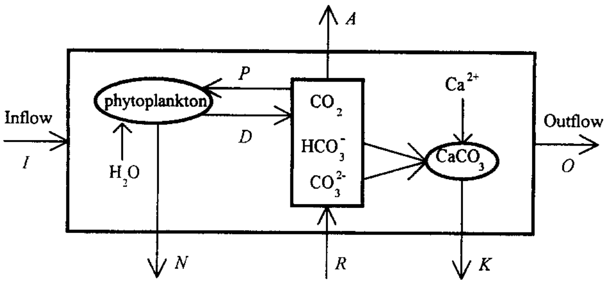

Fig. 7. The sources and sinks of carbon in the epilimnion. *I* and *O* are fluxes of DIC contained in inflowing and outflowing waters, respectively. *A* is the net flux of CO_2 from the epilimnion to the atmosphere. *P* is rate of photosynthetic assimilation of CO_2 by algae; *D* is rate of dark respiration. Net result of those two processes is net photosynthesis (*N*). *K* is rate of calcite precipitation.

The chemical and isotopic evolution of DIC was modeled within the framework of the idealized carbonate system consisting only of water and DIC. The presence of other dissolved species was taken into account by imposing on the calculations the pH and ionic strength values observed in the lake. Calculations were carried out in small time steps (20 min). In every step, adequate amounts of carbon related to the above-mentioned sources and sinks were added to and substracted from the epilimnetic pool. New concentrations of CO_2, HCO_3^-, and CO_3^{2-} were calculated using the equilibrium equations for the given temperature and the mass conservation equations for total carbon (see Appendix). The equilibrium constants were adopted from Plummer and Busenberg (1982) for carbonate species and from Harned and Hamer (1933) for water dissociation constant. Carbon isotope ratios of all DIC species were calculated assuming full isotope equilibrium. Isotope fractionation factors were taken from Zhang et al. (1995).

Mean rates of photosynthetic assimilation of CO_2 (*P*) and calcite production (*K*) were calculated from the sediment trap data. The amount of organic matter collected in the traps corresponds to the net photosynthesis (*N*). It was assumed that 12 h periods of photosynthesis and calcite precipitation alternate with 12 h periods when only dark respiration takes place. Under such conditions, the rate of CO_2 consumption (*P*) is greater than the net photosynthesis (*N*) by the rate of dark respiration (*D*). The rate of respiratory release of CO_2 by algae (*D*) was assumed to equal 20% of the rate of CO_2 assimilation (*P*) during the light period (Laws and Bannister, 1980; Laws et al., 1990). Photosynthetic activity of submerged macrophytes was not taken into account because these plants cover only the small, shallowest parts of the lake (Kępczyński and Noryśkiewicz, 1993) and their biomass is thus expected to be small in comparison with that of algae.

Other unknown parameters of the model are the isotope fractionation during assimilation of dissolved CO_2 by phytoplankton and the isotopic composition of CO_2 released to water during dark respiration. Photosynthetic discrimination of $^{13}CO_2$ depends on the availability of CO_2 and varies between 0‰ for low concentrations of dissolved CO_2 and −25 ÷ −30‰ for the excess of dissolved CO_2 (Degens et al., 1968; Deuser et al., 1968; Calder and Parker, 1973; Vogel, 1993). Given that photosynthesis in this lake was not CO_2 limited (cf. Fig. 2), the effective fractionation should be closer to the lower end of this range. Direct observations made in other eutrophic lakes (Hollander and McKenzie, 1991; Aritzegui and McKenzie, 1995) indicate that −20 is a reasonable approximation for the isotope fractionation between phytoplankton and DIC. Experimental results concerning the isotope fractionation during dark respiration are contradictory (O'Leary, 1981), but this fractionation is expected to be small (Vogel, 1993). In the model, it was assumed that dark respiration is nonfractionating, i.e., $\delta^{13}C$ of respired CO_2 = $\delta^{13}C$ of biomass (−25‰). Because the observed $\delta^{13}C$ values of DIC in Lake Gościąż were close to −5‰, $\delta^{13}C$ of phytoplankton and respired CO_2 should be about −25‰. The $\delta^{13}C$ values of organic matter collected in the sediment traps are not known, but $\delta^{13}C$ of organic matter from Lake Gościąż sediments deposited between ca. 1823 to 1965 AD (Goslar et al., 1994) varied between −27 and −29‰.

