Two hundred years of blue-green algae blooms in the Gippsland Lakes

A report prepared for the Gippsland Lakes Ministerial Advisory Committee

May 2013

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Executive summary

"When the natural entrance, three miles east of the present entrance, was blocked sometimes by a sandbar, the lakes water would be impounded and they would freshen up. At times a green scum would appear on the surface of the water." (J. Burgoyne, Bairnsdale Advertiser, 16/8/1949)

Nodularia blooms are a recurring problem in the Gippsland Lakes. Since 1986, there have been eight major blooms. Before 1986, however, blooms were rare, with only a handful of blooms reported in almost 200 years of European settlement. There are anecdotal reports of blue-green algae (cyanobacteria) blooms prior to the construction of the permanent entrance in 1886 (Carstairs 1937), but there are no data on their frequency or intensity or even the species involved. Effectively managing this ecosystem requires an historical perspective on how the lakes have functioned over time; this will better help us understand both our impact on bloom occurrence and the management actions that could mitigate this impact.

We collected intact sediment cores from 7 m deep water in north Lake King, which were then dated at the Lucas Heights nuclear facility. We ran tests for various markers of blue-green algae, such as pigments and stable isotopes of nitrogen and carbon, in order to determine the history of blue-green algal blooms in the Gippsland Lakes.

We found clear evidence for two periods of eutrophication (high nutrient enrichment) and blue-green algae blooms in the Gippsland Lakes – 1. The recent period after the Second World War and 2. Prior to the opening of the artificial entrance in 1889. The first piece of evidence for the recent period of eutrophication comes from the steady increase in sediment organic carbon content after the 1940s, and this organic material is consistent with inputs derived from phytoplankton. In 1987, the first of the recent series of severe *Nodularia* blooms occurred and this was reflected in the sediment record as a marked dip in the ratio of heavy to light nitrogen atoms, which we know is caused by an increase in nitrogen fixing blue-green algae, such as *Nodularia*. This period also coincided with a marked jump in the sum of the blue-green algae pigments.

The biogeochemical markers for the period before the opening of the entrance likewise suggest a period of eutrophication and intense blue-green algae blooms. The sediment organic content was high and derived from phytoplankton, the atomic nitrogen was light and the blue-green algae pigments were high. The lakes were a lot less saline before the opening of the entrance, and it may be that a freshwater species of blue-green algae such as *Anabaena* was blooming in the lakes then, rather than *Nodularia.* We hypothesis from these observations that the Gippsland Lakes were eutrophic (highly nutrient enriched) prior to the opening of the entrance, and this was probably due to low flushing and stagnant water, combined with nutrient inputs from localised burning and land clearing, potentially from both Aboriginal burning practices and European land clearing.

We believe that in both periods of eutrophication, water column stratification led to anoxia (no oxygen) in the bottom waters, which in turn led to a release of phosphorus, which drove the algal blooms.

Ascertaining a specific reason for the re-eutrophication of the Gippsland Lakes in modern times is difficult, but we can speculate that it is due to changing land practices, particularly high fertiliser use, irrigation, and river regulation. Climate change may cause more frequent droughts, floods and fires, which could further exacerbate the problem.

Introduction

Background

Nodularia blooms are a recurring problem in the Gippsland Lakes. Since 1986, there have been eight major blooms. Before 1986, however, blooms were rare, with only a handful of blooms reported in almost 200 years of European settlement. There are anecdotal reports of blue-green algae (cyanobacteria) blooms prior to the construction of the permanent entrance in 1886 (Carstairs 1937), but there are no data on their frequency or intensity or even the species involved. Effectively managing this ecosystem requires an historical perspective on how the lakes have functioned over time; this will better help us understand both our impact on bloom occurrence and the management actions that could mitigate this impact.

Paleolimnology

Paleolimnology is the reconstruction of lake, estuary and river histories using the physical, chemical, and biological information stored in sediments. It can show the range of natural variability within the system, the extent of human activities and our impact on the ecosystem, and is particularly valuable for periods with limited or no monitoring.

Paleolimnology is based on the concept that sediment accumulates on the bottom of lakes over time, and that each layer represents a snapshot of what was in the lake at the time the sediment was deposited.

