

A modern isotope record of changes in water and carbon budgets in a groundwater-fed lake: Blue Lake, South Australia

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Abstract

Groundwater is often a major component of lake water and chemical balances. Alteration in catchment subsurface water balances through land-use change and pumping can affect lake biogeochemical cycles through changes in groundwater flow rates. We present a modern (~200 yr) sediment isotope record ($\delta^{18}\text{O}_{\text{carb}}$, $\delta^{13}\text{C}_{\text{carb}}$, and $\delta^{13}\text{C}_{\text{org}}$) of changes to the water and carbon budget of Blue Lake, which is situated in karstic limestone in South Australia and is mostly fed by groundwater. The 3.5‰ decrease in $\delta^{18}\text{O}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{carb}}$ deposited in lake sediments since ~1850 reflects higher rates of groundwater through-flow due to rainfall variability, land-use change, and increased rates of pumping over the past 40 yr. Calculated water residence times, based on the isotopic data, were 23 ± 2 yr before 1850 and decreased by the late twentieth century to 8 ± 2 yr. Concomitant dissolved inorganic carbon (DIC) residence times were 3.8 and 2.2 yr, respectively. Although burial rates of CaCO_3 have increased by about threefold over the past 40 yr, there is no evidence that substantial changes in organic carbon deposition has occurred. The shorter DIC residence time is largely due to increased input and higher CO_2 evasion rates. About 88% of C_{carb} and ~96% of C_{org} generated within the water column is remineralized, but the isotopic composition is essentially unaltered in the sediments. The measured variations in $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$ of sediments are thought to reflect changes to DIC residence time and increased $\text{CO}_2(\text{aq})$ concentrations rather than changes in lake productivity.

The importance of the link between groundwater and many lakes is being increasingly recognized as the demands for water supply increase (Winter et al. 1999). The effects of land-use change on the long-term hydrological balance of groundwater-fed lakes and their consequent effects on the biogeochemical cycles of solutes and nutrients are poorly understood. Studies of lakes that have used sediment isotope records of carbonates (Li et al. 1997; Hodell et al. 1998; Hilfinger et al. 2001) and of organic matter (Bernasconi et al. 1997; Hodell and Schelske 1998; Meyers et al. 1998; Brenner et al. 1999) have shown that these techniques can

provide a reliable record of lake-level changes and nutrient inputs over the past several centuries. We compare $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ data from authigenic carbonates and $\delta^{13}\text{C}$ of organic matter from a high-resolution sediment core with sediment traps and water-column data from a groundwater-fed maar lake (Blue Lake) in a temperate part of southeastern Australia. These data are used to evaluate the effect of land-use change and pumping from the lake on the water and carbon residence times over the past 150 yr of European settlement. We show that the isotope proxy record of carbonates is a very robust method of providing a window into long-term subsurface hydrological processes in large watersheds. On the other hand, the organic carbon record reflects changes in the dynamics of isotope systematics between C_{org} and $\text{CO}_2(\text{aq})$ due to increased discharge of groundwater with high pCO_2 , rather than reflecting changes in trophic state or catchment vegetation.

Blue Lake is a monomictic, oligotrophic hard-water lake located in southeastern Australia ($37^\circ 43' \text{S}$, $140^\circ 50' \text{E}$; Fig. 1). It covers an area of $6.03 \times 10^5 \text{ m}^2$, has a volume of $3.5 \times 10^7 \text{ m}^3$ and a maximum depth of 74 m (Fig. 2), and has filled the vent of a 28,000-yr-old volcano in southeast South Australia (Leaney et al. 1995). The surrounding landscape is slightly undulating, and, because of the steep-sided nature of the extinct volcanic crater, the surface water catchment is

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Acknowledgments

We thank A. McPharlin and J. Cugley of the South Australian Environmental Protection Agency and F. Stadter and R. Mullan of the Dept. for Water, Land, and Biodiversity Conservation for assistance with sampling and for providing ancillary data. G. Hancock, CSIRO Land and Water, performed the sediment ^{210}Po and ^{226}Ra analyses. Careful and thorough reviews by P. DeDeckker, E. Krull, R. Ricketts, and one anonymous referee significantly improved the manuscript and are greatly appreciated.

This work was partly supported by Land and Water Australia Grant CWS7 under the auspices of the National Eutrophication Management Program.

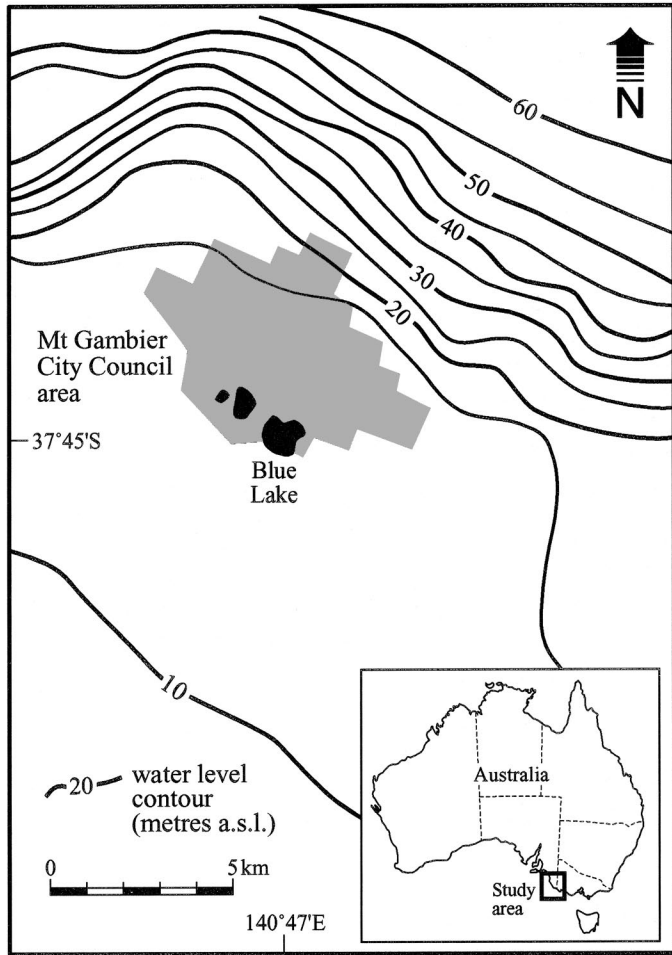


Fig. 1. Location of the study area (inset) and plan view of Blue Lake and groundwater level contours. The contours represent the hydraulic head of the Gambier Limestone aquifer (in meters above sea level). The inferred direction of groundwater flow (perpendicular to contours) is from northeast to southwest.

only 10% larger than the lake's surface area. The lake is mostly groundwater-fed, predominantly from the unconfined karstic Gambier Limestone aquifer (GL), with <20% input from the deeper, confined Dilwyn Formation aquifer (Turner et al. 1984; Ramamurthy et al. 1985). Water-table hydraulic gradients along the direction of groundwater flow across the lake are very flat (5 in 10,000) but are steeper northeast of the study area (6 in 1,000) (Fig. 1). There are no tributaries, and the only surface water input is via direct rainfall onto the lake surface (715 mm yr⁻¹; Bureau of Meteorology 1988). In this temperate environment, the mean annual evaporation rate from the lake surface is 1,198 mm yr⁻¹ (Turner et al. 1984), the mean relative humidity is 62 ± 3%, and the mean annual temperature is 14.5°C (Bureau of Meteorology 1988). Blue Lake provides all of the water to the local town of Mt. Gambier (population, ~23,000). The rate of withdrawal of water from the lake increased slowly during the first half of the 1900s to ~10⁶ m³ yr⁻¹ by 1950, followed by a rapid fourfold increase over the next 20 yr (Fig. 3) to the current pumping rate, which is ~3.6 × 10⁶ m³ yr⁻¹ (Department of Environmental and Natural Resources 1994).

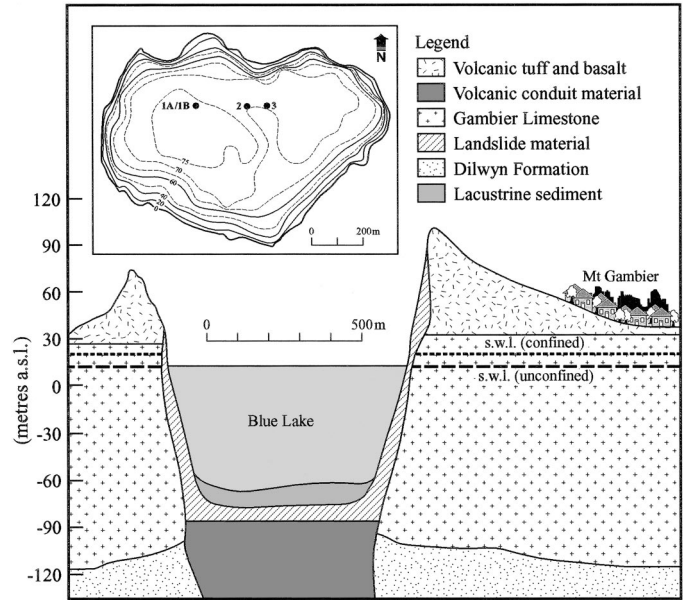


Fig. 2. Cross-section of Blue Lake, showing the standing water level (s.w.l.) of the unconfined Gambier Limestone and confined Dilwyn Sand aquifers, relative to lake water levels. Also shown is a lake morphometric map (inset) with contours in meters and the sampling location of sediment cores. The sediment traps were moored ~20 m south of site 1A/1B.

The lake level has dropped a total of ~8 m since records began in the late 1800s, with about half of that decrease occurring over the past 30 yr. The variation in lake levels prior to ~1940 is thought to have been due to rainfall variability over the same time period.