The model was run for time intervals between subsequent sampling campaigns. Table 1 summarizes the initial data for all intervals. The average values of water temperature, pH, concentration, and $\delta^{13}C$ of DIC in the epilimnion were calculated on the basis of the values measured during each sampling campaign. It was assumed that water temperature and pH vary monotonously between the values determined during subsequent samplings. For the groundwater inflow, the average values of DIC concentration and its isotopic composition measured in the monitored springs at the beginning and end of the given interval were used in calculations. Accurate evaluation of fluxes of carbon associated with waters flowing through the lake was not possible due to poorly defined inflow and outflow. These fluxes were calculated on the assumption that inflow and outflow are equal and constant in time. The average yield of springs was estimated at 50 L/s based on hydrological observations of Gierszewski (1993). Decomposition of organic matter in deep waters and in sediments was not subject to direct observations. The flux of carbon recycled to the epilimnion (*R*) and its $\delta^{13}C$ were left as unknown parameters of the model. They were searched by trial and error unless the calculated and measured concentrations and $\delta^{13}C$ of DIC in the epilimnion matched.

4.2. Results of Model Calculations

Table 2 summarizes fluxes of carbon to and from the epilimnion, estimated for all intervals. Of the two sources of carbon that could be responsible for maintaining relatively stable concentrations and $\delta^{13}C$ of DIC in the epilimnion, recycled DIC (*R*) and DIC contained in the groundwaters (*I*), the former seems to be crucial. For the entire studied period, *R* is equal to almost two-thirds of the total inorganic carbon input to the epilimnion. Groundwater inflow alone could not account for the observed DIC and $\delta^{13}C_{DIC}$ patterns because DIC concentrations in groundwaters are close or moderatly higher than in the epilimnion (Fig 2b). Calculations show that large (one order of magnitude higher than assumed in the model) groundwater inflow could replenish the epilimnion with DIC, but this would result in $\delta^{13}C_{DIC}$

Table 1. Input data used in the numerical model of the carbon cycle in Lake Gościaż.

Date	Temp (°C)[a]	pH[a]	DIC 10^{-3} (mol·l^{1})[a]	$\delta^{13}C_{DIC}$[a]	Net photosynthesis 10^{-11} (mol·l^{-1}·s^{-1})[b]	Calcite production 10^{-11} (mol·l^{-1}·s^{1})[b]
29 Apr	14.8	8.55	2.43	−5.5		
					0.9	0.4
4 Jun	21.5	8.16	2.46	−5.4		
					1.0	0.5
5 Jul	19.9	8.30	2.55	−4.7		
					1.1	0.6
5 Aug	22.3	8.36	2.13	−4.8		
7 Sep	15.7	8.26	2.21	−4.2	1.1	0.5
					1.5	0.9
19 Oct	10.0	8.22	2.07	−5.5		

[a] Mean values determined for the epilimnion on the basis of measurements carried out on the given days.

[b] Mean values calculated for the periods between the subsequent sampling campaigns, on the basis of the sediment trap data.

around −10‰. The net flux of carbon to the atmosphere (small when compared with other fluxes) is a result of two counteracting flows. The upward flux of CO_2 is 2–3 times bigger than the net flux.

The calculated fluxes of recycled carbon R are close for all periods, which suggests that patterns of carbon redistribution were similar, except for the period between 5 July and 5 August. The calculated $\delta^{13}C$ of R changes in a wide range (−29.7‰ to −16.1‰), but this variability does not contradict the assumption that this flux derives mainly from decomposition of organic matter. Recycled carbon is a mixture of DIC released during aerobic decomposition of organic matter ($\delta^{13}C \approx -28‰$), methanogenesis ($\delta^{13}C \approx +15‰$) and oxidation of methane ($\delta^{13}C \approx -60‰$), and dissolution of calcite ($\delta^{13}C \approx -2‰$). More positive $\delta^{13}C$ values point to increased extent of methanogenesis and/or dissolution of calcite. The most negative $\delta^{13}C$ value obtained for 7 September to 19 October, when thermal stratification weakened, indicates increased importance of oxic processes in production of DIC. The average $\delta^{13}C$ value of the recycled DIC for the whole studied period is −25.5‰ (or −22.2‰ when the interval from 5 July to 5 August is excluded). It is shifted from $\delta^{13}C$ of source organic matter towards the more positive values due to two processes: escape of methane to the atmosphere and dissolution of calcite.

