

# The trophic history of Myall Lakes, New South Wales, Australia: interpretations using $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of the sedimentary record

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**Abstract** In an attempt to determine the trophic history of the Myall Lakes complex (New South Wales, Australia)  $\delta^{13}\text{C}_{\text{org}}$ ,  $\delta^{15}\text{N}$  and  $\text{C}_{\text{org}}:\text{N}$  profiles were determined for bulk organic matter of two short sediment cores from Bombah Broadwater and Myall Lake.  $^{210}\text{Pb}$  profiles and sediment types indicate

significantly different trophic trajectories during the time periods examined.  $\delta^{13}\text{C}_{\text{org}}$  and  $\text{C}_{\text{org}}:\text{N}$  indicate Bombah Broadwater has been dominated by increasing inputs of terrestrial organic material over the last century, thought to be related to watershed disturbance including agricultural activity. Primary production appears to be dominated by phytoplankton.  $\delta^{15}\text{N}$  remained relatively stable at around 1‰ until the mid-1970s when there was a sharp increase to 4.7‰, interpreted as an influx of sewage-derived material. These observations offer an insight into the recent trophic changes at the site. Sedimentation rates are noticeably lower in Myall Lake and the most recent sediment is a flocculent organic rich deposit overlying mineral clay.  $\delta^{13}\text{C}_{\text{org}}$  and  $\text{C}_{\text{org}}:\text{N}$  values indicate a transition from plankton to macrophyte dominated primary production around 1800AD.  $\delta^{15}\text{N}$  values become increasingly negative from approximately 1900AD. This is interpreted as being due to increasing reliance by macrophytes on nitrogen recycled from decomposing sediments driven by natural infilling and eutrophication in this basin. The contrasting sedimentation rates, sediment types and geochemical profiles suggest the different basins of this water body are subject to substantially different internal and external influences which should be considered in management decisions.

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Guest editors: J. Wilson, L. Bowling & J. Tibby  
The Myall Lakes: patterns and processes in an unusual coastal lake system in eastern Australia

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**Keywords** Sediment · Lakes · Isotopes · Trophic · Carbon · Nitrogen

## Introduction

Myall Lakes is a series of four interconnected brackish lakes located on the lower north coast of New South Wales. In 1999 a major bloom of the potentially toxic cyanobacterium *Anabaena circinalis* Rabenhorst occurred in some areas of the lakes (Ryan et al. 2008).

The potential health risks and loss of amenity value associated with such blooms resulted in the initiation of several studies regarding the limnology and ecology of the sites in an attempt to identify the causes of the 1999 event (Dasey et al., 2004, 2005). While the mechanisms responsible for cyanobacterial blooms are not well understood the link with nutrient enrichment has been widely noted and researched (Cloern, 2001; Smith, 2003). Scheffer (1997) provided evidence that cyanobacteria are superior competitors for light in high nutrient conditions. Bianchi et al. (2000) showed that cyanobacteria populations respond to a reduction of the nitrogen–phosphorus ratio due to their ability to fix atmospheric nitrogen. Davis & Koop (2006) have highlighted the importance of physical conditions such as stratification and light availability in bloom initiation at sites across Australia.

The observed relationship between cyanobacterial blooms and nutrient imbalances has led to the suggestion that the 1999 bloom in Myall Lakes may be due to anthropogenic nutrient impacts. Known anthropogenic sources of nutrients to the lakes include agricultural activities in the watershed and sewage discharges into the Myall River (Dasey et al. 2004). However, modern data, and even time series monitoring collected over months to years span too short a period to cast useful insights into the reasons for the current configuration of a system. Modern manifestations of eutrophication may be due to conditions which were initiated before the period for which monitoring data are available (e.g. Anderson, 1995). Long-term nutrient records for Myall Lakes prior to 1999 are not available. Palaeo-studies of lake records are producing an increasing number of examples of sites subject to anthropogenic nutrient impacts (Schelske & Hodell, 1991; Bennion et al., 1996; Umbanhowar et al., 2003; Bennion et al., 2004) related to agricultural activities such as ploughing, dairy farming and the use of fertilizers. Such studies generally use biotic remains such as

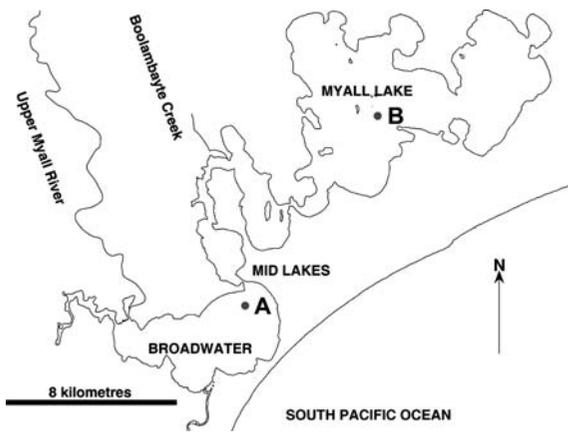
diatoms or chironomid head capsules to reconstruct nutrient levels. In recent years there has been increasing use of carbon and nitrogen stable isotope analysis of organic material from sedimentary records to cast insight into the trophic history of enclosed water bodies such as lakes and estuaries (Talbot, 2001).

To this end a study of the environmental history of the lakes was undertaken by analysing stable isotopes of carbon and nitrogen of the sediment record taken from two of the basins.  $\delta^{13}\text{C}$  of sedimentary material has been shown to be a proxy for primary production (Schelske & Hodell, 1991, 1995; Brenner et al., 1999) thought to be formed during increased uptake of  $^{13}\text{C}$  during conditions of inorganic C limitation, during bloom conditions (Fogel et al., 1992). Sedimentary  $\delta^{13}\text{C}$  has also been used as tracer of sources of terrestrial vs autochthonous organic matter based on differences in  $\delta^{13}\text{C}$  of these materials (Herczeg et al., 2001).  $\delta^{15}\text{N}$  is a proxy for the loading of inorganic nitrogen compounds (Hodell & Schelske, 1998; Brenner et al., 1999; Herczeg et al., 2001; Teranes & Bernasconi, 2000), a primary cause of eutrophication. In some instances this is due to additions of sewage material which has a  $^{15}\text{N}$  enriched signal (Savage et al., 2004; Kauppila et al., 2005) due to denitrification during sewage treatment. In other instances, the cause is inputs of  $^{15}\text{N}$  enriched dissolved inorganic N which is created during denitrification of agricultural fertilizers in the watershed (Voss & Struck, 1997; Kellman, 2005).