A variety of proxy measurements are used to build up a picture of the historic condition of the lakes. A recent study by Saunders, Hodgson *et al.* (2008) found a modern increase in chlorophyll *a* in Gippsland Lakes' sediment, and suggested that large blue-green algal blooms are therefore a recent occurrence. All primary producers (plants and algae) contain chlorophyll *a*, however (Bianchi 2007), and so there will often be a low correlation between chlorophyll *a* and blue-green algae blooms. Using chlorophyll *a* in conjunction with other biomarkers – such as algal pigments and atomic isotope ratios – provides a more reliable indicator of intense blue-green algae blooms (Das, Routh *et al.* 2009). The addition of other markers, such as charcoal (for bushfires), may help us better understand the causes of blooms (Bianchi, Engelhaupt *et al.* 2000; Brenner, Whitmore *et al.* 1999; Teranes and Bernasconi 2000).

While this is the first attempt to observe blue-green algae blooms in the sediment record prior to the opening of the entrance, there are anecdotal reports of blooms that are consistent with *Nodularia* or some other floating, toxic blue-green algae. For example, a report from the Bairnsdale Advertiser in 1949 stated:

"When the natural entrance, three miles east of the present entrance, was blocked sometimes by a sandbar, the lakes water would be impounded and they would freshen up. At times a green scum would appear on the surface of the water." (J. Burgoyne, Bairnsdale Advertiser, 16/8/49)

Likewise fisherman Jock Carstairs described what must have been an algal bloom in the 1880s (Coral Dow pers. comm.):

"In the early days about this time we had a few very dry seasons and the lake grass which was abundant started to rot and the old entrance being very shallow, the water up the (sic) became very stagnant, and the lakes became full of rotten green sediment. Looking over the lakes on a very fine

day was like looking over a green field; it was very poisonous and a fisherman named Charlie O'Neil, fell in and swallowed some water and afterwards died of poisoning. It was almost impossible to use the nets, the fish would not mesh and it was a job to haul the seine nets.... the fishing in consequence became very poor, it even killed tons of fish, many being washed up on the beach and a great many floating about almost dead ... after this having got a wet season the flood waters coming down the rivers and lakes cleaned the lakes out again."

And this contemporary report from 1889:

"The rain has sweetened the lakes by causing the scum and grass which had accumulated to travel out to sea, and our waters are beginning to entice fish in again, which is a good thing for all hands down here." (Our Cuninghame Lette, 13/6/1889)

There is therefore strong evidence of blooms during the early period of European settlement, however we have no information as to whether they took place prior to European settlement and how their frequency and intensity has changed. The aim of this study was to investigate the use of biogeochemical proxies of blue-green algae blooms to piece together a history of blooms over the past 200 years.

Stable isotopes of carbon and nitrogen

Nitrogen occurs in two stable forms, 'heavy' nitrogen (^{15}N) and 'light' nitrogen (^{14}N), and we know that atmospheric nitrogen is lighter than catchment derived nitrogen. By measuring the proportion of 'light' and 'heavy' nitrogen we can work out how much of the nitrogen comes from the catchment and how much from the air. We know from recent work in the Gippsland Lakes (Woodland *et al.* unpublished) that *Nodularia* gets its nitrogen almost exclusively from the air, and therefore we can infer from the ratio of 'light' to 'heavy' nitrogen how much *Nodularia* was in the water when the sediment was deposited. Likewise, by surveying different parts of the lakes, we can infer the areas which have had the highest concentrations of *Nodularia*, and hence the areas that are the likely source of future blooms.

Carbon also occurs in two stable forms, 'heavy' carbon (^{13}C) and 'light' carbon (^{12}C). Terrestrial plants get the majority of their carbon from atmospheric carbon dioxide, which is relatively light, whereas aquatic plants and algae get carbon from a variety of sources, such as dissolved bicarbonate and the breakdown of organic material, which tends to be relatively heavy. The carbon in aquatic plants will therefore be heavier than that found in terrestrial plants, and the analysis of the carbon isotope ratio thus gives an indication if the organic material in the sediment came largely from the catchment or within the lakes.

The proportion of 'heavy' to 'light' isotopes is denoted by the delta notation (e.g. $\delta^{13}C$, $\delta^{15}N$). Appendix A contains a full definition, but it suffices to know that the higher the number, the heavier the isotopes. For carbon, we are most interested in what is locked up in organic material, so we specifically measure only this portion, and denote it $\delta^{13}C_{org}$.