Abnormally low R estimated for the period between 5 July and 5 August reflects substantial drop in DIC concentration in the epilimnion. Parallel decrease was also observed for $[Ca^{2+}]$. The high accuracy of calcium concentration determination and small number of sources and sinks for this element make calcium budget easier to calculate and more reliable than the carbon budget. Table 3 shows fluxes of Ca^{2+}, analogous to R, that should have been added to the epilimnion to match the observed concentrations. These fluxes significantly increase over the whole studied period, except for 5 July–5 August when a substantial amount of Ca^{2+} was removed from the epilimnion. DIC and Ca^{2+} budgets reveal the same pattern; for the whole studied period, significant amounts of both substances were refluxed to the epilimnion. Apparently, this recycling was disturbed in July. The last column of Table 2 shows changes in the Ca^{2+} inventory in the hypolimnion expressed as net fluxes of Ca^{2+} out of the hypolimnion. In July, this net flux was much larger than for other periods reflecting reduced replenishment of the deep waters with Ca^{2+}. The decrease in Ca^{2+} inventory in the hypolimnion corresponds for the whole studied period to approximately a quarter of the flux feeding the epilimnion. The rest of this flux must have been derived from the dissolution of calcite and release of calcium previously bound in ion pairs, colloids, and adsorbed on other substances. Calcium

Table 2. Carbon budget of Lake Gościaż. Measured and calculated fluxes of carbon [mol/s] into and out of the epilimnion. Fluxes of carbon removed with organic matter (N) and calcite (K) are derived from the sediment trap data. Net CO_2 flux into the atmosphere (A) calculated from the diffusion film model (Appendix, Eqn. 7).

Interval	Inflow (I)	Outflow (O)	Orgnanic matter (N)	Calcite (K)	Net CO, flux into the atmosphere (A)	DIC recycled into the epilimnion[a] (R)	Incoming fluxes ($R + I$)	Outgoing fluxes ($A + N + K + O$)
29 Apr–4 Jun	0.1213	0.1224	0.1353	0.0643	0.0276	0.2359 (−22.4)	0.3572	0.3496
4 Jun–5 Jul	0.1429	0.1246	0.1505	0.0763	0.0339	0.3170 (−16.1)	0.4599	0.3853
5 Jul–5 Aug	0.1307	0.1124	0.1610	0.0940	0.0171	0.0120 (−[b])	0.1427	0.3845
5 Aug–7 Sep	0.1303	0.1083	0.1635	0.0793	0.0169	0.3005 (−17.6)	0.4308	0.3680
7 Sep–19 Oct	0.1272	0.1074	0.2203	0.1395	0.0246	0.3308 (−29.7)	0.4580	0.4918
29 Apr–19 Oct	0.1300	0.1147	0.1686	0.0929	0.0241	0.2457 (−22.2)	0.3757	0.4003

[a] In brackets $\delta^{13}C$ of supplementary carbon derived from decay of organic matter in the sediments.

[b] Calculated value of $\delta^{13}C$ (−392.0) is not interpreted as reflecting recycled DIC (see text).

Table 3. Calculated fluxes of Ca^{2+} [mol/s]. In the first column are fluxes of Ca^{2+} that must have been added to the epilimnion to match the observed concentrations of Ca^{2+}; these fluxes are analogous to R. In the second column are changes in the Ca^{2+} inventory in the hypolimnion expressed as fluxes of Ca^{2+} from the hypolmnion.

Interval	Ca^{2+} refluxed to the epilimnion	Ca^{2+} flux from the hypolimnion
29 Apr–4 Jun	0.0059	0.0058
4 Jun–5 Jul	0.0143	0.0000
5 Jul–5 Aug	−0.0326	0.0246
5 Aug–7 Sep	0.0470	−0.0067
7 Sep–19 Oct	0.0874	0.0083
29 Apr–19 Oct	0.0281	0.0064

budget concerns only Ca^{2+} because ion selective electrode is not sensitive to other forms of dissolved calcium. The additional source of calcium to the epilimnion corresponds to 23% of the calcite flux registered in traps (flux K in Table 1). This figure is an upper estimation for dissolution of settling calcite.