Because nitrate concentrations in the surrounding GL aquifer are very high (typically 750 ± 350 μmol L⁻¹; Dillon 1989) because of the disposal of agricultural waste directly into the aquifer over the past 100 yr, the lake also has ele-

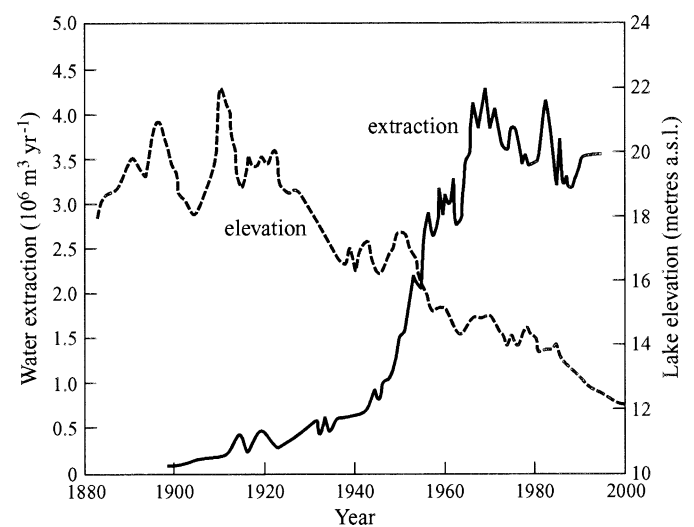


Fig. 3. Change in lake surface water elevation (meters above sea level) and rate of pumping of lake water (in millions of m³ yr⁻¹) since 1880.

vated nitrate levels (currently, $250 \mu\text{mol L}^{-1}$; Department of Environmental and Natural Resources 1994; Lamontagne 2002). Despite the high nitrate concentrations, the lake remains oligotrophic because of very low dissolved phosphorus concentrations ($<0.15 \mu\text{mol L}^{-1}$). Increased groundwater input to a surface-water body can affect biogeochemical cycles by altering the nutrient loading rates as well as transformation rates between inorganic and organic forms of N and C. For example, implicit in reduced water residence time is the decreasing importance of gas exchange (e.g., CO_2 , O_2 , and N_2), as well as reduced contact time, which can affect sediment-water interfacial processes.

Materials and methods

Freeze core sampling—Three short cores (350–400 mm) were collected at a water depth of 60–70 m using a freeze core design similar to that described by Crusius and Anderson (1991). An aluminum box, $\sim 1,000$ mm in length, tapered over the bottom 350 mm to a wedge shape, was filled with a slurry of dry ice/ethyl alcohol and rapidly lowered through the water column to just above the sediment–water interface. The corer was then lowered slowly into the sediment and left for 10 min before quickly being raised to the surface. The dry ice slurry was removed, and lake water was placed into the box to partially defrost a thin layer of water on the outside of the box, which allowed the entire frozen slab to slide off into an ice chest filled with dry ice. On return to the laboratory, the outside layer of frozen water was scraped off, and the three cores were sectioned into 5-mm intervals for the first 120 mm of core, then 10 mm intervals thereafter, and subsamples were taken for bulk density, dating, and isotopic measurements.

Sediment particle traps—Three sediment particle traps were deployed for a total of 15 months at 15, 40, and 70 m from a buoy moored ~ 20 m south of site 1A/1B near the deepest part of the lake. The trap construction and sampling details are described in Telfer (2000). In brief, the traps consisted of 102-mm diameter, 750-mm long cylinders that were emptied monthly (except on two occasions when they were deployed for 50 and 59 d, respectively) and collected between 0.032 and 1.64 g of material. Analytical methods for determining the fractions of carbonate C, organic C, and residual silicate material are described in Telfer (2000).

Dating—Subsamples of sediment from core 1B were split for bulk density by placing ~ 35 – 45 g of wet sediment into tared plastic containers and weighed. These samples were oven dried at 110°C and then reweighed. The bulk density was calculated using the estimates of water loss and an assumed dry sediment density of 2.5 g cm^{-3} . The resultant dry mass was not corrected for precipitated salts from pore water, because those contribute $<0.5\%$ of the total mass. A further 10 g of subsample from each section was washed, oven dried at 60°C , and analyzed by conventional alpha and gamma spectrometry for ^{210}Pb and ^{226}Ra , respectively, at the Canberra Laboratories of CSIRO Land and Water.

Percentages of CaCO_3 and organic matter (OM)—Subsamples from the core and sediment traps were placed in sealed glass tubes, and 1 ml of concentrated H_3PO_4 was added to convert CO_3 to $\text{CO}_2(\text{g})$. The gas pressure was measured with a calibrated manometer and converted to percentage carbonate. The percentage of OM for the sediment core samples were calculated by subtracting the value for the percentage of CaCO_3 from total loss on ignition at 850°C . The uncertainties were $\pm 2\%$ for CaCO_3 and, overall, 5% for the percentage of OM. The percentage of C_{org} for the sediment trap samples was estimated from the percentage of C determined with the mass spectrometry run of the noncarbonate fraction (see below) and had a nominal uncertainty of 3%.

Mass spectrometry—Subsamples of sediment were washed in distilled water to remove interstitial pore water, oven dried, and ground to a fine powder with a mortar and pestle. About 0.5 g of sample was placed in a 35-ml Vacutainer and sealed with a septum. One milliliter of 98% H_3PO_4 was added through the septum, and the samples were placed in a water bath/shaker overnight at 30°C . Analysis of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of the CO_2 gas was done on a Europa Scientific GEO 20-20 mass spectrometer by conventional dual-inlet techniques and expressed as parts per thousand relative to the Pee Dee Belemnite (PDB) scale. The precision for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of carbonates were 0.15‰ and 0.2‰, respectively. The acidified sediment residue was then rinsed several times in deionized water and again oven dried at 60°C . Next, 10–20 mg of sediment was placed in tin capsules and analyzed for C:N ratios and $\delta^{13}\text{C}$ of the residual fraction by combustion using continuous-flow mass spectrometry. Precision rates for these analyses were ± 0.1 and 0.15‰, respectively, and were based on replicate internal standards and samples. $\delta^{13}\text{C}_{\text{DIC}}$ was analyzed by first precipitating all dissolved inorganic carbon (DIC) from 250 ml water samples using saturated ammoniacal SrCl_2 to form SrCO_3 , according to the method described by Bishop (1990). The solid material was acidified in closed glass ampules, and the CO_2 gas was analyzed as described above for sediment carbonates.

Results

Sediment accumulation rates—The total ^{210}Pb concentrations in the sediments of core 1B showed a typical exponential decline in ^{210}Pb over the top 100 mm of core (Fig. 4A). ^{210}Pb concentrations were relatively low (10–80 Bq kg^{-1}) because of the large fraction of authigenic carbonate material that dilutes the atmospheric ^{210}Pb signature and because of core compaction. The volumetric porosity of core 1B ranged 0.835–0.875 throughout most of the core, yielding a volumetric dry bulk density of 0.125–0.165 g cm^{-3} . Porosity increased to 0.910 over the top 25 mm, with a corresponding decrease in bulk density to 0.090 g cm^{-3} at the top of the core. Under the assumption of a dry sediment density of 2.5 g cm^{-3} , the profile of excess ^{210}Pb as a function of cumulative dry mass was replotted as the logarithm of $^{210}\text{Pb}_{\text{ex}}$ as a function of cumulative dry bulk density, which yielded mass accumulation rates of 0.0387–0.0664 g cm^{-2}

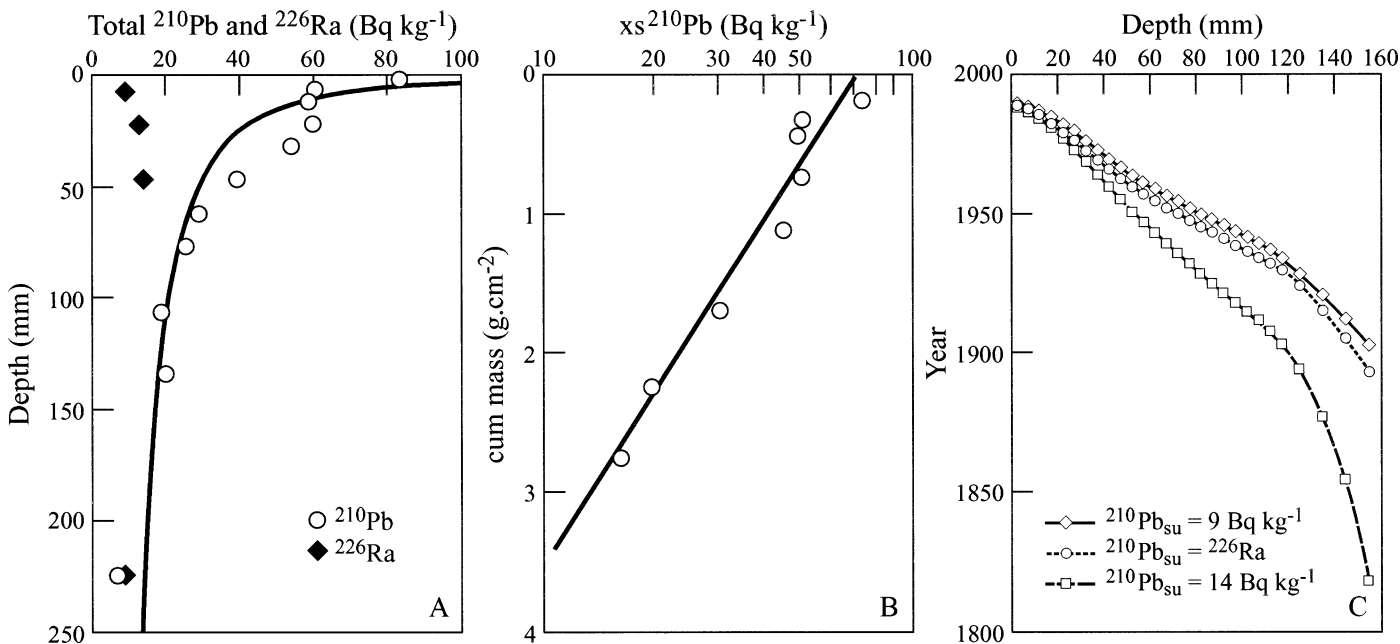


Fig. 4. (A) Total ^{210}Pb and ^{226}Ra levels, in Bq kg $^{-1}$ of total sediment as a function of depth for Blue lake core 1B. (B) "Excess" ^{210}Pb in log $_2$ Bq kg $^{-1}$ of total sediment as a function of cumulative mass for Blue lake core 1B. (C) Calculated age (in calendar year) vs. depth for the three scenarios for supported ^{210}Pb with values of 9 or 14 Bq kg $^{-1}$ or interpolating between measured values of ^{226}Ra as a proxy for supported ^{210}Pb .

yr $^{-1}$ (Fig. 4B,C), depending on which of the supported values of ^{210}Pb we used (see below).