Many studies have shown that stable isotope analysis can be used to relate sediment cores to the sedimentation of organic matter from past water column processes (Appendix A describes these processes in detail). For example, a decrease in $\delta^{15}N$ can indicate the presence of blue-green algae blooms through the input of fixed nitrogen (Bianchi, Engelhaupt *et al.* 2000; Brenner, Whitmore *et* *al.* 1999; Teranes and Bernasconi 2000). Increased $\delta^{13}C_{org}$ can indicate an increase in phytoplankton productivity (Herczeg, Smith *et al.* 2001; Kauppila, Weckström *et al.* 2005; Meyers 2003). Changes in charcoal (fire indicator) can also provide evidence of forest destruction, slope instability and erosion due to increased fire regimes (McWethy, Whitlock *et al.* 2010; Whitlock, Higuera *et al.* 2010).

The two major contributors to changes in the sediment will be floods and *Nodularia* blooms. Recent *Nodularia* blooms have been associated with high rainfall periods (Cook and Holland 2012; Stephens, Biggins *et al.* 2004) so we expect to see a combination of the effects of floods and blooms. Organic material brought in with a flood will have relatively low $\delta^{15}N$, high C_{org}:N (Meyers 1994) and very low $\delta^{13}C_{org}$. A *Nodularia* bloom, on the other hand will contribute material with very low $\delta^{15}N$, but will not greatly impact other measurements. A lot of this material will be further processed in the lake water and in the sediment, with a significant proportion being removed from the system. We expect that the major observable signal will be a drop in $\delta^{15}N$ largely due to *Nodularia*, and a drop in $\delta^{13}C_{org,}$ largely from the flood. If there is a flood and no bloom, there will be no major change to $\delta^{15}N$, and if there is a bloom and no flood, then $\delta^{13}C_{org}$ will remain stable.

Algal Pigments

Algal pigments also provide a means by which to distinguish the types of phytoplankton that accumulate in the sediment. Phytoplankton produce accessory pigments to enhance the spectrum of light that can be harvested, as well as protecting them from excessive light. Different phytoplankton groups produce different pigments and the concentrations of these pigments within the sediment can be used as an indicator of the relative dominance of different groups. In the case of blue-green algae, the pigments zeaxanthin, canthaxanthin and echinenone are commonly used as markers. Pigments are commonly used to reconstruct bloom histories in the Baltic Sea (e.g. Bianchi *et al.* 2000).

Study Aims

The aims of this study were to

1. Use a combination of core dating and biogeochemical proxies for blue-green algae blooms to reconstruct bloom history at a site in Lake King, known to experience *Nodularia* blooms in the past 30 years
2. Undertake a lake wide survey to $\delta^{13}C$ and $\delta^{15}N$ to evaluate these proxies as a means to identify the spatial footprint of recent *Nodularia spumigena* blooms.

Methods

Sample Collection

Sediment cores were taken from Lake King North (LKN; 37.875620° S, 147.757280° E, Figure 1) at a depth of 7 m on the 15th of March 2012. The first core, LKN1 (56 cm) was retrieved by a piston corer and sectioned in the field, in 0.5 cm layers, giving a high resolution chronology of recent changes in the sediment. 1-2 g subsamples from each section were stored in glass vials, with the rest of the sample stored in zip lock bags. These were kept in a cold ice box and on returning to the laboratory the bags were transferred to the refrigerator (4 °C) and the vials were frozen until later processing for stable isotope analysis. Wet samples were kept in darkness in order to reduce light exposure that could change the sediment composition.

The second core (LKN2) was actually a series of cores retrieved by a 50 cm D-section corer (0-42, 42-92, 95-145, 145-195 and 195-200 cm). These cores were collected to investigate long term changes in the sediment. Additional cores were also retrieved by a D-section corer at depths 0-45 and 145-200 cm respectively. All cores were stored in halved PVC pipes, wrapped in cling film and aluminium foil and kept cool until refrigerated in the laboratory. The cores were sectioned into 1 cm layers using a blade and spatula, and stored as per LKN1. Extra cores were stored undisturbed in the refrigerator (4 °C) for further analysis if necessary.

A lakes-wide sediment survey was conducted in September 2012 (Figure 1). Sediment cores (approximately 15 cm deep) were collected from thirty four sites, and two 1 cm slices were taken from the top of the core, placed in zip-lock bags, stored on ice and returned to the lab where they were wrapped in foil and refrigerated.