Carbon and calcium budgets for the period between 5 July and 5 August reveal that for both substances, their fluxes recycled to the epilimion were exceptionally low. This feature can be explained by the decrease in vertical mixing intensity. Vertical mixing is driven by wind action and thermal convection. Reduction of this external forcing results in decreased vertical mass fluxes and in stronger density stratification, which limits release of dissolved substances from the sediments (Imboden and Wüest, 1995). Such a situation promotes development of anoxic conditions which slow down decomposition of organic matter and dissolution of calcite. This positive feedback further reduces fluxes of DIC and Ca^{2+} to the epilimnion and lowers $\delta^{13}C$ of released DIC. There is, however, no direct evidence for the occurrence of the described mechanism over this period. Depth profiles of $\delta^{13}C_{DIC}$ in the hypolimnion seem to condradict the presented explanation because, except for DIC and $[Ca^{2+}]$, there was no dramatic change of $\delta^{13}C_{DIC}$ for 5 August. However, removal of DIC from the hypolimnion by means of mixing does not result in isotopic fractionation. A direct result of recycled DIC flux reduction should be a decrease in $[CO_2]$ in the surface waters. Low pCO_2 favours two processes having direct impact on $\delta^{13}C_{DIC}$: reduced fractionation during algal photosynthesis and chemically enhanced invasion of isotopically light CO_2 from the atmosphere (Herczeg and Fairbanks, 1987). Calculations show that both phenomena together could account for the DIC and $\delta^{13}C_{DIC}$ values observed in the epilimnion on 5 August. Short-term observations made between 5 and 9 July 1994 confirm that replenishment of the epilimnion with calcium and DIC is not a continuous phenomenon and depends on weather conditions. The morphology of the Lake Gościąż basin facilitates fast recycling of carbon. The lake is generally shallow (mean depth 4.5 m) with two relatively small areas of deep water. Because the thermocline is located between 5 and 6 m, most of the bottom is exposed to the epilimnetic waters during summer stratification. Thus, DIC released during respiration of settling organic matter may be quickly returned to the surface waters.

For the studied period, the flux of DIC removed from the epilimnon with settling organic matter (N) averaged only two-thirds of the recycled flux of DIC (R). Assuming that 23% is the upper estimation for dissolution of precipitated calcite (K), the organic matter production rate equaled maximally 75% of decomposition rate. The actual figure must be lower also because a part of settled organic matter is buried in the sediments. Therefore, substantial amounts of organic matter must be delivered to the lake and subsequently decomposed, giving an additional flux of DIC into the epilimnion. Possible sources for this additional organic carbon are (1) organic carbon dissolved in the groundwaters feeding the lake (DOC), (2) surface runoff transporting organic detritus (POC), (3) remnants of emerged plants growing in the littoral zone, using atmospheric CO_2 for photosynthesis, and (4) leaves fallen from trees growing along lake shores. Decomposition of previously buried organic matter cannot be a significant source of DIC because, in such a case, the organic matter content in the sediments should decrease with depth, which is not observed for the entire sediment column (Wicik, 1993).

There are three external sources of carbon for the lake: inorganic carbon dissolved in the inflowing groundwaters (50% contribution of the whole input, $\delta^{13}C$ between −15‰ and −11‰), terrestial biomass (30% contribution, $\delta^{13}C \approx -28‰$), and CO_2 invaded from the atmosphere (20% contribution, $\delta^{13}C \approx -9‰$). By assuming the estimated fluxes from all three sources as revealed by the model, the resulting $\delta^{13}C$ should be −16‰. It should be noted that this value is considerably more negative than $\delta^{13}C_{DIC}$ of lake waters, which fluctuates between −10‰ to −4‰. This discrepancy results from the escape of methane and, to some extent, of CO_2 from the lake into the atmosphere.