Age at depth was estimated using the constant rate of supply (CRS) model (Binford 1990). The unsupported ^{210}Pb fraction was estimated using three different scenarios: (1) supported $^{210}\text{Pb} = 9 \text{ Bq kg}^{-1}$ (lowest measured ^{226}Ra and ^{210}Pb activities), (2) supported $^{210}\text{Pb} = 14 \text{ Bq kg}^{-1}$ (highest measured ^{226}Ra activity), and (3) supported ^{210}Pb proportional to ^{226}Ra at each depth (with linear extrapolation for depths where ^{226}Ra activity was not measured). We calculated the age-versus-depth relationship using the cumulative dry volumetric density for each of the above scenarios (Fig. 4C). The three models showed reasonably good agreement over the past 40 yr, with the model assuming the highest supported ^{210}Pb (14 Bq kg $^{-1}$) deviating the most with increasing age and depth.

An assumption inherent to the CRS model for ^{210}Pb dating is that the annual flux of unsupported ^{210}Pb remains constant through time (Binford 1990). In Blue Lake, the main sources of unsupported ^{210}Pb would be atmospheric deposition of particle-bound ^{210}Pb (Binford 1990) and possibly groundwater discharge of ^{222}Rn (Norton et al. 1985), a precursor to ^{210}Pb . The contribution of more than one source of unsupported ^{210}Pb to lake sediment has no impact on dating as long as the total supply is constant. However, in Blue Lake, the discharge of groundwater (and possibly ^{222}Rn) has not remained constant, especially during the period affected by pumping. The concentration of ^{222}Rn in the GL aquifer ranged 2.5–7 Bq L $^{-1}$, which is relatively low but still significant (Herczeg and Dighton unpubl. data). Estimates of ^{222}Rn loading rate to the Blue Lake (assuming no evasion of ^{222}Rn to the atmosphere) have suggested that groundwater

accounted for <1%–7% of the ^{210}Pb load before 1900 and for 11%–40% in 1970, at the peak in the pumping withdrawal rate. Thus, the supported ^{210}Pb load may have increased from 1900 to the present. The true contribution of groundwater ^{222}Rn is probably less than suggested here, because some ^{222}Rn will be lost to the atmosphere after entering the lake. However, if the input of groundwater ^{222}Rn is a significant proportion of the unsupported ^{210}Pb load, our estimated ages will tend to overestimate "true" ages in the uppermost portion of the core profile.

The chronological age of individual sediment layers up to a depth of 130 mm can be reasonably well established by the ^{210}Pb -derived mass accumulation rate estimates (140 mm depth corresponds to about the year 1915). Below that depth, the chronology has much higher uncertainties because of the smaller difference between measured ^{210}Pb activity and supported ^{210}Pb activity. It is also likely that mass accumulation rates had increased since 1940 because of the accelerated pumping rates, which are thought to have induced a higher flux of Ca^{2+} and HCO_3^- from the groundwater to the lake, and this is also reflected in lower carbonate contents in the core below 150 mm (see below). Extrapolating the $^{210}\text{Pb}_{x_s}$ -derived mass-accumulation rate below the dating range of ^{210}Pb may therefore lead to an overestimation of the mass-accumulation rate to 350 mm, an underestimation of the age at the bottom of the core, and a higher uncertainty in ages assigned to the bottom half of the core. Thus, we do not claim to have great confidence in the chronology of the lower half of the core and consider it to be older than 1920. The bottom of the core would have an age somewhere between 1800 (assuming the modern accumulation rate) and ~1600, which is based on a Holocene ^{14}C chronology of a 2-m-long

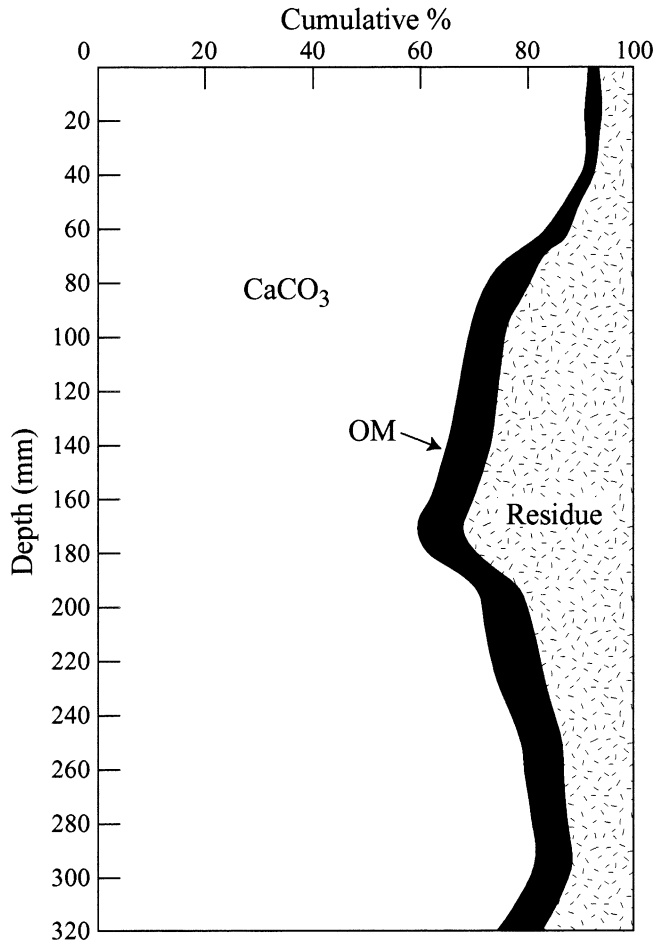


Fig. 5. Mass percentage of CaCO_3 , organic matter (OM), and residue as a function of depth for Blue Lake sediment.

core from Blue Lake (Leaney et al. 1995) that estimated an accumulation rate a factor of ~ 3 – 4 lower than those measured by ^{210}Pb .

Sediment cores—The carbonate content was 90%–92% in the top 30 mm of the core, then decreased to 58% at 160 mm, followed by an increase to 78% over the bottom 100 mm (Fig. 5). The OM content was lowest at the top of the core (2.5%–3.2%) and increased to 8.5% at the bottom of the core. The highest concentrations of residual material (acid-insoluble ash residue) were at a depth of 150–200 mm, where they made up 30% of the mass of the core. The sediment color became noticeably lighter further up the core, corresponding to an increase in carbonate content, and there were noticeable fine, possibly annual, laminations in the top 80–100 mm.

The depth profile of oxygen isotopes of the carbonate fraction of Blue Lake sediments showed a variation of nearly 3.5‰ (Fig. 6A). Near the bottom of the core, the $\delta^{18}\text{O}_{\text{carb}}$ level was roughly constant at $1.3 \pm 0.1\text{‰}$. The data showed a decrease of $\sim 1.8\text{‰}$ in $\delta^{18}\text{O}$ from about the mid-1800s to 1900, followed by a gradual decline to -0.9‰ in 1960. A further 1.5‰ decrease was observed from 1960 to ~ 1980 , which corresponds to the time during which of high rates of

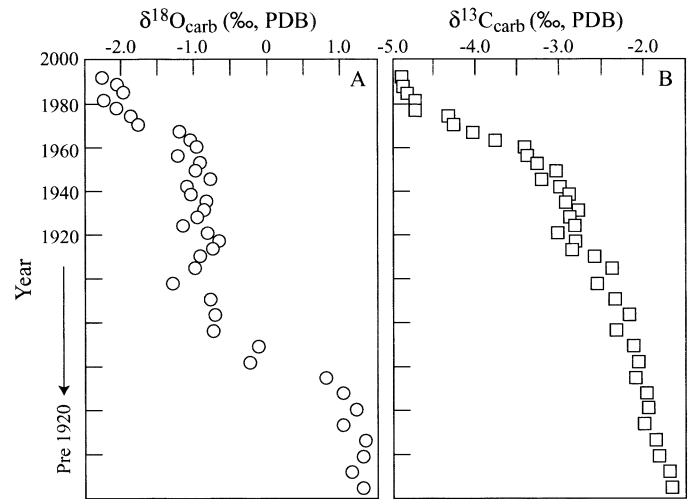


Fig. 6. (A) $\delta^{18}\text{O}_{\text{carb}}$ and (B) $\delta^{13}\text{C}_{\text{carb}}$ for Blue Lake sediment, with the depth scale converted to approximate year, derived from the mass accumulation rates (Fig. 4).

pumping of lake water to the town of Mt. Gambier occurred (Fig. 3).