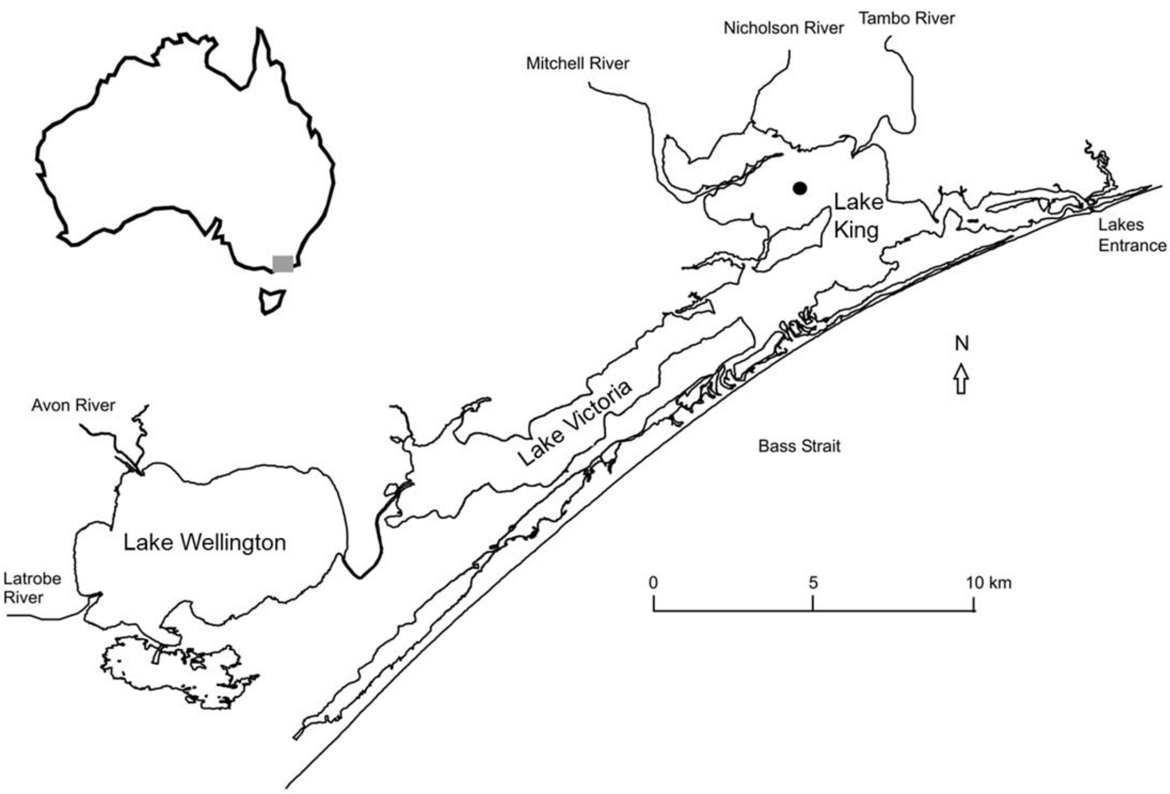

Figure 1: The Gippsland Lakes, south-eastern Australia. The cores were collected at site LKN.

Dating

The sediment was dated at the Australian Nuclear Science and Technology Organisation (ANSTO) using the lead 210 (^{210}Pb) dating method. Alpha spectrometry was used to determine unsupported ^{210}Pb activities on ten subsamples from core LKN1. Details on the sample processing procedure can be found in Harrison 2003. The CIC (Constant Initial Concentration) model was used to calculate the ages of the sediment samples (Appleby 2001). The ^{210}Pb chronology was validated with reference to caesium 137 (^{137}Cs), which is known to give a distinct peak in 1963, due to global atmospheric nuclear weapons tests (Leslie and Hancock 2008). ^{137}Cs activities in 8 subsamples were determined by gamma spectrometry.

Charcoal

Wet sediment (1 ml) was sub-sampled into a 50 ml Falcon tube. 25 ml of 10% tetra sodium pyrophosphate ($Na_4P_2O_7$) was added to the tube, the contents shaken vigorously and left to sit. After 30 minutes, 25ml of 12.5% sodium hypochlorite (NaOCl) was added, and the tube was again shaken vigorously and then left to sit for 14-18 hours. The samples were then sieved through 250 µm and then 125 µm mesh, rinsed and placed on a water filled petri dish where the total number of charcoal and grass charcoal particles were enumerated under a dissecting microscope.