## Materials and methods

### Site description

Myall Lakes is a lake complex comprising four shallow, interconnected, brackish lakes located on the lower north coast of New South Wales (Fig. 1). The two largest basins are Myall Lake in the north and Bombah Broadwater in the south, which are connected by Two Mile Lake and Boolambayte Lake. They are 2 km inland from the Tasman Sea to which they are connected via the Lower Myall River flowing 25 km south west into the bay of Port Stephens. Lake surface area is between 100–150 km<sup>2</sup> depending on water levels and the catchment size is 780 km<sup>2</sup>. This means that flushing time is relatively



**Fig. 1** Myall Lakes showing the two basins sampled and locations of cores A and B.

long (400–880 days) (DPWS 1999) and marine influence is limited. Dissolved oxygen levels are reported to be high throughout the water column for Myall lake and salinity levels are between 2000 and 5000  $\mu\text{S cm}^{-1}$  (Dasey et al., 2005). Much of the catchment is forested and the lakes are found within the Myall Lakes National park. Freshwater is received from the Myall River which discharges into the most southerly basin of Broadwater, and Boolambayte Creek which empties into the mid-section.

The Broadwater is characterised by low visibility and populations of macrophytes restricted to shallower areas (Dasey et al. 2004). In contrast, Myall Lake has higher water column visibility with abundant populations of macrophytes throughout the lake (Dasey et al., 2004).

The site was originally inhabited by the Worimi aboriginal people. European settlement of this area occurred during 1800–1830 and was linked with deforestation for timber (especially cedar) and agricultural and urban development (NPWS, 1991). Sawmills were in use throughout the area from the 1860s (Great Lakes Council, 2003). In 1840, Bula-hdelah was established at the junction of the Crawford and Myall Rivers. The timber industry eventually declined due to depletion of the resource, and beef and dairy production became established during the early 1900s. Dairying activities have continued till the present day with several dairies still active. Much of the catchment is now protected by National Park designation, or managed as State Forests, and the biggest local industries are currently

retail and tourism services (ABS, 2001). A sewage treatment plant (STP) for Bula-hdelah began discharging effluent into a tributary of Myall River in 1968. Secondary treatment began in the early 1970s and tertiary treatment was initiated in 1996 (Mid Coast Water, pers comm.).

A palaeoecological study of Flett (2003) used  $^{210}\text{Pb}$  dating to determine a sedimentation rate of 0.47  $\text{cm year}^{-1}$  in Broadwater and 0.16  $\text{cm year}^{-1}$  in Myall Lake. Other results from that study showed that the species of cyanobacteria involved in the recent blooms did not produce cysts which preserve in sediment, and consequently the past cyanobacterial populations in the Myall Lakes could not be directly reconstructed (Flett, 2003).

### Sample collection

Two sediment cores were collected in March 2003, one from each of Broadwater and Myall Lake (Fig. 1). Cores were collected from a boat using a push corer with a core barrel 78 mm in diameter and 900 mm long. At the Broadwater site, a 40 cm core was collected from 2.5 m depth. At the Myall Lake site, a 38 cm long core was collected from a water depth of 1.5 m. To develop a chronology, these cores were taken at the sites core-sampled by Flett (2003) and for which  $^{210}\text{Pb}$  profiles are available. The Broadwater core was taken at the site coded BW1 ( $32^{\circ} 38' 48.5'' \text{ S } 15.2^{\circ} 18' 49'' \text{ E}$ ), and the Myall Lake core at the site coded ML4 ( $32^{\circ} 25' 37'' \text{ S } 15^{\circ} 23' 49'' \text{ E}$ ) by Flett (2003). Upon collection cores were extruded from the barrel, sliced into 1 cm sections and placed in polythene zip lock bags. Samples were stored in a coolbox on ice and frozen at  $-20^{\circ}\text{C}$  upon return from the field.

A sub-sample of sediment (approximately 4–5  $\text{cm}^3$ ), was taken from each core slice and oven dried at  $60^{\circ}\text{C}$ . After drying, samples were ground in a pestle and mortar before being split. One split was treated with 2N HCL to remove any carbonates which might affect  $\delta^{13}\text{C}$  values (Schubert & Nielsen, 2000; Lorrain et al., 2003) and % carbon readings (Nieuwenhuize et al., 1994) before being re-dried as above. This was then used for  $\delta^{13}\text{C}$  and  $\text{C}_{\text{org}}$  analysis. The untreated split was used for  $\delta^{15}\text{N}$  and % N analysis. Samples were loaded into tin capsules before isotope analysis.

Samples (one per core slice) were run on a SL 22 Europa mass spectrometer coupled with a Carlo Erba/Fisons 1108 CHN analyser. Samples were run against an internal standard (flour). One standard was run every 6 samples to test machine precision and correct for drift. Instrumental precision of the mass spectrometer, derived from variation in the standards, showed a standard deviation of 0.32‰ for  $\delta^{15}\text{N}$  and 0.12‰ for  $\delta^{13}\text{C}_{\text{org}}$ . Nitrogen isotope ratios were calculated using the formula

$$\delta^{15}\text{N}_{\text{‰}} = \left[ \frac{(^{15}\text{N}/^{14}\text{N})_{\text{sample}}}{(^{15}\text{N}/^{14}\text{N})_{\text{reference}}} - 1 \right] \times 10^3$$

Carbon isotope ratios were calculated using the same formula with the necessary substitutions.

A historical increase in fossil fuel consumption has contributed to a disproportionate increase in  $^{12}\text{C}$  of atmospheric carbon dioxide (The Seuss effect). Using the chronologies available the  $\delta^{13}\text{C}_{\text{org}}$  data were corrected for this effect using the model developed by Schelske & Hodell (1995).

$$\delta^{13}\text{C}_{\text{org}} = -4577.8 + 7.3430t - 3.9213 \times 10^{-3}t^2 + 6.9812 \times 10^{-7}t^2$$

The calculated time dependant depletion in  $\delta^{13}\text{C}$  since 1840 was added to the measured  $\delta^{13}\text{C}_{\text{org}}$  for each sediment section analysed. It should be noted that semi-continuous monitoring of the  $\delta^{13}\text{C}$  of atmospheric  $\text{CO}_2$  ( $\text{CO}_{2\text{atmos}}$ ) in Schauinsland Germany between 1996 and 1997, suggests a smaller decrease due to fossil fuels than predicted for the same period by the model used for correction here (Levin & Kromer, 1997). However, in the absence of  $\text{CO}_{2\text{atmos}}$   $\delta^{13}\text{C}$  data from sites proximal to Myall Lakes, the model of Schelske & Hodell (1995) is used here as an approximate correction for historical increases in fossil-fuel-derived  $^{12}\text{C}$  in the atmosphere.