The $\delta^{13}\text{C}$ of the carbonate fraction showed a steady decrease in $\delta^{13}\text{C}$ of $\sim 1.8\text{‰}$ from the bottom of the core to 1950 and a more rapid decrease of almost 2‰ during the last 50 yr of the sediment carbonate record (Fig. 6B). The $\delta^{13}\text{C}$ record did not display the large decrease during the latter half of the nineteenth century, as was observed for the $\delta^{18}\text{O}$ data (Fig. 6A).

$\delta^{13}\text{C}_{\text{org}}$ values were -30‰ at the bottom of the core and increased to a maximum of about -26‰ by ~ 1920 (Fig. 7A). The $\delta^{13}\text{C}_{\text{org}}$ values decreased by almost 10‰ over the past 80 yr, to about -35.5‰ . C:N mass ratios (Fig. 7B) generally ranged 10–12.5, except for four samples with slightly higher values, up to 14. The relatively low C:N ratios suggest that almost all of the OM deposited in the sediments of Blue Lake are derived from autochthonous al-

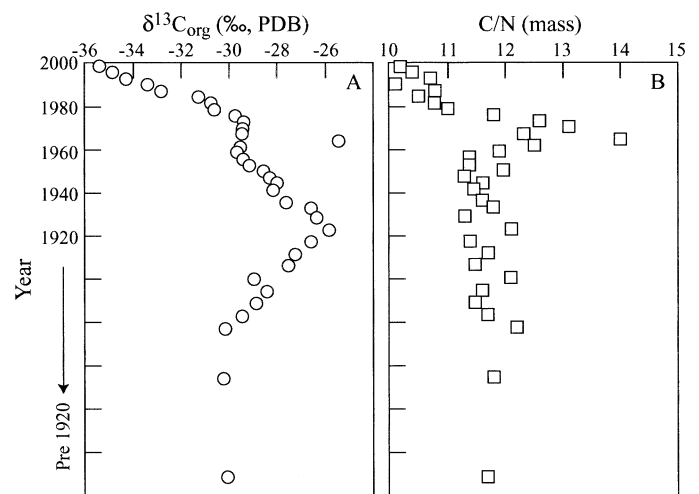


Fig. 7. (A) $\delta^{13}\text{C}_{\text{org}}$ and (B) C:N_{org} for Blue Lake sediment, with the depth scale converted to the approximate year derived from the mass accumulation rates (Fig. 4).

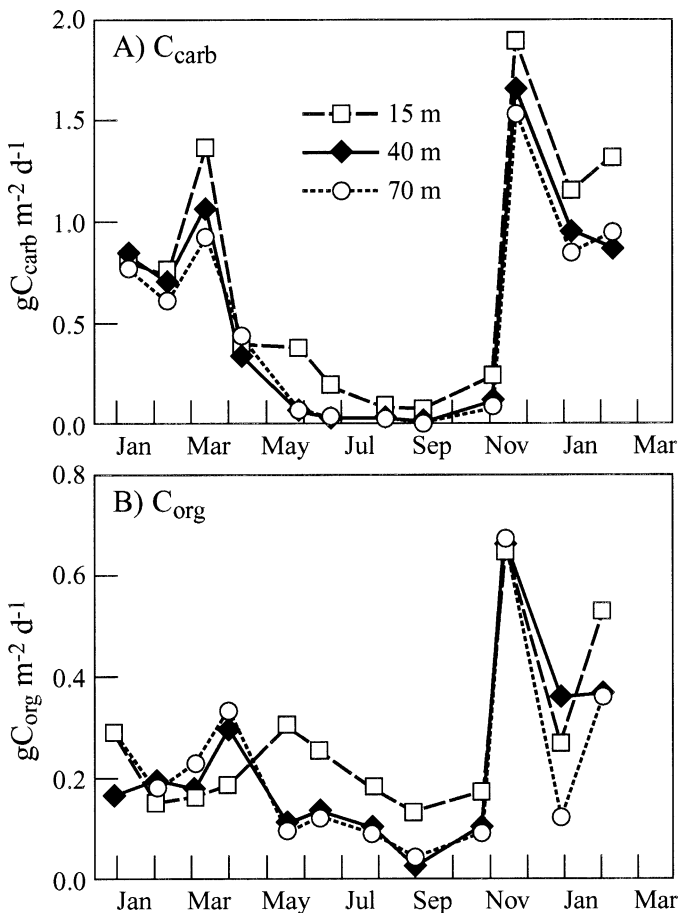


Fig. 8. Computed mean daily carbon mass fluxes for (A) carbonate C and (B) organic C at the three sediment traps deployments at 15, 40, and 70 m (original data from Telfer 2000).

gal or bacterial production rather than from terrestrial OM, which has C:N ratios >20 (Meyers 1997). Although low C:N ratios can also be characteristic of soil OM (Goni et al. 1998; Onstad et al. 2000), most of the organic carbon is lake-derived because of the negative $\delta^{13}\text{C}$ values (see above).

Sediment traps—The total mass flux of material collected in each of the sediment traps at 15, 40, and 70 m varied from <0.1 to $22 \text{ g m}^{-2} \text{ d}^{-1}$ (Telfer 2000). The highest total mass flux was recorded during December ($17\text{--}22 \text{ g m}^{-2} \text{ d}^{-1}$), with somewhat lower fluxes through the rest of the summer to March ($8\text{--}15 \text{ g m}^{-2} \text{ d}^{-1}$).

Much lower particle C fluxes were recorded throughout autumn–spring (April–November; $0.2\text{--}5 \text{ g m}^{-2} \text{ d}^{-1}$). Figure 8A,B shows that the seasonal change in particle C flux was mostly due to the much higher flux of carbonate minerals in summer, which appeared to be generated in the epilimnion and subsequently sank through the water column and partially dissolved. The $\delta^{13}\text{C}$ level of sediment trap carbonate material ranged -3.2‰ to -5.1‰ and was systematically more negative with increasing depth. The $\delta^{13}\text{C}$ composition of carbonate in the sediment traps varied with depth in the water column and with season (Fig. 9A). There was a general tendency for the carbonates in the 15-m trap to be 0.4‰

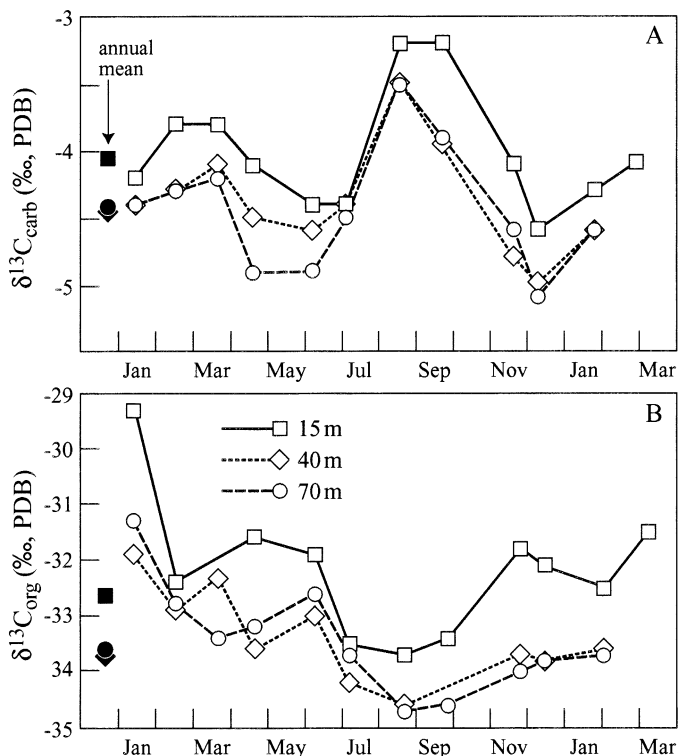


Fig. 9. (A) $\delta^{13}\text{C}_{\text{CaCO}_3}$ and (B) $\delta^{13}\text{C}_{\text{org}}$ for sediment traps at 15, 40, and 70 m throughout 1994.

more enriched in ^{13}C than those at 40 and 70 m, and this was also reflected in the annual amount weighted mean difference (-4.1‰ at 15 m and -4.5‰ at 40 and 70 m). The greatest difference from top to bottom was 0.9‰ , during the period of stratification (November–May). $\delta^{13}\text{C}_{\text{org}}$ values from the sediment traps showed a minimum during the winter and tended to be systematically enriched in ^{13}C in the 15-m trap, compared with the two deeper traps, by $\sim 0.5\text{--}1.5\text{‰}$ (Fig. 9B). The total range in $\delta^{13}\text{C}_{\text{org}}$ for all but two samples was between -31.5 and -34.8‰ . There was a -0.3‰ difference in $\delta^{13}\text{C}_{\text{carb}}$ and a -1.6‰ difference for $\delta^{13}\text{C}_{\text{org}}$ between the core top and weighted mean of sediment trap material collected at 70-m depth in the water column. C:N_{org} for all three sediment traps ranged 6.4–10.5 (Telfer 2000), with the exception of two samples from the 15-m trap that had values of ~ 13 . The amount weighted mean at the 70-m trap of 7.5 ± 0.9 was slightly lower than the sediment core top value of 10.2.

$\delta^{13}\text{C}_{\text{DIC}}$ of lake water—The water column $\delta^{13}\text{C}_{\text{DIC}}$ data (Fig. 10) showed a uniform composition of $-7.2 \pm 0.1\text{‰}$ during winter. By the end of the stratified period in April, there was a $2.6 \pm 0.2\text{‰}$ difference between 1 and 60 m due to preferential ^{12}C loss via gas exchange and photosynthesis from the DIC pool in the epilimnion and preferential addition of ^{12}C to the DIC pool in the hypolimnion due to oxidation of sinking OM ($\delta^{13}\text{C} = -32 \pm 3\text{‰}$; see below). The mean $\delta^{13}\text{C}_{\text{DIC}}$ composition of lake water was $\sim 2\text{‰}$ less than the weighted mean isotopic composition of carbonates in the sediment traps (Fig. 9A).