Carbon and nitrogen analysis

Each sediment slice was analysed via mass spectroscopy for % nitrogen, % carbon, C_{org}:N, δ^{15}N and δ^{13}C.

Samples were dried at 60 °C for 30-50 hours and placed in 1.7 ml Eppendorf tubes along with Qiagen Tungsten Carbide Beads (3 mm). Samples were shaken for 6-10 minutes at 25 Hz using a Retsch Mixer Mill MM 200 until a fine, homogeneous powder was produced. Samples for carbon ($\delta^{13}C_{org}$) were weighed in silver capsules and placed on a hotplate (60-80 °C) to undergo acidification. 20 µL aliquots of 10% HCl were sequentially added to capsules until no effervescence was recorded. Samples for nitrogen (δ^{15}N) analysis were weighed in tin capsules. Once each capsule was prepared it was pinched-closed and pressed into a disk using a pelletiser. Each sample was analysed at the Water Studies Centre (Monash University) on an ANCA GSL2 elemental analyser interfaced to a Hydra 20-22 continuous-flow isotope ratio mass-spectrometer (Sercon Ltd., UK). Stable isotope data were expressed in the delta notation ($\delta^{13}C_{org}$ and δ^{15}N) relative to the stable isotopic ratio of Vienna Pee Dee Belemnite standard (R_VPDB = 0.0111797) and the air standard (R_Air = 0.0036765), for carbon and nitrogen respectively.

$$\delta^{H}X = (R/Rstd - 1) \times 1000,$$

where X is C or N and

$$R = {}^{H}X/{}^{L}X$$

The heavy (H) to light (L) isotope ratio measured in the sample and in the standard (VPDB or air). Analytical precision was ±0.1 ‰ for both $\delta^{13}C_{org}$ and δ^{15}N (SD for n=5).

Pigments

Pigments were analysed at 5 cm intervals from 0-41 cm and every 10 cm through to 2 m. Freeze-dried sediments were extracted in pure acetone overnight and stored in dark at -22 °C. They were then filtered, dried and re-dissolved, and then injected into a Shimadzu high performance liquid chromatography (HPLC) system. The separation conditions were modified from Mantoura and Llewellyn (1983) and Chen et al. (2001) using the 4.6 × 150 mm, 3 µm C8 (Luna, Phenomenex) column. Pigment peaks were identified by retention times and spectra, and then quantified by peak areas at maximum absorbance wavelength using calibrated curves from phytoplankton pigment standards DHI (Denmark). *Canthaxanthin* was measured at 475 nm, and the carotenoids *Lutein-Zeaxanthin, Diadinoxanthin, Diatoxanthin*, and *Echinenone* were measured at 450 nm. *Chlorophyll a* was measured at 665 nm. Concentrations are reported in micromoles of pigment relative to the organic material in the sediment as estimated by loss-on-ignition at 550 °C.

Other Data

The historical records of major fires and floods in East and West Gippsland came from the Department of Sustainability and Environment website (www.dse.vic.gov.au).

Results

Age model

There was a linear relationship between cumulative mass and the natural log of unsupported ^{210}Pb (Figure 2a, R^2= 0.96), allowing the use of the CIC model. A polynomial regression was fitted to the calculated age against depth (Figure 2b, R^2= 0.99). Ages estimated outside the fitted polynomial (depth > 90 cm) must be taken as approximate. The mass accumulation rate calculated from the CIC model was 1.0 ± 0.2 g cm^{-2} y^{-1} (R^2 = 0.91), calculated from Figure 2a. In the top 5 cm, ^{210}Pb did not exhibit a decay profile which may be due to sediment mixing.

These calculated ages were validated by ^{137}Cs, with the 1963 peak found in the 25-30 cm sediment layer, dated to 1964-1969. A further validation is the peak in charcoal concentration (24 ml^{-1}) at depth 61 cm (Figure 5), which corresponds to approximately 1939, the date of major bushfires in the catchment (Department of Sustainability and Environment).