The chronology used in this study was developed by correlating cores A and B with cores taken at the same locations (Flett, 2003) using magnetic susceptibility and loss on ignition data. The same  $^{210}\text{Pb}$ -derived sedimentation rates used in that study, calculated at the Australian Nuclear Science and Technology Organisation (ANSTO), were then applied to the new cores.

To determine the ages using  $^{210}\text{Pb}$ , approximately 2 g of each oven-dried sediment sample was crushed

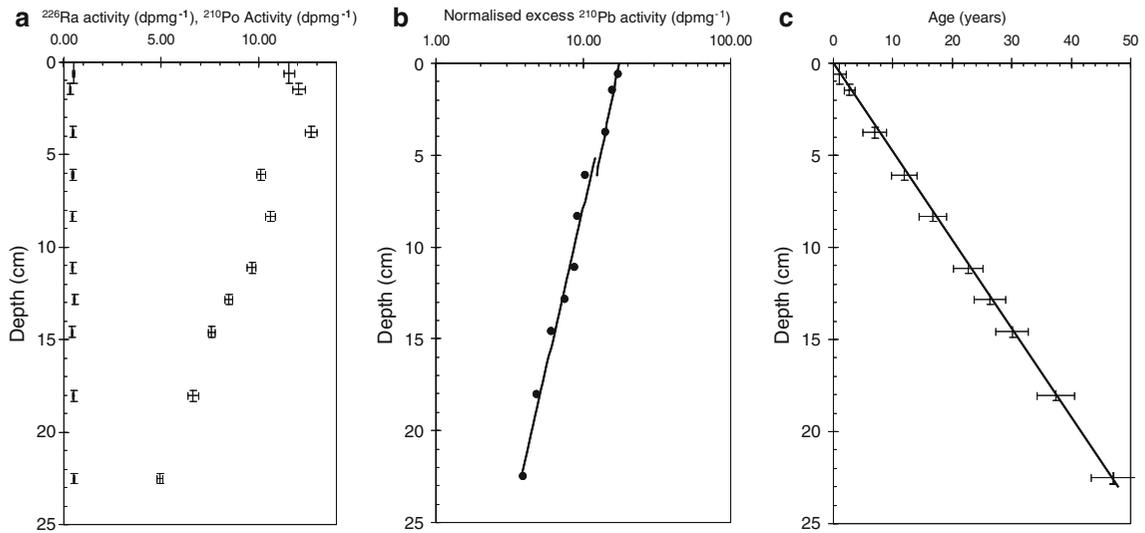
and  $^{133}\text{Ba}$  and  $^{209}\text{Po}$  tracers were added. Organic matter, clays and other solids were removed in several stages with concentrated acids. Polonium was auto-deposited onto polished silver discs, and then  $^{210}\text{Po}$  activity was determined by alpha spectrometry. Radium and  $\text{BaSO}_4$  were precipitated and filtered from the remaining solution, then the activity of  $^{133}\text{Ba}$  was measured by gamma detection, and this figure used to estimate the chemical recovery achieved by the treatment. The  $^{226}\text{Ra}$  activity was detected by alpha spectrometry. The unsupported  $^{210}\text{Pb}$  activity in each sediment slice was calculated by subtracting the  $^{226}\text{Ra}$  activity, an approximation of the supported  $^{210}\text{Pb}$  activity, from the  $^{210}\text{Po}$  activity, which is in equilibrium with the total  $^{210}\text{Pb}$  of each slice (Appleby, 2001). The results were then normalised by grainsize, and modelled using a modified version of the Constant Initial Concentration (CIC) model (Appleby & Oldfield, 1983; Harrison et al., 2003).

## Results

### Broadwater core

A 40 cm core (A) was collected in approximately 2 m depth of water. The core was composed of a relatively homogeneous grey–brown silty clay. Distinctive features such as laminations, macrophytes or mollusc remains were not observed. The sediment surface had no covering of benthic algal turf or other material.

From the Flett (2003) core (BW1), ten samples were dated using the  $^{210}\text{Pb}$  method described above. Figure 2a shows the  $^{226}\text{Ra}$  and  $^{210}\text{Po}$  activities.  $^{226}\text{Ra}$  activities were close to constant at around 1 dpm  $\text{g}^{-1}$ .  $^{210}\text{Po}$  activities were as high as 13 dpm  $\text{g}^{-1}$  at 0 cm and decreased down the core to around 5 dpm  $\text{g}^{-1}$  at 22.5 cm. Results were normalised for grainsize variability between samples, which has been shown to affect  $^{210}\text{Pb}$  uptake (He & Walling, 1996). The corrected excess  $^{210}\text{Pb}$  profile is shown in Fig. 2b. Two sedimentation rates were determined by applying a modified version of the CIC model. The sedimentation rate is  $0.54 \pm 0.15 \text{ cm year}^{-1}$  for the top mixed layer, down to 5 cm, and a slightly slower rate of  $0.47 \pm 0.034 \text{ cm year}^{-1}$  for the core below 5 cm. Since the two rates are probably due to