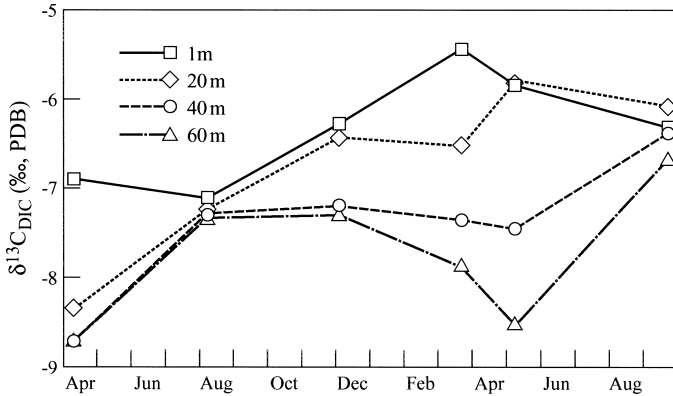


Fig. 10. $\delta^{13}\text{C}_{\text{DIC}}$ vs. water depth for Blue Lake over an 18-month period.

Discussion

Isotope record of hydrological changes—The $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ signature of precipitated carbonate is widely used as a proxy for changes to the water and DIC balance of lake systems (Talbot 1993; Li et al. 1997; Ricketts and Anderson 1998; Terranes and McKenzie 2001). The $(^{18}\text{O}:^{16}\text{O})_{\text{carb}}$ ratio reflects that of the water from which it precipitates and is determined by the relative amount and isotopic composition of inflow waters as well as by the relative fraction of losses via outflow and evaporation. The $^{13}\text{C}:^{12}\text{C}$ ratio of precipitated carbonate will also be dependent on the water budget parameters and the associated DIC concentrations and isotopic composition. It also incorporates carbon transfer via gas exchange between surface waters and the atmosphere and the net losses by sedimentation of carbonate minerals and OM. The changes in stable isotope composition of O and C in carbonates reflect changes in the relative mass flux components of the respective balances and are explicitly considered below.

The hydrological balance of a groundwater-fed lake such as Blue Lake (which has no surface drainage apart from direct rainfall) reflects the balance between groundwater inflow and loss by groundwater outflow, evaporation, and pumping (Eq. 1), where

$$\delta V/\delta t = Q_{\text{in}} + P - Q_{\text{out}} - E - Q_{\text{p}} \quad (1)$$

where $\delta V/\delta t$ is the change in lake volume over time; Q_{in} , Q_{out} , and Q_{p} are the groundwater inflow, groundwater outflow, and pumping; P is rainfall on the lake surface; and E is evaporation.

The stable isotope mass balance is written as

$$\partial(VR_L)/\partial t = Q_{\text{in}}R_{\text{in}} + PR_P - Q_{\text{out}}R_L - Q_{\text{p}}R_L - ER_E \quad (2)$$

where R is the $^{18}\text{O}:^{16}\text{O}$ ratio, expressed as $R = [(\delta^{18}\text{O}:1000) + 1]$, and the subscripts “L,” “in,” “P,” and “E” refer the isotopic ratios in the lake, groundwater inflow, rainfall, and moisture lost via evaporation, respectively.

The term R_E is the most difficult of the isotopic parameters to estimate and is usually approximated by the expression derived from Craig and Gordon (1965) in terms of $\delta^{18}\text{O}$ units as

$$\delta^{18}\text{O}_E = \left[\frac{1}{(1-h+\Delta\varepsilon)} \right] \left(\frac{\delta^{18}\text{O}_L - \varepsilon}{\alpha} - h\delta^{18}\text{O}_a - \Delta\varepsilon \right) \quad (3)$$

where h is the relative humidity (expressed as a fraction of unity); $\Delta\varepsilon$ is the enrichment factor, $14.2(1-h)$ Gonfiantini (1986); $\delta^{18}\text{O}_L$ is the isotopic composition of lake surface water; $\delta^{18}\text{O}_a$ is the isotopic composition of air vapor above the lake; α is the equilibrium fractionation factor ($\text{H}_2\text{O}_{\text{vap-liq}}$); and $\varepsilon = 1 - \alpha$. This expression implicitly accounts for both net loss of the lighter isotope due to evaporation, as well as vapor exchange between surface water and atmospheric water vapor.

The value of $\delta^{18}\text{O}_E$ is estimated from the equilibrium fractionation factor at the mean temperature of lake surface water (Friedman and O'Neill 1977), mean annual relative humidity (h) recorded at Mt. Gambier (62%), and $\delta^{18}\text{O}_a = -14.8 \pm 0.5\text{‰}$, which is assumed to be in isotopic equilibrium with the amount of weighted mean rainfall measured at Adelaide (Hughes and Allison 1983; J. C. Dighton unpubl. data) normalized to the mean annual lake surface water temperature of 14°C . The change in lake volume was calculated from the hypsographic curve, $\text{Vol} (\text{m}^3 \cdot 10^7) = 2.812 + 0.05773\text{AHD} + 0.00011\text{AHD}^2$, where AHD is the height of Blue Lake water level expressed as Australian height datum (AHD) in meters, which is the local convention standardized to mean intertidal sea level.

Given that the measured $\delta^{18}\text{O}$ of lake water (-2.2 to -2.8‰ ; Turner et al. 1984) was similar to that measured in carbonates at the top of the sediment core (Fig. 6), we assume that the $\delta^{18}\text{O}_{\text{carb}}$ measured in the sediment cores is a reliable proxy for changes in the isotopic composition of lake water. Because most of the carbonates are formed in the epilimnion in the warmer months at $\sim 18^\circ\text{C}$, the correction required between the carbonate $\delta^{18}\text{O}_{\text{carb}}$ (‰, PDB scale) and $\delta^{18}\text{O}_{\text{water}}$ (‰, SMOW [standard mean ocean water] scale) is within the analytical uncertainty (Friedman and O'Neill 1977) and was not applied. Furthermore, because each of the 5–10 mm subsections of core represents a 3–8-yr time period, we assumed that the volume of the lake was at steady state over that time interval (i.e., $\delta V/\delta t = 0$), given that the volume change during that time interval was $<2\%$. Equations (1 and 2) can be solved analytically for two unknowns for each of the 38 5–10-mm intervals, under the assumption of an instantaneous change in $\delta^{18}\text{O}$ of lake water from one step to the next.

Because rainfall, evaporation, and pumping rates are known reasonably well, we solved Eqs. 1 and 2 for groundwater inflow (Q_{in}) and outflow (Q_{out}) over the isotope record. The $\delta^{18}\text{O}$ of inflowing groundwater was estimated to be -4.8‰ from a mean of nearby water wells and observation boreholes (Love et al. 1994). The rainfall rate used in our model was based on meteorological parameters measured at Mt. Gambier (715 mm yr^{-1}), evaporation was estimated by an energy balance method by Turner et al. (1984) to be $1,198 \text{ mm yr}^{-1}$, and pumping rates were either those measured or estimated (Department of Environmental and Natural Resources 1994; Fig. 3). By isolating Q_{in} in the steady-state water balance expression, we substituted these data into Eq. 2 to get an explicit estimate of Q_{out} for each value of R_L and

substituted that back into Eq. 1 to get Q_{in} . Thus, we estimated both Q_{in} and Q_{out} as a function of time over the record. The largest source of uncertainty in the calculations of groundwater input and outflow was in the estimates of E and $\delta^{18}O_E$; however, the relative changes in Q_{in} and Q_{out} as a function of time were not greatly affected by varying the value of $\delta^{18}O_a$ and h that were used to derive this parameter in Eq. 3.

A pair of expressions similar to those used above for the water balance could be generated for the carbon mass balance using DIC concentrations and $\delta^{13}C_{DIC}$ via Eqs. 4 and 5:

$$\begin{aligned} \partial(V[DIC]_L)/\partial t = & Q_{in}[DIC]_{in} - Q_{out}[DIC]_L - S_{carb} - S_{org} \\ & - netEv \end{aligned} \quad (4)$$

and the isotopic mass balance as

$$\begin{aligned} \frac{\partial(V[DIC]_L R_L)}{\partial t} = & Q_{in}[DIC]_{in} R_{in} + Inv R_{CO_2(atm)} \\ & - Q_{out}[DIC]_L R_L - S_{carb} \alpha_{carb} R_L - S_{org} R_{org} \\ & - Ev R_{CO_2(L)} \end{aligned} \quad (5)$$

where $[DIC]_L$ and $[DIC]_{in}$ are the DIC concentrations in lake water and groundwater, respectively; S_{carb} and S_{org} are the annual losses of carbonate C and organic C, respectively, to sediments; $netEv$ is the net CO_2 loss from the lake via gas evasion; R_x is the isotope ratio ($^{13}C:^{12}C$) in the respective reservoirs; Inv is the total invasion of CO_2 from the atmosphere; Ev is the total evasion of CO_2 from the lake; and α is the fractionation between DIC and precipitated carbonate.