The dating method that we used accurately dates sediment as far back as the 1920s, but can only provide a rough approximation prior to this. Biogeochemical proxies can, however, be used to pinpoint dates when major changes are known to have occurred in the Gippsland Lakes. We can predict that the 1889 opening of the artificial entrance is found at ~130 cm, as there is a major, sustained decrease in the percentages of carbon and nitrogen in the sediment at this point, indicating a reduction in the sedimentation of organic matter to Lake King North. This could be due to a reduction in algae or due to changes to the hydrology of the system; both of these would occur following the opening of the entrance. The increase in C_{org}:N above 130 cm suggests a greater contribution of catchment derived material and less production in the lakes themselves. Consistent with this, there was a drop in pigment concentrations at around the 130 cm mark, indicating less phytoplankton (Figure 6).

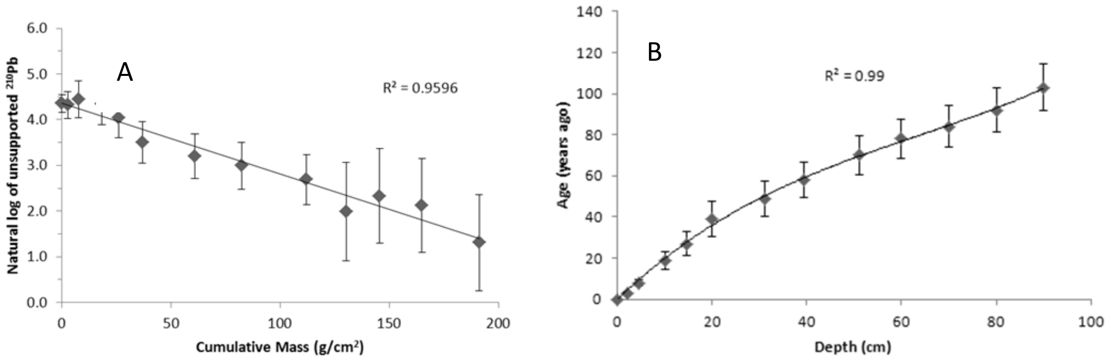

Figure 2: a) Linear relationship between cumulative mass and the natural log of unsupported ^{210}Pb, corrected for grainsize differences. b) Age vs. depth model based on unsupported ^{210}Pb values using the CIC model.

Core LKN1 (1942-2012)

(shown in Figure 3)

Over this period, %N and %C_{org} increased from approximately 0.2 to 0.5 and 2.6 to 4.3, respectively. C_{org}:N showed an initial decreased and then stabilised at around 10.

During the late 1940s, δ^{15}N increased sharply from ~4 to ~6 ‰, while there was a concurrent decrease in $\delta^{13}C_{org}$ from -22 to -24 ‰. Other variables do not noticeably change during this period.

In the 1950s the data shows a lot of year to year variation, especially in the carbon measurements.

Between 1964 and 1968 there was a drop in $\delta^{13}C_{org}$, %N and %C_{org}, whilst δ^{15}N and C_{org}:N remained relatively stable. During 1965, the first *Nodularia* bloom was reported (Solly 1966). Prior to this occurrence there was a major fire and flood in the catchment (Stephens, Biggins *et al.* 2004).

1971 was one of the largest floods on record with 199.1 mm recorded at the Bairnsdale Airport in December 1970 (Bureau of Meteorology), but there is little evidence of this in the sediment, apart from an increase in C_{org}:N. Following this flood was a bloom reported in 1973 (Stephens, Biggins *et al.* 2004), however no variables showed any noticeable change.

During the late 1980s there was a marked decrease in δ^{15}N, $\delta^{13}C_{org}$, %N and %C_{org}, and a spike in C_{org}:N. During this period there were four *Nodularia* blooms, occurring in 1987, 1988, and two in 1989, with 1987 the most widespread bloom on record (Stephens, Biggins *et al.* 2004). There was a flood in 1985 and another major flood event in 1989.

Between 1993 and 1994, there was a drop in δ^{15}N and spike in C_{org}:N which was not associated with a *Nodularia* bloom. Other variables remained stable. There was a flood in 1993, and a blue-green algae bloom in Jones Bay, but the species was *Microcystis* (Cook and Holland 2012), which does not fix nitrogen and would not be expected to affect sediment δ^{15}N.