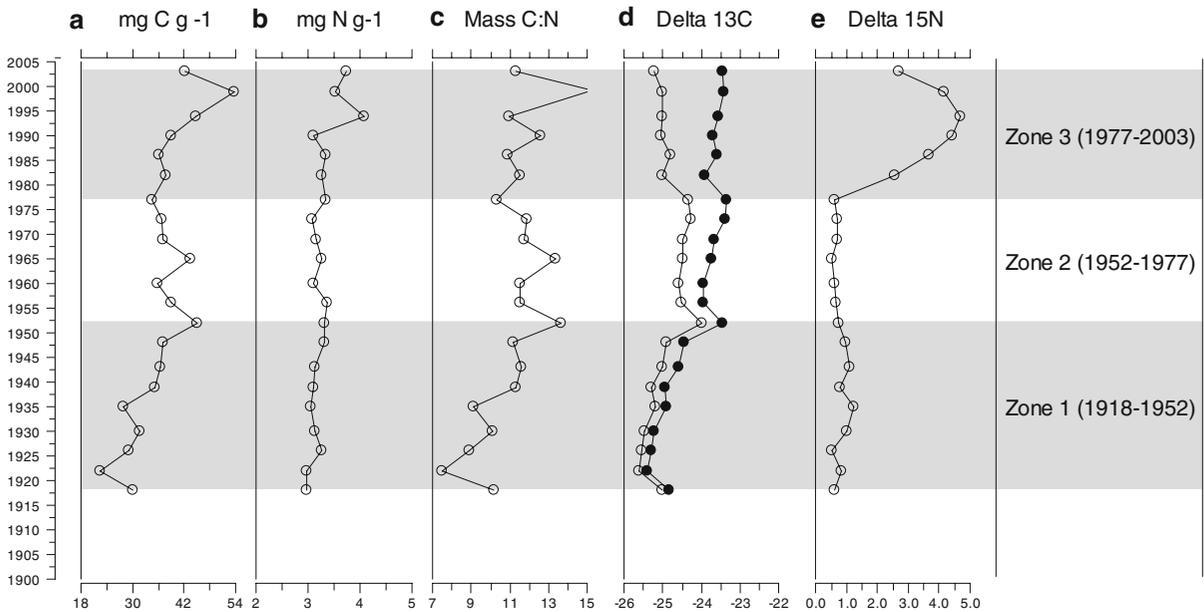


**Fig. 2** Broadwater (Core BW1) chronology. (a)  $^{226}\text{Ra}$  activities and  $^{210}\text{Po}$  activities measured on ten samples in  $\text{dpm g}^{-1}$ . Ra activities are the marks on the left, the lowest marks at each

depth. (b) Excess  $^{210}\text{Pb}$  profile, corrected for grain size differences. (c) Age depth model based on CIC modelled sedimentation rate of  $0.47 \pm 0.034 \text{ cm year}^{-1}$ .

differential compaction (and the errors mean they are virtually indistinguishable), the more conservative sedimentation rate of  $0.47 \pm 0.034 \text{ cm year}^{-1}$  has been graphed for the whole core in Fig. 2c. Using this sedimentation rate, the base of the 40 cm core A is estimated to be  $85 \pm 6$  years old, which corresponds to approximately 1918 AD.

Analytical profiles for the Broadwater (Fig. 3) could be divided into three broadly comparable time periods based on a visual assessment of simultaneous changes. While this zonation scheme is open to subjective interpretation, it is used here to aid discussion and comparison of the profiles. Zones 1 (1918–1952 AD), 2 (1952–1977 AD) and 3 (1977–2003 AD)



**Fig. 3** Stratigraphic diagram showing analytical profiles taken from core A, Bombah Broadwater. a =  $\text{mg C g}^{-1}$ . b =  $\text{mg N g}^{-1}$ . c = C:N. d =  $\delta^{13}\text{C}_{\text{org}}$  (filled circles denote  $\delta^{13}\text{C}_{\text{org}}$  values corrected for the Seuss effect). e =  $\delta^{15}\text{N}$ .

are labelled on the diagram (Fig. 3). These zones were chosen to reflect three periods of environmental change evident from synchronous changes in the analytical profiles.

Three parameters demonstrated distinct increases throughout Zone 1.  $C_{\text{org}}$  content (Fig. 3a) increased from ca.  $30 \text{ mg g}^{-1}$  circa.1918 to  $45 \text{ mg g}^{-1}$  circa 1952. Corrected  $\delta^{13}C_{\text{org}}$  (Fig. 3d) also increased from  $-25\%$  to  $-23.9\%$ .  $C_{\text{org}}:N$  (3c) showed an overall increase from 10.1 to 13.6, largely driven by the increase in organic C content while N (Fig. 3b) content remained unchanged. In contrast  $\delta^{15}N$  (Fig. 3e) remained relatively stable, increasing by  $0.5\%$  to  $\sim 1\%$  before returning to  $\sim 0.6\%$ .

$\delta^{15}N$  (Fig. 3e) and N content (Fig. 3b) remained stable in Zone 2 at  $0.6\%$  and  $3.2 \text{ mg g}^{-1}$ , respectively.  $C_{\text{org}}$  content (Fig. 3a) showed no overall trend during this period but fluctuated around  $36 \text{ mg g}^{-1}$ . This relative stability was reflected in the  $C_{\text{org}}:N$  data (Fig. 3c) which varied around 12.  $\delta^{13}C_{\text{org}}$  (Fig. 3d) was the only analysis which showed any significant changes and increased from  $-23.9\%$  to  $-23.3\%$ .

Zone 3 was marked by a noticeable increase in  $\delta^{15}N$  (Fig. 3e) from approximately  $1\%$  to a peak of  $4.7\%$  at 2 cm depth ( $\sim 1994$ ) before decreasing to  $2.7\%$  in the surface section. N content (Fig. 3b) did not show changes in concert with  $\delta^{15}N$  but there was an increase to  $4 \text{ mg g}^{-1}$  at 2 cm depth ( $\sim 1994$ ) and higher values were maintained in the overlying sections. Organic C (Fig. 3a) also showed a pronounced increase to a peak of  $53 \text{ mg g}^{-1}$  in the late 1990s, just below the surface section, which in turn drove the slight upward trend in  $C_{\text{org}}:N$ . Similarly, following a drop of  $0.6\%$  to  $-23.9\%$  between 1977 and 1982,  $\delta^{13}C_{\text{org}}$  values (Fig. 3d) continued a trend towards enrichment to approximately  $-23.5\%$  in the surface section.

### Myall Lake core

A 38 cm core (B) was recovered from Myall Lake in a water depth of 1.5 m and largely comprised a flocculent green–brown material. This material is known as ‘gyttja’ (Wetzel, 1975) and is considered to be a stage in the breakdown of macrophytes which are seasonally abundant in this lake (Skilbeck et al., 2005). Accordingly, organic content appeared to be high and mineral content low. The surface layer consisted of uncompacted gyttja but the integrity of

the surface was not disrupted. The bottom 6 cm comprised a grey–brown mineral mud which plugged the bottom of the corer.