The isotopic composition of DIC therefore reflects the balance between the amount and isotopic composition of inflowing groundwater DIC, the permanent burial of inorganically precipitated $CaCO_3$ and organic carbon in sediments, and gas exchange. For the DIC mass balance (Eq. 4), we need only consider net evasion, because there is a net flux of CO_2 out of the lake, given that the pCO_2 level of inflowing groundwater is 10–20 times that of the atmosphere (Love et al. 1994) and the lake surface water always has a higher pCO_2 level than the atmosphere (Turner 1979). However, both total CO_2 gas invasion and evasion need to be explicitly determined in the isotope mass balance (Eq. 5), because invasion from the atmosphere adds CO_2 with $\delta^{13}C = -9\%$, whereas evasion removes CO_2 with $\delta^{13}C \sim -14\%$. Increasing groundwater input would tend to make the lake water $\delta^{13}C_{DIC}$ levels more negative for similar reasons as that of the $\delta^{18}O$ mass balance described above. A shorter water residence time decreases the relative importance of gas exchange, and, because gas exchange tends to force the lake DIC toward atmospheric equilibrium ($\sim 1\%$), the net effect is similar to that of reduced evaporation. Thus, one can approach the application of the $\delta^{13}C_{carb}$ record in the same way as that used for the $\delta^{18}O_{carb}$ to explicitly calculate groundwater inflow and outflow rates. The additional parameters needed in Eqs. 4 and 5 are estimates of the gas exchange rates, which were determined by a hydrological study of Blue Lake by Turner et al. (1983). The permanent burial rates of inorganic and organic C are calculated from sediment mass accumulation rates (Fig. 4) and the measured C content of the sediment (Fig. 5).

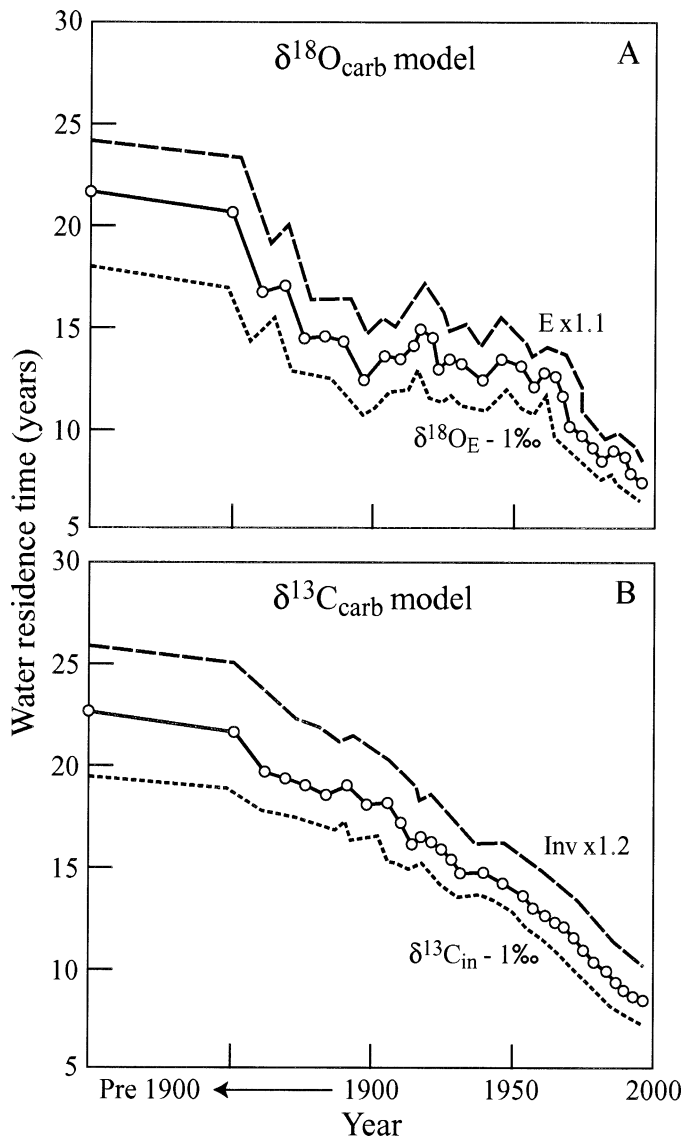


Fig. 11. Calculated water residence time (volume/ Σ outflow) shown as circles, as a function of time for Blue Lake based on (A) $\delta^{18}O_{carb}$ and (B) $\delta^{13}C_{carb}$ using Eqs. 1–5 in the text. Also shown are the sensitivity of the calculated water residence times to two of the parameters (E and $\delta^{18}O_E$ in the case of $\delta^{18}O_{carb}$ and Inv and $\delta^{13}C_{in}$ for the $\delta^{13}C_{carb}$) by 10%, -1% , 20%, and -1% , respectively.

The results of the O and C isotope mass balance calculations (Fig. 11) are expressed in terms of variation in water residence time for Blue Lake $[V/(Q_{in} + P)]$ over the sediment record. In each case, we have shown upper and lower curves that show the sensitivity of the model to two parameters to which either have the largest uncertainty or the largest impact on estimated water residence time (these are, respectively, E and $\delta^{18}O_E$ for the $\delta^{18}O$ mass balance, CO_2 invasion rate, and $\delta^{13}C_{DIC}$ of inflow for the $\delta^{13}C$ model). In each case, the absolute numbers are different to the “best estimate,” but the trends are nearly identical. We have summarized the range of sensitivity of the water residence time estimates derived using Eqs. 2–5 for a number of input parameters in Table 1.

Table 1. Sensitivity of the $\delta^{18}\text{O}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{carb}}$ isotope mass balance models to variation in a number of input parameters. The trends shown in Fig. 11 are for those that are most sensitive (e.g., E and $\delta^{18}\text{O}_E$ for the $\delta^{18}\text{O}$ mass balance and CO_2 inversion rate (Inv) and $\delta^{13}\text{C}_{\text{DIC(in)}}$ of the $\delta^{13}\text{C}$ mass balance).

| Parameter | Change in parameter | % change in water residence time |
|-----------------------------------------------|-------------------------------|----------------------------------|
| $\delta^{18}\text{O}$ mass balance | | |
| E | $\pm 10\%$ | 12–15 |
| h | $\pm 10\%$ | 2–5 |
| $\delta^{18}\text{O}_E$ | $\pm 1.0\text{‰}$ | 10–18 |
| $\delta^{18}\text{O}_I$ | $\pm 0.4\text{‰}$ | 7–12 |
| $\delta^{13}\text{C}$ mass balance | | |
| CO_2 invasion rate (INV) | $\pm 20\%$ | 15–20 |
| $\text{C}_{\text{carb+org}}$ sed rate | $\pm 20\%$ | 1–4 |
| $[\text{DIC}]_{\text{in}}$ | $\pm 0.5 \text{ mmol L}^{-1}$ | 7–11 |
| $\delta^{13}\text{C}_{\text{DIC}}(\text{in})$ | $\pm 1\text{‰}$ | 10–13 |

DIC: dissolved inorganic carbon; sed rate: sedimentation rate.

The estimated water residence time in the early part of the record (before settlement of the area by Europeans), based on the $\delta^{18}\text{O}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{carb}}$ mass balance, was $\sim 22 \pm 2$ yr (Fig. 11A,B), which then decreased to 7 ± 2 yr by the late 1990s. The changes in residence time calculated from both isotope models were generally similar for the beginning and latter part of the record but differed significantly during the second half of the nineteenth century. Water residence times estimated from the $\delta^{13}\text{C}_{\text{carb}}$ data tended to follow a smooth trend throughout the entire record, whereas there was an apparent rapid decline in water residence time during the latter part of the 1800s when the $\delta^{18}\text{O}$ data were used. The reason for the discrepancy between the calculations is related to the rapid 2‰ observed decrease in $\delta^{18}\text{O}$ that was not replicated in the carbon isotopic record. From 1850 to ~ 1890 , the apparent mean $\delta^{18}\text{O}$ of the lake water decreased by $\sim 2\text{‰}$, (to -1‰ ; see Fig. 6), with a concomitant change in calculated water residence time to 14 ± 1 yr, which remained roughly constant through the first half of the twentieth century.

The decrease in the $\delta^{18}\text{O}$ of lake water during the late 1800s may have been caused by a combination of increased recharge to the unconfined GL aquifer after the clearing of native vegetation and higher rainfall relative to evaporation from 1860 to 1910 (long-term rainfall records from Mt. Gambier show that this period from was $\sim 20\%$ wetter than average; Bureau of Meteorology 1998). Increased recharge would lead to higher groundwater heads up-gradient of the lake and, consequently, higher rate of through-flow across the lake. The shorter lake water residence time leads to a decrease in the relative influence of evaporative enrichment of ^{18}O , and the lake water isotopic composition would tend to approach the groundwater value of -4.5‰ . It is also reasonable to expect that evaporation may have been lower during relatively wetter years (and humidity higher), thus leading to less evaporative enrichment of water and more negative isotopic composition of surface waters from which the carbonates precipitated. A decrease in the $\delta^{18}\text{O}$ of “re-

charge water” to the groundwater may also have been associated with higher recharge rates and greater proportions of winter rainfall (which tend to have more negative $\delta^{18}\text{O}$ levels than annual mean) reaching the top of the GL aquifer. However, the large volume of groundwater surrounding the lake would tend to buffer short-term changes to the point where no observable change in $\delta^{18}\text{O}_{\text{gw}}$ contributing to the lake is likely on the timescale of our study. Even though our sampling interval covered a time span of $\sim 6\text{--}9$ yr in that part of the record, the time lag and dampening in the groundwater system would be on the order of centuries, especially given that much of groundwater inflow appeared to occur at 45 m depth (Telfer 2000). The smoother trend observed for the $\delta^{13}\text{C}_{\text{carb}}$ data in the late 1800s may be related to the much shorter residence time for DIC compared with H_2O within the lake (see below).

The gradual decrease in $\delta^{18}\text{O}_{\text{carb}}$ values from ~ 1910 to 1960, compared with the previous half-century, is thought to be a reflection of the lake water residence time having reached a quasi steady state. Although pumping of the lake water had begun by 1900, the amount was not yet a major component of the water balance and may have had just a slight influence on lake isotopic composition by inducing higher groundwater through-flow. Fluctuations in the isotopic record on a timescale of $\sim 20\text{--}25$ yr through the first half of the twentieth century (Fig. 6A) may reflect interannual to decadal changes in rainfall to the lake that is superimposed on the pumping-induced slow decline in $\delta^{18}\text{O}$.