During the late 1990s and early 2000s, δ^{15}N, $\delta^{13}C_{org}$, %N and %C_{org} all decreased, while C_{org}:N spiked. During this period were 5 reported *Nodularia* blooms; 1996, 1997, 1999, 2001 and 2002 (Cook and Holland 2012). In 1998, a major flood event occurred. There was also a minor bushfire in the

Gippsland region during 1997. The $\delta^{15}N$ was consistently low during this intense bloom period, while the $\%C_{org}$ drop did not occur until after the 1998 flood.

Around 2007, there was a spike in C_{org}:N and $\%C_{org}$, and a dip in %N. In 2006-2007 major bushfires occurred in the East Gippsland catchment, as well as a major flood in 2007.

Core LKN2 (pre European-2012)

(shown in Figure 4)

The data from this core has been divided into six periods of interest, based on changes present in the data, in particular $\delta^{15}N$ due to its relationship with *Nodularia*: Section A (200 – 141 cm: prior to the 1860s), B (141 – 130cm: late 1860s - mid 1880s), C (130 – 101cm: mid 1880s - mid 1910s), D (101 – 80cm: mid 1910s – late 1920s), E (80 – 37 cm: late 1920s – mid 1950s) and F (37 – 0cm: mid 1950s – 2012).

Section A (200 – 141 cm: prior to the 1860s)

Compared to the other sections, charcoal concentrations were high, with peaks at depths 195, 192, 175, 170, 167 and 161 cm, with a maximum concentration of 133 ml^{-1}. $\delta^{15}N$, $\delta^{13}C_{org}$, C_{org}:N, %N and $\%C_{org}$ all showed a lot of variability during this period.

$\delta^{15}N$ was often low, at levels that were equal to or lower than those occurring during the modern drop. $\delta^{13}C_{org}$, C_{org}:N, %N and $\%C_{org}$ were quite variable, but were broadly similar to the values occurring since the mid 1980s.

Section B (141 – 130cm: late 1860s – mid 1880s)

There is distinct dip in $\delta^{15}N$, as well as concurrent increases in $\delta^{13}C_{org}$, %N and $\%C_{org}$. C_{org}:N remained stable. Charcoal concentrations were slightly elevated.

Section C (130 – 101cm: mid 1880s - mid 1910s)

This period is characterised by high $\delta^{15}N$ and C_{org}:N, low $\delta^{13}C_{org}$, %N and %C, and very low charcoal concentrations. At depth 122 cm, in Section B, there was dip in $\delta^{15}N$ and C_{org}:N, and spike in $\delta^{13}C_{org}$, %N, $\%C_{org}$ and charcoal concentration.

Section D (101 – 80cm: mid 1910s – late 1920s)

$\delta^{13}C_{org}$, $\delta^{15}N$, %N and %C were all low, while C_{org}:N was particularly high. There was a spike in charcoal at 91 cm of 72 ml^{-1}. Major fires occurred in 1914 (Department of Sustainability and Environment).

Section E (80 – 37 cm: late 1920s – mid 1950s)

This period had stable, high $\delta^{15}N$, while $\delta^{13}C_{org}$ and C_{org}:N were variable. %N and %C showed a steady increase over this period, and charcoal was generally low, apart from a spike around 1940.

Section F (37 – 0cm: mid 1950s – 2012)

The record for the past 60 years is characterised by a recent drop in $\delta^{15}N$, along with an increase in C_{org}:N, %N and $\%C_{org}$. Charcoal concentrations were low during this period.

Pigments

Pigments that are characteristic of diatoms (diatoxanthin) and blue-green algae (canthaxanthin and echinenone) all showed trends broadly similar to the chlorophyll *a* signal, which is a pigment found in all algae (Figure 5). There was a distinct pattern, where the pigment concentrations were high at the top of the core, and then declined over the first ~50 cm, and then there was a large peak at around 150 cm and an even larger peak below 170 cm. The drop in pigments from about 140 cm coincides with the opening of the permanent entrance. The peak at 40 cm is about 1970 and may relate to the reported blooms in 1965 and 1973. The sustained increase from 22 cm coincides with the 1988 *Nodularia* bloom onwards.

Lake sediment survey

The sediments with medium to high $\delta^{13}C_{org}$ and very low $\delta^{15}N$ are likely to be the most influenced by *Nodularia* (see Appendix A). The 2011-2012 bloom occurred throughout Lake King, but was most severe in Bunga Arm. The sediment most influenced by *Nodularia* is in Bunga Arm, with other parts of Lake King also showing a strong influence. Closer to Lakes Entrance the sediment has very high $\delta^{13}C_{org}$ is influenced by marine inputs and seagrass, while Lake Wellington and Jones Bay have very low $\delta^{13}C_{org}$, which indicates that they are strongly influenced by catchment inputs.