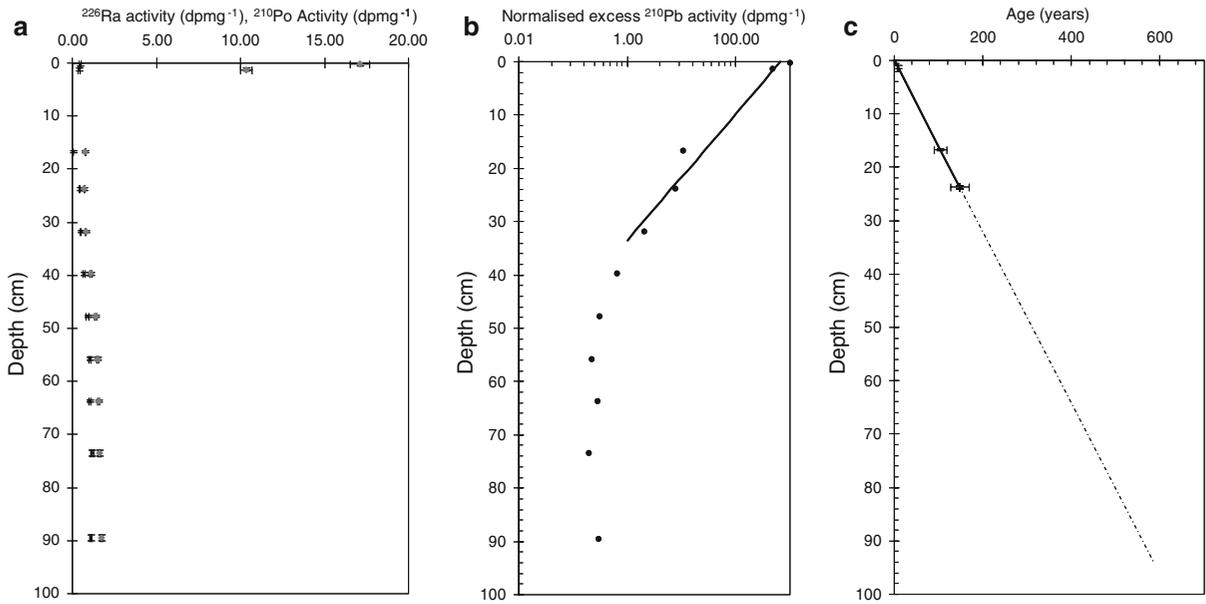
The chronology of the Upper Myall Core was determined by correlation with the core (ML4) previously dated by Flett (2003), which was recovered from the same location. Ten samples from ML4 were analysed for  $^{210}Pb$  as described in the methods, but only the top three samples showed detectable activities of  $^{210}Po$ . These activities ranged from  $\sim 17 \text{ dpmg}^{-1}$  at 0 cm to  $\sim 0.7 \text{ dpmg}^{-1}$  at 17 cm (Fig. 4a).  $^{226}Ra$  activities were low and reasonably constant through time. The unsupported  $^{210}Pb$  activities resulting from subtracting  $^{226}Ra$  activities from  $^{210}Po$  activities for each sample were normalised for grainsize differences and plotted in Fig. 4b. The sedimentation rate of  $0.161 \pm 0.022 \text{ cm year}^{-1}$  (Fig. 4c) was determined using the CIC model. When applied to the Upper Myall core from this study, this sedimentation rate yielded a basal age of  $236 \pm 33 \text{ years BP}$  or  $\sim 1767 \text{ AD}$ .

Analytical profiles (Fig. 5) were divided into three zones based on a visual assessment of synchronous variations. Zone 1 covers the period 1767–1804 AD, Zone 2 marks 1804–1904 AD and Zone 3 marks 1904–2003 AD.

The transition from clay mud to gyttja between Zones 1 and 2 was reflected in the analyses with a large increase in organic carbon (Fig. 5a) from approximately  $94 \text{ mg g}^{-1}$  to  $164 \text{ mg g}^{-1}$ . N content (Fig. 5b) also showed a relatively large increase from  $\sim 8 \text{ mg g}^{-1}$  to  $\sim 13 \text{ mg g}^{-1}$ .  $\delta^{13}C_{\text{org}}$  (Fig. 5d) increased from  $-20\%$  to  $-18\%$  while  $\delta^{15}N$  fluctuated around  $0\%$  (Fig. 5e).

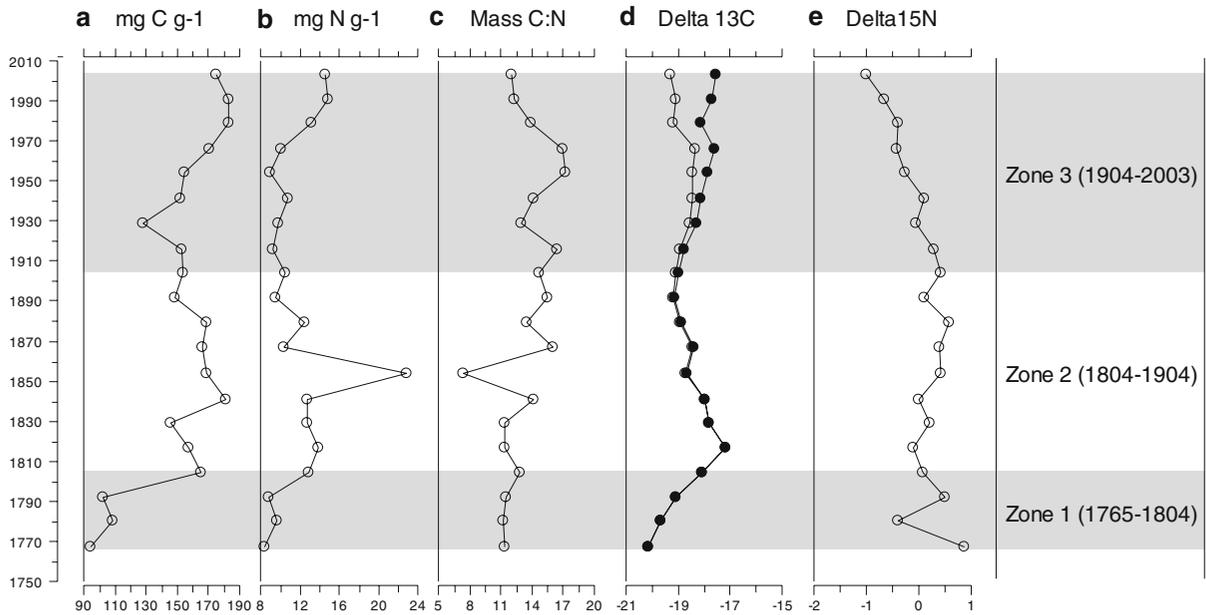
Zone 2 was characterised by an overall increase in  $C_{\text{org}}:N$  (Fig. 5c).  $\delta^{15}N$  (Fig. 5e) remained relatively stable at just above  $0\%$ . Similar to Zone 1,  $C_{\text{org}}$  content (Fig. 5a) and  $\delta^{13}C_{\text{org}}$  (Fig. 5d) corresponded quite closely.  $C_{\text{org}}$  content showed an overall decline from  $180 \text{ mg g}^{-1}$  to  $\sim 150 \text{ mg g}^{-1}$  while  $\delta^{13}C$  decreased from  $-18.0\%$  to  $-18.9\%$ . With the exception of a sharp spike to  $22.81 \text{ mg g}^{-1}$  in the mid-1800s, N content (Fig. 5b) showed a decreasing trend from  $\sim 13 \text{ mg g}^{-1}$  to  $10 \text{ mg g}^{-1}$ . This was reflected in the  $C_{\text{org}}:N$  ratio data (Fig. 5c) which showed an overall increase during this period.