The greatly accelerated rate of pumping from ~ 1945 onward corresponds to lower lake water levels (Fig. 3) and became the major outflow component of lake water, with groundwater outflow (Q_{out}) either totally eliminated or very low (Table 2). The result is that the lake water $\delta^{18}\text{O}$ levels had, by the mid-1990s, decreased by 3.5‰ since European settlement of the area and, by the end of the twentieth century, only 2.5‰ more enriched in ^{18}O than the incoming groundwater. Water residence times estimated from both the O and C isotope mass balance were 7 ± 2 yr by 1995 and appear to be on a declining trend.

Another way to formulate the water balance is to group groundwater inflow plus rainfall into one inflow term ($Q_{\text{in}} + P = \Sigma Q_{\text{in}}$) and group the outflow terms except evaporation (pumping plus groundwater outflow; $Q_{\text{out}} + Q_{\text{p}}$) and solve a modified form of Eq. 2. By using this approach, a first-order approximation of the relative importance of water loss by evaporation relative to all other losses can be estimated, without the need to explicitly solve for the individual fluxes, and there are fewer assumptions required. The results of a conceptual model curve are shown in Fig. 12, with the ratio $(Q_{\text{out}} + Q_{\text{p}})/\Sigma Q_{\text{in}}$ on the x-axis plotted against $\delta^{18}\text{O}_{\text{water}}$. A value of $(Q_{\text{out}} + Q_{\text{p}})/\Sigma Q_{\text{in}} = 1$ would correspond to 100% loss by groundwater outflow plus pumping (i.e., evaporation = 0). If all water is lost by evaporation, data would plot at the upper right-hand side of the curve (outflow plus pumping would be zero). The range of $\delta^{18}\text{O}_{\text{carb}}$ values for the Blue Lake core is toward the 100% through-flow end of the spectrum, and this is shown in more detail in Fig. 12. We estimate that $\sim 25\text{--}30\%$ of all inflow was lost to evaporation prior to any pumping, and the remainder was lost by groundwater outflow. By the mid-1990s, pumping had induced in-

Table 2. Water balance terms for selected years, determined from the $\delta^{18}\text{O}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{carb}}$ mass balance model (Eqs. 1–5).

| Year | Water flux $\delta^{18}\text{O}_{\text{carb}}$ ($\text{m}^3 \text{ yr}^{-1}$) $\times 10^6$ | Water flux $\delta^{13}\text{C}_{\text{carb}}$ ($\text{m}^3 \text{ yr}^{-1}$) $\times 10^6$ |
|---------------------------|-----------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------|
| Rainfall, all years | 0.434 | 0.435 |
| Evaporation, all years | 0.724 | 0.724 |
| Pumping | | |
| 1850 | 0 | 0 |
| 1910 | 0.11 | 0.11 |
| 1953 | 2.5 | 2.5 |
| 1995 | 3.5 | 3.5 |
| Q_{in} | | |
| 1850 | 1.63 | 1.77 |
| 1910 | 2.82 | 1.85 |
| 1953 | 2.84 | 2.78 |
| 1995 | 4.80 | 4.34 |
| Q_{out} | | |
| 1850 | 1.92 | n/a |
| 1910 | 2.48 | |
| 1953 | 0.53 | |
| 1995 | 0.73 | |
| Water residence time (yr) | | |
| 1850 | 20.8 | 21.7 |
| 1910 | 13.8 | 16.9 |
| 1953 | 13.4 | 13.7 |
| 1995 | 7.5 | 8.3 |

creased groundwater inflow to the lake, the fraction of that lost to the atmosphere was reduced to 5%–10%, and almost all of the remainder was pumped out. Although the present analysis does not explicitly estimate groundwater outflow component, previous estimates have suggested that this is now <20% of total water losses (Table 2).

Impact of increased through-flow on DIC cycling—Changes to DIC residence time (defined as the total lake DIC inventory divided by total input) over the 200 yr of record can also be calculated from Eq. 4 and 5, as well as using the water balance parameters derived from the $\delta^{18}\text{O}_{\text{carb}}$ mass balance. The results of these fluxes are given in Table 3, and the calculated DIC residence time is plotted as a function of time in Fig. 13. The early part of the record shows an estimated DIC residence time of $\sim 3.8 \pm 0.3$ yr; by the mid-1990s, this had decreased to $\sim 2.2 \pm 0.2$ yr. Thus, the reduction in DIC residence time is only $\sim 40\%$, compared with the concomitant decrease in water residence time by a factor of ~ 3 (from 22 to 8 yr). The much shorter residence time of DIC, and the modest change in response in increased groundwater input, is because a substantial fraction of the total DIC inventory is replaced each year because of the large CO_2 gas exchange fluxes (Table 3). Thus, the change in DIC residence time as a result of higher groundwater through-flow is not as significant as the change in water residence time. Most of the increased incoming DIC flux via groundwater inflow is lost by increased net evasion to the atmosphere. Although there is thought to be an increase in the rate of C removal by increased CaCO_3 deposition (see

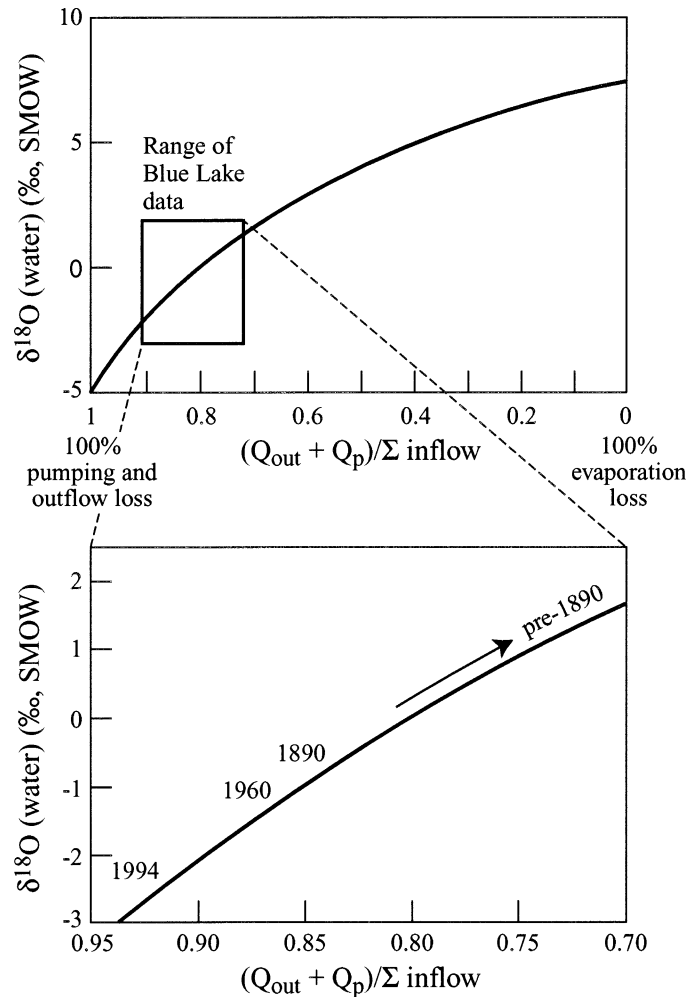


Fig. 12. Computed outflow:inflow ratio, expressed in terms of (groundwater outflow + pumping) divided by total inflow plotted against sediment $\delta^{18}\text{O}_{\text{carb}}$ data. If all water is lost by pumping + groundwater outflow, data would plot at the bottom left, and, if all was lost by evaporation, at the top right of the curve. The range of Blue Lake data are shown in more detail in the bottom panel, which indicates that, prior to ~ 1890 , $\sim 15\%$ – 25% of total water inflow was lost to evaporation. Because of increased pumping after the 1950s, the fraction of inflow lost by E decreased to 5%–10% by the mid-1990s.

below), the relative fraction of DIC lost to the sediments is <5% of the net evasion of CO_2 (Table 3).

The present-day rates of recycling of carbonate C and organic C produced within a lake can be estimated by comparing the particle fluxes estimated from sediment traps with that permanently buried in the sediment. We also need to assess whether the sediment record of $\delta^{13}\text{C}$ reflects that of the C_{carb} and C_{org} produced in the water column and of the DIC. Particle fluxes of C_{org} estimated from the 14-month sediment trap deployment in 1994 ranged <0.1 – $0.3 \text{ g m}^{-2} \text{ d}^{-1}$ throughout all months except December, when it was $\sim 0.7 \pm 0.1 \text{ g m}^{-2} \text{ d}^{-1}$. The flux of C_{carb} is of the same order as the C_{org} flux from April to November but is a factor of 2–3 higher during summer (December–March), when it reaches values up to $1.8 \text{ g m}^{-2} \text{ d}^{-1}$ just after the onset of

Table 3. Dissolved inorganic carbon (DIC) budget, determined from $\delta^{13}\text{C}_{\text{carb}}$ data, and water balance terms, determined from $\delta^{18}\text{O}_{\text{carb}}$ and Eqs. 1–5 in the text.