The main conclusions of this work, which concern cycling of carbon in the lake, are based on estimations of the fluxes and $\delta^{13}C$ of DIC recycled into the epilimnion (R). Therefore, the reliability of these estimations must be addressed. The overall uncertainty of the calculated fluxes results from analytical errors of the input parameters as well as from simplifications of the conceptual model. Analytical errors for samples from two subsequent sampling campaigns have a cumulative effect for the estimated fluxes of recycled carbon (R) and their isotopic compositions which were adjusted to match the observed parameters in the epilimnion. Of all the analytical uncertainties, that which is associated with alkalinity determination influences R most significantly. All calculated fluxes, presented in Table 2, are only slightly sensitive to uncertainties in pH and temperature. Table 4 shows sensitivity of R to errors of alkalinity determination. The extreme cases of error propagation are when errors of alkalinity determination (1σ) for the subsequent samplings have the opposite signs. This can lead to both decrease and increase in R. It can be seen from Table 4 that the flux of recycled carbon depends almost linearly on estimated DIC inventory in the epilimnion. Table 5 shows the large sensitivity of the estimated $\delta^{13}C$ of R to analytical errors (1σ) in the epilimnetic $\delta^{13}C_{DIC}$. Further errors are introduced when the locally measured parameters are used as the representative ones for the whole epilimnion. However, chemical and isotopic parameters of water (Wachniew, 1995), sedimen-

Table 4. Evaluation of sensitivity of R and its $\delta^{13}C$ to analytical errors of alkalinity (1σ). Values in the middle column are the same as in Table 2. Values in the left and right column represent extreme under- and overestimation of R associated with superposition of errors for two subsequent samplings.

Interval	$R - \Delta R$	R	$R + \Delta R$
29 Apr–4 Jun	0.1413 (−33.7)	0.2359 (−22.4)	0.3310 (−18.0)
4 Jun–5 Jul	0.2048 (−22.0)	0.3170 (−16.1)	0.4296 (−13.6)
5 Jul–5 Aug	−0.0918 (+46.1)	0.0120 (−392.0)	0.1150 (−45.1)
5 Aug–7 Sep	0.2139 (−22.3)	0.3005 (−17.6)	0.3963 (−15.9)
7 Sep–19 Oct	0.2584 (−36.6)	0.3308 (−29.7)	0.4020 (−25.3)

tation rates, and chemical composition of the sediments (Kentzer and Żytkowicz, 1993) showed small spatial variability. Short-time variability of the model parameters was also not accounted for. In reality, water temeprature and pH do not change monotonously as was assumed in the model.

Fluxes of carbon removed into the atmosphere (A) and with precipitated calcite (K) have relatively small influence on the whole-lake carbon budget (Table 1). Their accurate evaluation is not critical for reliability of the carbon budget. Relevant parameters, for example, isotopic enrichment during precipitation of calcite or wind speed, need not to be determined accurately. DIC concentrations in the inflowing groundwaters are close to the epilimnetic concentrations. Therefore, the net result of groundwater inflow (I) and surface outflow (O) on DIC content in the lake is smaller than could be expected from the size. Unfortunately, more accurate evaluation of both fluxes is impossible for Lake Gościąż. Reliable evaluation of the carbon budget relies most of all on estimations of DIC concentration and $\delta^{13}C$ in the epilimnion, as well as on estimations of the amount and $\delta^{13}C$ of organic matter removed from the epilimnion. These parameters are crucial for the model and should be estimated with great credibility. In particular, our study lacks direct estimation of isotopic fractionation between DIC and POC. Tables 4 and 5 show large sensitivity of the estimated fluxes and isotopic compositions of recycled carbon to analytical uncertainties. However, the main qualitative conclusions of the model should not be affected by analytical errors. They do not weaken the conclusion that carbon released from decomposition of organic matter is a crucial element of the carbon budget of the lake.

5. CONCLUSIONS

Although carbon is the most abundant nutrient in aquatic ecosystems, comprehensive studies of pathways and fluxes of this element are rare, mainly due to complexity and dynamics of the carbonate system. Quantification of the carbon budget of lakes has two important aims: (1) it helps to better understand the effects of eutrophication and acidification of lakes, which is a serious problems in many parts of the world, and (2) it provides a basis for quantitative paleoenvironmental interpretation of carbon isotope records preserved in the sediments, both in the form of organic and inorganic carbon-bearing substances. The presented study was aimed at quantifying the carbon budget of a temperate, groundwater-fed lake, using the isotopes of carbon as the major tool. The combination of chemical and isotope tools turned out to be an efficient way of quantifying the pathways and fluxes of carbon in this particular lake system.