Zone 3 exhibited a distinct reduction in  $\delta^{15}N$  (Fig. 5e) from approximately  $0.5\%$  to  $-1\%$  which



**Fig. 4** Myall Lake (Core ML4) chronology. (a)  $^{226}\text{Ra}$  activities (black) and  $^{210}\text{Po}$  activities (grey) measured on eleven samples in  $\text{dpm g}^{-1}$ . Ra activities are the marks on the left, the lowest

marks at each depth. (b) Excess  $^{210}\text{Pb}$  profile, corrected for grain size differences. (c) Age depth model based on CIC modelled sedimentation rate of  $0.161 \pm 0.022 \text{ cm year}^{-1}$ .



**Fig. 5** Stratigraphic diagram showing analytical profiles taken from core B, Upper Myall Lake. a =  $\text{mg C g}^{-1}$ . b =  $\text{mg N g}^{-1}$ . c = C:N. d =  $\delta^{13}\text{C}_{\text{org}}$  (filled circles denote  $\delta^{13}\text{C}_{\text{org}}$  values corrected for the Suess effect). e =  $\delta^{15}\text{N}$ .

was accompanied by an overall increase in N content (Fig. 5b) from  $9 \text{ mg g}^{-1}$  to  $14.5 \text{ mg g}^{-1}$  at the surface. This increase drove a fall in the  $\text{C}_{\text{org}}:\text{N}$

ratio (Fig. 5c) from 14.6 to 11.9.  $\text{C}_{\text{org}}$  (Fig. 5d) content and  $\delta^{13}\text{C}_{\text{org}}$  (Fig. 5d) both showed notable increases.

## Discussion

### Broadwater core

Various attempts have been made to independently confirm the sedimentation rates and age models determined by  $^{210}\text{Pb}$  in Flett (2003).  $^{137}\text{Cs}$  results from a third parallel, correlated core from the BW1 location confirmed that the sediments at  $22 \pm 2$  cm depth were deposited around 1985, which is within the error of the sedimentation rate determined by  $^{210}\text{Pb}$  (Tibby, pers comm). Ideally, a comparison would have been made with the Constant Rate of Supply (CRS) model for determining the sedimentation rate, but this model requires that  $^{210}\text{Pb}$  activities be calculated for the whole core, and unsupported  $^{210}\text{Pb}$  was still present in the bottom sample tested (Appleby, 2001). When compared with the cores from Myall Lake, the sedimentation rate calculated for the Broadwater was much faster, but this was expected since it was close to the mouth of the Upper Myall River (Fig. 1). Very little fluvial or marine material currently enters the upper lakes of the system, although earlier Holocene deposits in Myall Lake are estuarine in nature (Skilbeck et al., 2005).

The rise in all analytical profiles (other than N content) in Zone 1 indicated a period of significant change in the Broadwater. There are two likely causes of  $\delta^{13}\text{C}_{\text{org}}$  increase over this period. The first is an increase in primary production (Cifuentes et al., 1988; Schelske & Hodell, 1991; Brenner et al., 1999) which lowers concentrations of  $\text{CO}_2(\text{aq})$ , thus driving a decreasing fractionation of C fixed by phytoplankton. The second is increases in inputs of exogenous material, probably of terrestrial origin, e.g. soil organic matter which has an enriched  $\delta^{13}\text{C}_{\text{org}}$  in comparison to autochthonous material from the lake (e.g. Bratton et al. 2003). The concurrent increases in  $\text{C}_{\text{org}}:\text{N}$  (Fig. 3c) appear to confirm a rise in contributions of terrestrial organic material (Emerson et al., 1988; Meyers et al., 1994; Meyers & Lallier-Verges, 1999).  $\text{C}_{\text{org}}:\text{N}$  values of greater than 11 throughout the core are indicative of terrestrial or macrophyte material (Meyer, 2003). The rise in both  $\text{C}_{\text{org}}:\text{N}$  (Fig. 3c) and  $\delta^{13}\text{C}_{\text{org}}$  (Fig. 3d) in the Broadwater is in contrast to sites where historical increases in  $\delta^{13}\text{C}_{\text{org}}$  are accompanied by a concomitant decrease in sedimentary  $\text{C}_{\text{org}}:\text{N}$  driven by increases in phytoplankton production (Herczeg et al., 2001; Kauppila

et al., 2005). These observations indicate that Zone 1 represents a period of increasing terrestrial or sewage inputs to Broadwater Lake.  $\delta^{15}\text{N}$  (Fig. 3e) increased slightly during this period which may represent an influx of nutrients (Bratton et al., 2003; Savage et al., 2004). However, the magnitude of this change is less pronounced than the sudden increases in  $\delta^{15}\text{N}$  in the 1970s–1990s. The Broadwater is characterised by relatively high turbidity with macrophyte populations restricted to shallow areas (Dasey et al., 2004). If this state has been maintained during the last century then it would seem likely that human activities in the watershed such as ploughing or clearing may be the cause (Bratton et al., 2003; McFadden et al., 2004). However there is no supporting analytical or historical evidence for this. Unfortunately the initiation of these changes occurred earlier than the dates represented in this core which hampers speculation regarding their magnitude, timing and causes.

$\delta^{13}\text{C}_{\text{org}}$  changes in Zone 2 suggest an apparent increase in primary production (Cifuentes et al., 1988; Schelske & Hodell, 1991; Brenner et al., 1999).  $\text{C}_{\text{org}}:\text{N}$  data provide some support for this interpretation, showing an overall decrease throughout the zone indicative of increasing phytoplankton production (Meyer, 2003). However there is some variation in this parameter and its causes are not evident as  $\delta^{15}\text{N}$  remained constant.