| Year | DIC flux $\delta^{13}\text{C}_{\text{carb}}$ (mol yr ⁻¹) × 10 ⁶ |
|------------------------------|----------------------------------------------------------------------------------------------|
| Invasion, all years | 18.1 |
| Evasion | |
| 1850 | 23.8 |
| 1910 | 26.3 |
| 1953 | 26.5 |
| 1995 | 32.4 |
| Pumping | |
| 1850 | 0 |
| 1910 | 0.33 |
| 1953 | 8.3 |
| 1995 | 11.6 |
| Q_{in} | |
| 1850 | 10.6 |
| 1910 | 11.1 |
| 1953 | 17.0 |
| 1995 | 28.8 |
| Q_{out} | |
| 1850 | 5.8 |
| 1910 | 8.2 |
| 1953 | 1.8 |
| 1995 | 2.4 |
| S_{carb} | |
| 1850 | 0.4 |
| 1910 | 0.5 |
| 1953 | 0.7 |
| 1995 | 0.9 |
| S_{org} , all years | 0.18 |
| DIC residence time (yr) | |
| 1850 | 3.9 |
| 1910 | 3.2 |
| 1953 | 3.1 |
| 1995 | 2.2 |

stratification in early December. The aggregated annual C fluxes for the three sediment traps and the sediment mass accumulation rates (Table 4) showed that ~39% of the annual C_{carb} and 22% of the C_{org} particle flux, respectively, are recycled within the water column. Most of the remaining C is recycled at or near the sediment water interface, with 88% and 96% of the total C_{carb} and C_{org} , respectively, produced within the water column recycled. The high rate of organic carbon mineralization at depth is surprising, because it is usually mineralized within the water column before making it to the bottom sediments. One possible reason for this may be seen from the correlation between carbonate and OM flux rates (Fig. 8), which suggests that the OM may be removed rapidly from the water column by “coaggradation” with carbonates, at least during summer. It is then mineralized over time via anaerobic redox processes at the sediment-water interface.

The mean $\delta^{13}\text{C}_{\text{CaCO}_3}$ levels in the sediment traps (Fig. 9) were $2 \pm 0.5\text{‰}$ more positive than the corresponding $\delta^{13}\text{C}_{\text{DIC}}$

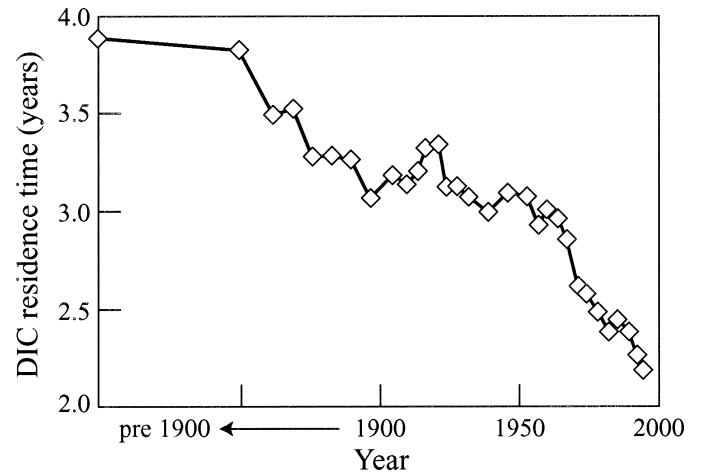


Fig. 13. Calculated dissolved inorganic carbon (DIC) residence time (volume × $[\text{DIC}]_L / \Sigma \text{DIC input}$) as a function of time for Blue Lake, based on $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ (for water fluxes) using Eqs. 4 and 5 in the text.

levels (Fig. 10). This difference is of the order of equilibrium and kinetic fractionation effects during calcite precipitation (Friedman and O’Neil 1977; Turner 1982; Zhang et al. 1995). The most ^{13}C -enriched carbonates are formed during late winter and early spring, shortly after lake overturn, when the total amount of CO_2 loss to the atmosphere would be the highest, which results in a preferential loss of ^{12}C . Core top $\delta^{13}\text{C}_{\text{CaCO}_3}$ values are very close to summertime sediment trap values, which are expected given the much higher carbonate production rates during summer (Fig. 9). The 0.4‰ lower $\delta^{13}\text{C}$ values recorded in the 40- and 70-m traps compared with that at 15 m may reflect preferential dissolution of $\text{Ca}^{13}\text{CO}_3$ calcite as it sinks through the water column, because the mass flux of C_{carb} declined with depth (Fig. 11) rather than with the additional production of ^{13}C -depleted calcite with depth. The dissolution occurred because of undersaturation with respect to calcite imposed by the addition of CO_2 below the thermocline, as well as lower temperatures and higher pressures with depth, which both increase the carbonate mineral solubility. The added $\text{CO}_2(\text{aq})$ is a result of a combination of mineralization of OM at depth and a buildup in the hypolimnion groundwater with high $p\text{CO}_2$ in-pit at 40 m.

Table 4. Carbon flux, calculated from sediment trap and sediment mass accumulation rates and fraction of carbon recycled.

| Measurement | C_{carb} (gC m ⁻² yr ⁻¹) | C_{org} (gC m ⁻² yr ⁻¹) |
|------------------------------|-------------------------------------------------------------|------------------------------------------------------------|
| Depth (m) | | |
| 15 | 190 | 77 |
| 40 | 145 | 60 |
| 70 | 115 | 60 |
| Sediment C-accumulation rate | 22.8 | 3.1 |
| % C recycled in water column | 39 | 22 |
| % C recycled at sediment | | |
| water interface | 49 | 74 |
| Total % C recycled | 88 | 96 |

$\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$ record: Trophic state or artefact of hydrological change?—The $\delta^{13}\text{C}$ composition of carbonate and OM in sediments have been extensively used to evaluate long-term changes in trophic state and C cycling due to nutrient loading (Meyers and Ishawitari 1995; Bernasconi et al. 1997; Hodell and Schelske 1998) or land-use change (Brenner et al. 1999; Herczeg et al. 2001). In addition to changes in water residence time discussed above, there has been increased loading of nitrates to Blue Lake as a consequence of increased inflow of the high NO_3^- groundwater (Lamontagne 2002). Any changes in trophic state as a result of nutrient enrichment inferred from the $\delta^{13}\text{C}_{\text{org}}$ sediment record are contingent on there being no (or at least well-known) diagenetic or metabolic effects on the isotopic signature (Macko et al. 1993; Meyers 1997).

Although there is a -2% difference between the level of OM at the top of the sediments and that of the suspended OM, we can assume that the offset is constant over time and that the overall trends in the sediment $\delta^{13}\text{C}_{\text{org}}$ are significant despite the estimated 96% recycling of C_{org} to DIC (see above). Keeping in mind that the C_{org} mass flux is higher during summer than winter (Fig. 8), the core top values are essentially the same as the weighted mean of the particle flux at 40 m but are $\sim 2\%$ more negative than the amount weighted mean flux at 70 m, which indicates a preferential loss of ^{13}C during diagenesis. If we assume that OM in Blue Lake is derived entirely from autotrophic production, then the calculated fractionation between $\delta^{13}\text{C}_{\text{DIC}}$ ($-6.5 \pm 1.2\%$) and the OM ($-32 \pm 2\%$) is about -27% under current conditions.

There are two main trends for the carbon isotopic record of OM in the sediments depicted in Fig. 7: an increase of 4.5% from 1850 to 1900, then a 9.5% decrease through the twentieth century. In the former case, the only significant local perturbation was the clearing of native *Casuarina* and *Eucalyptus* vegetation and replacement by pastures (Lange 1983). At the same time, there was a decrease in the percentage of C_{org} in the sediments (Fig. 5), and, during the same time, the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ carbonate records (see above) suggest a decrease in the water residence time. The -2.5% change in apparent $\delta^{13}\text{C}$ of the DIC, as indicated by $\delta^{13}\text{C}$ of carbonates, can only partly explain the -10% shift in $\delta^{13}\text{C}_{\text{org}}$ of OM observed in the sediments. That is, the suspended particulate organic carbon (POC) would change from -26% to -28.5% , under the assumption that, in the first instance, the fractionation between DIC and autotrophic POC is constant over time.

The increased flux of terrestrial OM ($\delta^{13}\text{C} = -24 \pm 2\%$) cannot be responsible for a decrease in $\delta^{13}\text{C}_{\text{org}}$ of sediments to -36% . The most likely explanations for the -7% to -8% shift in the difference between DIC and POC deposited in the lake since 1900 is through an increase in discrimination between DIC and POC as a result of increased lake $\text{CO}_2(\text{aq})$ concentrations. The 10% decrease in $\delta^{13}\text{C}_{\text{org}}$ throughout the twentieth century corresponds to increased rates of DIC input via groundwater, which in turn has $p\text{CO}_2$ levels of $10^{-1.4}$ – $10^{-2.8}$ atm. (Love et al. 1994) with consequent lake-water $p\text{CO}_2$ levels of $10^{-2.94}$ – $10^{-3.1}$ atm. (Turner 1979). Higher concentrations of $\text{CO}_2(\text{aq})$ may lead to an increase in the discrimination against ^{13}C by phytoplankton

(Hollander and McKenzie 1991; Rau et al. 1997), even though DIC is not limiting. The increase in available $\text{CO}_2(\text{aq})$ due to the higher groundwater flux would not necessarily alter the lake trophic state, despite there being relatively high $p\text{CO}_2$ levels prior to pumping. The implications are that the $\delta^{13}\text{C}_{\text{org}}$ record, even in an oligotrophic lake, reflects the availability of $\text{CO}_2(\text{aq})$ and, in turn, hydrological processes, rather than in-lake metabolism. Given that the $\delta^{13}\text{C}_{\text{carb}}$ data do not suggest major changes in trophic state (McKenzie 1985; Hodell and Schelske 1998) and are generally consistent with the hydrological balances, adds support the above explanation. Furthermore, there has been no apparent change in the C_{org} sedimentation rate during past two centuries, and increased sediment accumulation has almost entirely been contributed by higher C_{carb} sedimentation rates, which is also consistent with higher rates of DIC input from groundwater.

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Received: 22 August 2002

Amended: 12 May 2003

Accepted: 17 May 2003