The characteristic feature revealed by observations of the water column was a relatively small increase in the epilimnetic $\delta^{13}C_{DIC}$ despite intensive photosynthetic assimilation of ^{12}C-enriched CO_2 by algae. Our model describing the evolution of DIC in the epilimnion showed that DIC released by decomposition of organic matter in the sediments and in the hypolimnion replenishes ^{12}C in the surface waters. Other sources of carbon—DIC contained in the groundwaters and CO_2 invaded from the atmosphere—have lesser influence on concentration and isotopic composition of DIC in the epilimnion. For the entire observed period, which extends from April to October, recycled carbon accounted for two-thirds of all DIC influx to the epilimnion: its average $\delta^{13}C$ was −25.5‰. Dissolution of calcite in the sediments and in undersaturated deep waters leads to recycling of calcium. The maximum extent of calcite dissolution was found to equal 23% of its production. The important role of recycled carbon and calcium for the whole-lake budget of these substances on an annual scale may be a common feature of many lakes. Our results confirm earlier observations (e.g., McConnaughey et al., 1994) that fluxes recycled from sediments are important components of carbon and calcium budget for temperate lakes. Decomposition of organic matter within the lake exceeds primary production of biomass by at least one-third. Therefore, substantial amounts of organic matter must be delivered to the lake from its surroundings in the forms of POC and DOC. The excess carbon delivered to the lake allows continuous replenishment of the surface waters with isotopically light DIC and their supersaturation with CO_2, in spite of intensive photosynthetic activity of algae. The lake is thus a net source of CO_2. The flux of CO_2 into the atmosphere, calculated for the whole studied period (Table 2) corresponds to about 6 tons of carbon. The excess of respiration over production of organic matter seems to be a common feature of most lakes located in various climatic settings (Quay et al., 1986; Cole et al., 1994), pointing to an additional source of CO_2 previously not accounted for in the studies of the global carbon cycle. Of the external sources of carbon, groundwater inflow contributes 50%, terrestial biomass, 30%, and atmospheric CO_2, 20% of the total carbon input to the lake. This should result in an average $\delta^{13}C_{DIC}$ equal to −16‰ while the observed values fluctuate between −10‰ and −4‰. This discrepancy is due to the escape of ^{12}C-enriched CH_4 and, to some extent, of CO_2 to the atmosphere.

Although our model of the carbon cycling in Lake Gościąż

Table 5. Minimum ($-\Delta$) and maximum ($+\Delta$) values of $\delta^{13}C_R$ reflecting analytical errors (1σ) of $\delta^{13}C_{DIC}$ values put to the model.

Interval	$-\Delta$	$\delta^{13}C_R$	$+\Delta$
29 Apr–4 Jun	−25.4	−22.4	−19.9
4 Jun–5 Jul	−18.7	−16.1	−13.4
5 Jul–5 Aug	−385.5	−392.0	−325.7
5 Aug–7 Sep	−19.9	−17.6	−15.3
7 Sep–19 Oct	−31.3	−29.7	−28.0

is limited by analytical errors of model parameters and a number of simplifying assumptions, it provides quantitative information on the relative importance of sources and sinks of carbon determining the $\delta^{13}C_{DIC}$ in the epilimnion and, consequently, of the sedimentated authigenic calcite. The $\delta^{13}C$ records of authigenic calcite preserved in lacustrine sediments are generally interpreted in terms of variations in the photosynthesis-respiration cycle within the given lake and/or as an indicator of varying intensity of CO_2 exchange between the lake and the atmosphere. The results of the model calculations suggest that for hard-water lakes dominated by groundwater inflow, the carbon isotope signature of authigenic calcite is also linked to the mean residence time of water in the system. On the other hand, changes in the hydrological cycle of the lake are also imprinted in the oxygen isotopic composition of authigenic calcite. This adds a new perspective, which needs to be further explored, for a combined interpretation of both carbon and oxygen isotope signatures of calcite deposited in lakes.

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APPENDIX

The carbon conservation equations for the modelled volume of the lake are as follows:

$$C_T^{i+1} = C_T^i + \Delta I + \Delta R - \Delta K - \Delta P - \Delta A - \Delta O \quad (1)$$

$$^{13}C_T^{i+1} = {}^{13}C_T^i + \Delta^{13}I + \Delta^{13}R - \Delta^{13}K - \Delta^{13}P - \Delta^{13}A - \Delta^{13}O \quad (2)$$

where C_T^i, C_T^{i+1} ($^{13}C_T^i$, $^{13}C_T^{i+1}$) are molar concentrations of DIC (DI^{13}C) in the epilimnion for two subsequent iterations, and Δ denotes a small amount of carbon in a given form (in moles per unit volume) added to or subtracted from the epilimnion in a one time step. In general, these amounts may vary from one step to another. It was assumed that primary production occurs exclusively within the epilimnion, which is homogenous with respect to the concentrations and isotopic compositions of the dissolved species as well as the rates of phytoplankton and calcite production. For dark periods rate of dark respiration, ΔD was substituted for the rate of CO_2 assimilation ΔP.