The slight increase in  $\delta^{13}\text{C}_{\text{org}}$  in Zone 3 is accompanied by a similar increase in  $\text{C}_{\text{org}}:\text{N}$  suggesting a period of increasing inputs of allochthonous material or increased inputs of macrophyte material. The timing of the initiation of these changes would suggest they began at some point between the mid-1970s and the early 1980s. There is no known history of large increases in macrophyte populations in the Broadwater during this period, and while this material could be of terrestrial origin (similar to that seen in Zone 1) it would appear that these changes were driven by introduction of new sources of material which were relatively enriched in  $^{15}\text{N}$  (Fig. 3e). These  $\delta^{15}\text{N}$  values fall within the range seen for a similar brackish European sites suffering eutrophication due to sewage loading (Savage et al., 2004; Kauppila et al., 2005) and could indicate material processed at the waste water treatment plant at Bulahdelah on the Myall River. Secondary and tertiary treatment of sewage, initiated in Bulahdelah would result in organic material enriched in  $^{15}\text{N}$  by

denitrification. Alternatively, increases in inorganic nitrogen from agricultural sources in the catchment can result in elevated levels of denitrification within the watershed and in the water column of the receiving water body leading to deposited organic material enriched in  $^{15}\text{N}$  (Voss & Struck, 1997, Kellman, 2005). To date a record of the nutrient discharges of this facility has not been gathered to allow the testing of this hypothesis.

While the Zone 3 isotopic enrichment (suggested to be driven by nutrient additions) is relatively rapid, the reduction in  $\delta^{15}\text{N}$  since the mid-1990s may reflect an amelioration of the problem. However, this mechanism for reduction in  $\delta^{15}\text{N}$  should be interpreted with caution. It may be due, in some part, to the introduction of atmospheric nitrogen fixed by recently documented blue green algal blooms at these sites (Dasey et al., 2004). Atmospheric dinitrogen gas is the standard against which samples are measured and has a value of 0‰. There is published evidence for this process at work in the sedimentary record in lakes (Gu et al., 1996; Brenner et al., 1999) and the Baltic Sea (Bianchi et al., 2000). Cyanobacterial zeaxanthin pigment analysis would be required to support this hypothesis (e.g. Bianchi et al., 2000).

In summary it seems reasonable to conclude that Broadwater is sensitive to human activity in the watershed.  $\delta^{13}\text{C}_{\text{org}}$  and  $\text{C}_{\text{org}}:\text{N}$  indicate increasing inputs of terrestrial organic matter over the last 100 years with a respite between the 1950s and 1970s.  $\delta^{15}\text{N}$  indicates a nutrient impact in the recent history (1970s–1990s) of the site. The sources of this impact are unknown and their elucidation would require further investigation but it is possible that a sewage treatment plant at Bulahdelah may be the source. Any relationship between this impact and the 1999–2000 cyanobacterial blooms in Myall Lakes is uncertain as the introduction of this new material was initiated over 20 years ago. However, it is suggested that if  $\delta^{15}\text{N}$  does represent sewage-derived N inputs, the reduction in  $\delta^{15}\text{N}$  since the mid-1990s may represent a period of a change in the N:P ratio of Broadwater (assuming that water column P remains relatively constant). Under such conditions, N would become the limiting nutrient and the N-fixing *Anabaena* sp. (observed in the blooms of 1999–2000) would have a competitive advantage in the phytoplankton community of the lake (Bianchi et al., 2000).

## Myall Lake core

Throughout Myall Lake, the depth of the uppermost gyttja layer varies. It has also been shown that this layer is being deposited at different rates around the basin and that there is usually a gradual transition from the estuarine clay unit below (Skilbeck et al., 2005). A radiocarbon date of  $580 \pm 50$  cal.year BP at the bottom of the gyttja facies (1 m) in the ML11B core of Skilbeck et al. (2005), indicates that the sedimentation rate at this location is about  $0.17 \text{ cm year}^{-1}$ . This is very close to the rate of  $0.16 \text{ cm year}^{-1}$  determined for the Myall Lake cores referred to in this paper, but the greater thickness of the unit at ML11B means there is a  $\sim 300$  year discrepancy between the basal ages dated by the two different methods. However, the cores at the ML4 location used in this study gave similar ages for the base of the gyttja facies as another Myall Lake core, ML5, which had a faster sedimentation rate and thicker gyttja unit ( $\sim 0.25 \text{ cm year}^{-1}$  and 50 cm; Flett, 2003). The pollen analysis of ML5 also provided an opportunity for independent age control. The exotic *Plantago* first appeared in the pollen record at 45 cm, with *Pinus* appearing at 25 cm. These taxa are used as markers of European impact in many Australian records (D'Costa & Kershaw, 1997; Haberle et al., 2006), and in the Myall Lakes region *Plantago* and *Pinus* introductions are likely to be associated with the first European impact ( $\sim 1816\text{AD}$ , NPWS, 2001) and then the first pine plantations (unknown, but around 1875–1900 AD in other NSW forests: Tibby, 2003), respectively.

These approximate controls confirm the basis of the ML5 age model (Flett, 2003) and the similarity in age of the facies change between ML4 and ML5 can be seen as confirmation of the ML4 chronology. This chronology, when applied to the Upper Myall core would suggest that the initiation of conditions responsible for the gyttja sediments found in Upper Myall appeared before significant European influence on the area. The transition to gyttja sediments occurred during the late 1700s whereas the first European exploitation of forestry in the area, cedar logging, began in 1816 (NPWS, 2001). The agreement between initial increases in organic C content (Fig. 5a) and  $\delta^{13}\text{C}_{\text{org}}$  (Fig. 5d) are explained by the transition from inorganic clay to the highly organic sediment, gyttja (the boundary between Zones 1 and 2).

Speculation regarding the ultimate cause of this change has been offered by Flett (2003), and includes changes in climate and/or the hydrology of the basin. A further explanation may lie with the developmental model offered by Munsterhjelm (1997). As basins become more isolated they become nutrient traps dominated by macrophytes which produce organic rich gyttja sediments.