Concentrations of both isotopes of carbon are related by the equation:

$$^{13}C_T^i = \alpha_T^i R_{HCO_3^-}^i \, {}^{12}C_T^i \quad (3)$$

where $\alpha_T^i = (x_{CO_2}^i \alpha_{CO_2-HCO_3^-}^i + x_{HCO_3^-}^i + x_{CO_3^{2-}}^i \alpha_{CO_3^{2}-HCO_3^-}^i)$ is the fractionation factor between DIC and HCO_3^-, $R_{HCO_3^-}^i$ is carbon isotope ratio ($^{13}C/^{12}C$) in HCO_3^-, and x denotes the mole fraction of the given carbon species. $R^{i+1}_{HCO_3^-}$ and then $\delta^{13}C^{i+1}_{DIC}$ may be calculated from Eqns. (1) to (3), assuming $C^i_T = {}^{12}C^i_T + {}^{13}C^i_T$. When carbon is added or subtracted with no accompanying isotope fractionation (for ΔI, ΔR, ΔO), the resulting change of ^{13}C content in the system is expressed by the total amount of added carbon and its isotope ratio, e.g., for carbon transported to the epilimnion with inflowing waters:

$$\Delta^{13}I = \frac{R_I}{1 + R_I}\Delta I \tag{4}$$

Photosynthetic assimilation of CO_2 and precipitation of calcite are associated with the following isotope fractionations related to HCO_3^-:

$$\Delta^{13}P = \frac{\alpha_P\alpha_{CO_2-HCO_3^-}R_{HCO_3^-}}{1 + \alpha_P\alpha_{CO_2-HCO_3^-}R_{HCO_3^-}}\Delta P \tag{5}$$

$$\Delta^{13}K = \frac{\alpha_{calc-HCO_3^-}R_{HCO_3^-}}{1 + \alpha_{calc-HCO_3^-}R_{HCO_3^-}}\Delta K \tag{6}$$

where $\alpha_P = \epsilon_P - 1$ is the overall isotope fractionation factor between dissolved CO_2 and produced organic matter.

The net amount of CO_2 exchanged between the lake and the atmosphere in one step (ΔA) is calculated according to the diffusion film model (Stumm and Morgan, 1981; Wannkinkhof et al., 1985):

$$\Delta A = \frac{([CO_2] - [CO_2]_{eq})(1 - e^{-(k/h)\Delta t})}{S\Delta t} \tag{7}$$

where $[CO_2]$ is the initial concentration of CO_2 dissolved in the homogenous epilimion, $[CO_2]_{eq}$ is the concentration of CO_2 dissolved in water at equilibrium with atmospheric CO_2, k is exchange rate constant, h is the average depth of the epilimnion, S is the lake surface, and Δt is the time step. The rate constant k was calculated for the given wind velocities according to the empirical formula (Upstil-Goddard et al., 1990) obtained for two small English lakes. Partial pressure of CO_2 in the atmosphere was assumed to be 360 ppm, its $\delta^{13}C = -7.5‰$. The net amount of ^{13}C transferred through the air-water interface is expressed by the following equation:

$$\Delta^{13}A = \frac{[CO_2]_{eq}\dfrac{\alpha_{aw}R_{atm}}{1 + \alpha_{aw}R_{atm}} - [CO_2]\dfrac{\alpha_{wa}R_{HCO_3^-}}{1 + \alpha_{wa}R_{HCO_3^-}}}{[CO_2]_{eq} - [CO_2]}\Delta A \tag{8}$$

where α_{aw} and $\alpha_{wa} = \alpha_{CO_{2g}HCO_3^-}\alpha_{aw}$ are the overall fractionation factors for downward and upward fluxes of CO_2, respectively, and R_{atm} is the $^{13}C/^{12}C$ ratio in atmospheric CO_2. The values of α_{wa} for different temperatures were interpolated from the results of Zhang et al. (1995).