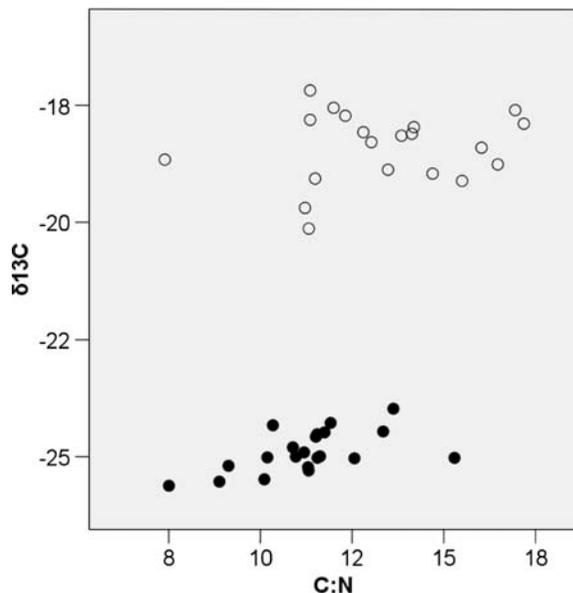
The shift to gyttja sediments also coincided with a large rise in  $\delta^{13}\text{C}_{\text{org}}$  values. This may have been due to overall increases in primary productivity during this period and been affected by the same mechanism described by Cifuentes et al. (1988) and Schelske & Hodell (1991), i.e. reduced discrimination against  $^{13}\text{C}$  fractionation during photosynthesis in the water column due to an increase in  $\text{CO}_2$  limitation driven by higher levels of primary production. However, there is also evidence that macrophytes are relatively enriched in  $^{13}\text{C}$  due to  $\text{CO}_2$  being limited in the boundary layer at the surface of the plant (France & Holmquist, 1997).  $\delta^{13}\text{C}_{\text{org}}$  and  $\text{C}_{\text{org}}:\text{N}$  are significantly higher (Fig. 6) in Upper Myall Lake than in the Broadwater possibly indicating higher levels of total production in this lake or, as seems more likely from observations of sediment types, greater contributions to total production by macrophytes which

have higher levels of structural carbon (Kenney et al., 2002; Meyers, 2003). This is in contrast to the suggestion that gyttja sediments in Myall Lake primarily comprise cyanobacterial remains (Dasey et al., 2005). These observations support the observation of a fundamentally different basis in primary production with Myall Lake being dominated by macrophytes and the Broadwater dominated by phytoplankton production (Dasey et al., 2004).

The increase in  $\text{C}_{\text{org}}:\text{N}$  data in Zone 2 suggests two potential scenarios as explanations: an increasing influx of terrestrial organic matter (Meyers, 1994) or an increase in macrophyte populations (Brenner et al., 1999, Meyers, 2003). In support of the first hypothesis is the timing of the initiation of the  $\text{C}_{\text{org}}:\text{N}$  increase in Zone 2, i.e. the early 1800s which corresponds to the onset of cedar logging in this area. Given the current abundant populations of macrophytes, lack of riverine inputs and small catchment area, the second scenario seems more likely and appears to have been initiated during the transition from mineral to gyttja sediments.

Reasons for the fall in  $\delta^{13}\text{C}_{\text{org}}$  throughout Zone 2 are unclear. Species turnover in the newly established macrophyte populations may be responsible. Alternatively incorporation of  $^{12}\text{C}$  enriched, microbially respired  $\text{CO}_2$ , into new primary production resulting from high levels of dissolved organic carbon (France, 1999) could be important during this period when logging was occurring and runoff was increased. The slight increase in  $\delta^{15}\text{N}$  during this period may also indicate an increase in nutrient inputs from catchment disturbance supporting the hypothesis that logging may be responsible. Further support is provided in the observation that the upper limit of this zone corresponds to the end of this period of catchment clearing.

The timing of the increases in  $\delta^{13}\text{C}_{\text{org}}$  in Zone 3 was roughly mirrored by the reductions in  $\delta^{15}\text{N}$  suggesting a possible relationship with changes in N processing. The transition to unusually low values of  $\delta^{15}\text{N}$  could be indicative of fast recycling of N in the form of  $\text{NH}_4^+$ . Low  $\delta^{15}\text{N}$  values have been observed in primary producers entirely reliant on N recycled as  $\text{NH}_4^+$  (Doi et al., 2004) or in situations where N recycled from the sediments is the most abundant form of N (Teranes & Bernasconi, 2000). Inputs of nutrients are thought to be minimal at this site due to the reduced watershed and restricted connection to The Broadwater. This



**Fig. 6** Biplot showing  $\text{C}_{\text{org}}:\text{N}$  vs  $\delta^{13}\text{C}_{\text{org}}$  for organic matter of Broadwater Lake (core A = ●) and Myall Lake (core B = ○).

increases reliance of macrophyte populations on  $\text{NH}_4^+$  derived from decomposing sediments (Munsterhjelm, 1997). Dasey et al., (2005) report greatly elevated has shown greatly elevated levels of  $\text{NH}_4^+$  in gyttja sediments in Myall Lake. Lack of significant new N inputs could lead to an attenuation of  $^{15}\text{N}$  which is fixed in the component of macrophyte remains which are not decomposed and form part of the sediment. Further more, algal utilisation of ammonia is associated with a larger fractionation of N isotopes resulting in greater depletion of  $^{15}\text{N}$  in the growing plants (Waser et al., 1998).

It is notable that the geochemical evidence presented here suggests the two basins examined in this body of water exhibit fundamentally different conditions governing primary production. Sediments in Broadwater indicate phytoplankton primary production with significant inputs of terrestrial organic matter, probably supplied via the Myall River. Myall Lake sediments are indicative of an organic fraction dominated by macrophyte inputs.

These observations appear to support the hypothesis of alternating stable states for primary production in shallow lakes with differing nutrient inputs (Scheffer et al., 1993). The initiation of macrophyte domination in Myall Lake appears to have begun at some point around 1800 and the development of macrophyte populations appears to have become increasingly reliant on nutrients recycled from the sediment. This hypothesis may explain observations of occasional peaks in ammonia which are of concern to managers (Dasey et al., 2004; Wilson 2008) but appear to be a natural feature of this basin. There is no further evidence that this basin is experiencing deleterious anthropogenic impacts.

The Broadwater appears to be more sensitive to human activities in the watershed with increases in inputs of terrestrial organic matter since the early 1900s. Since the 1970s there have been significant additions of a new source of nitrogen. This is most likely sewage material from the Bulahdelah sewage treatment plant which discharges material into the Myall River. While this impact appears to have been ameliorated since the late 1990s the ecological effects on this water body, including eutrophication, should be considered by managers and would be better understood with further investigation. It is unclear whether the sewage impact is connected with the recent cyanobacterial bloom in this basin. The

initiation of sewage inputs to the site began in the 1970s and it seems unlikely that it would take more than twenty years before cyanobacterial populations were affected. However it is possible that the apparent reduction in N inputs would have altered the N:P ratio in the Broadwater, temporarily creating the conditions necessary for N-fixing species *Anabaena circinalis* to prosper briefly as observed in the blooms of 1999–2000.

**Acknowledgements** Many thanks to Matt Dasey for help in recovering the cores. Susan Waldron gave valuable advice during discussions of the data. Gillian Taylor provided technical assistance in isotope analysis. Jennifer Harrison and Atun Zawadski helped with fieldwork and analysis. Three reviewers provided comments which significantly improved the original manuscript.

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