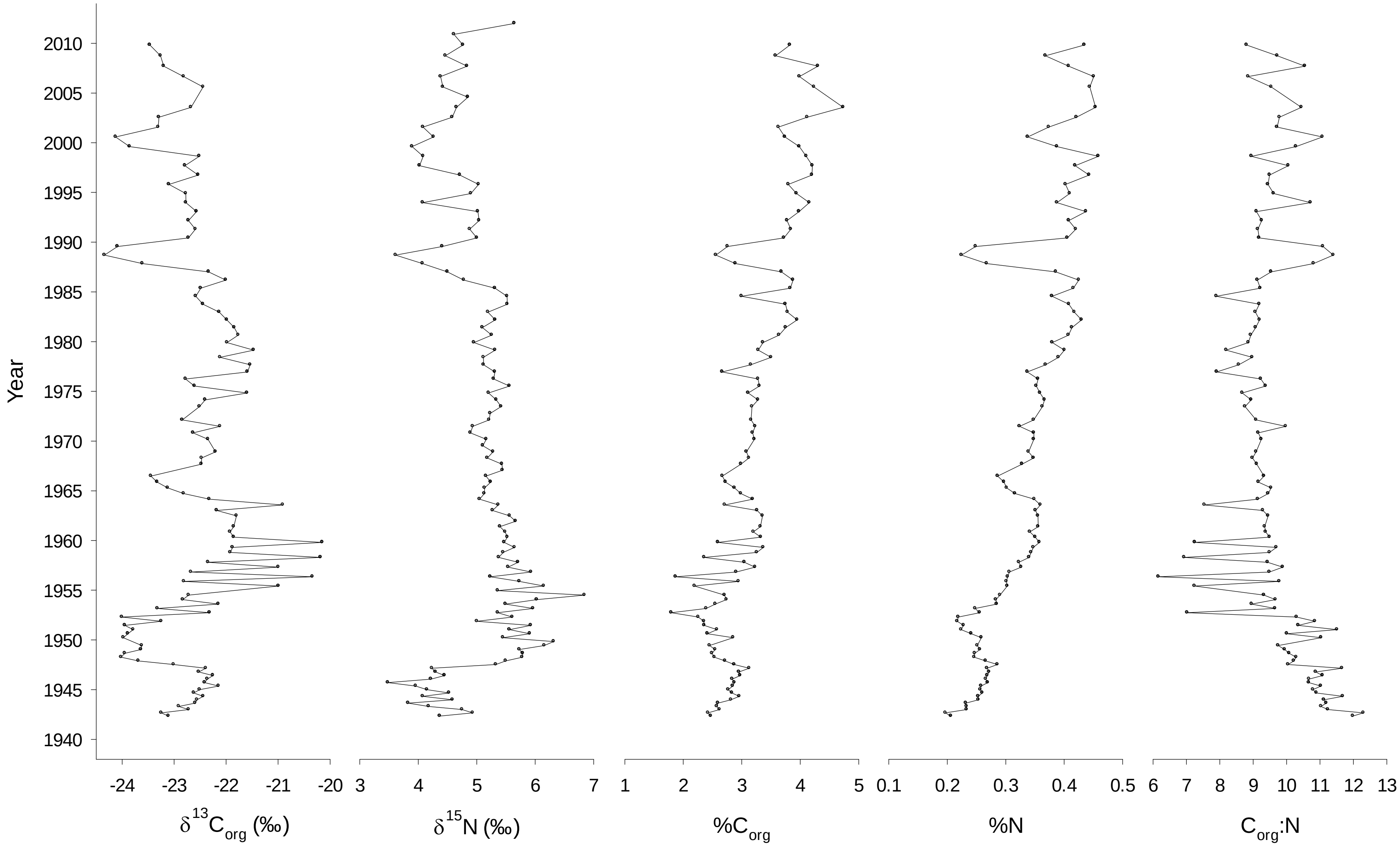

Figure 3: LKN1. Sediment, $\delta^{13}C_{org}$, $\delta^{15}N$, $\%C_{org}$ %N and C_{org}:N plotted against year. Year calculated using Figure 3b.

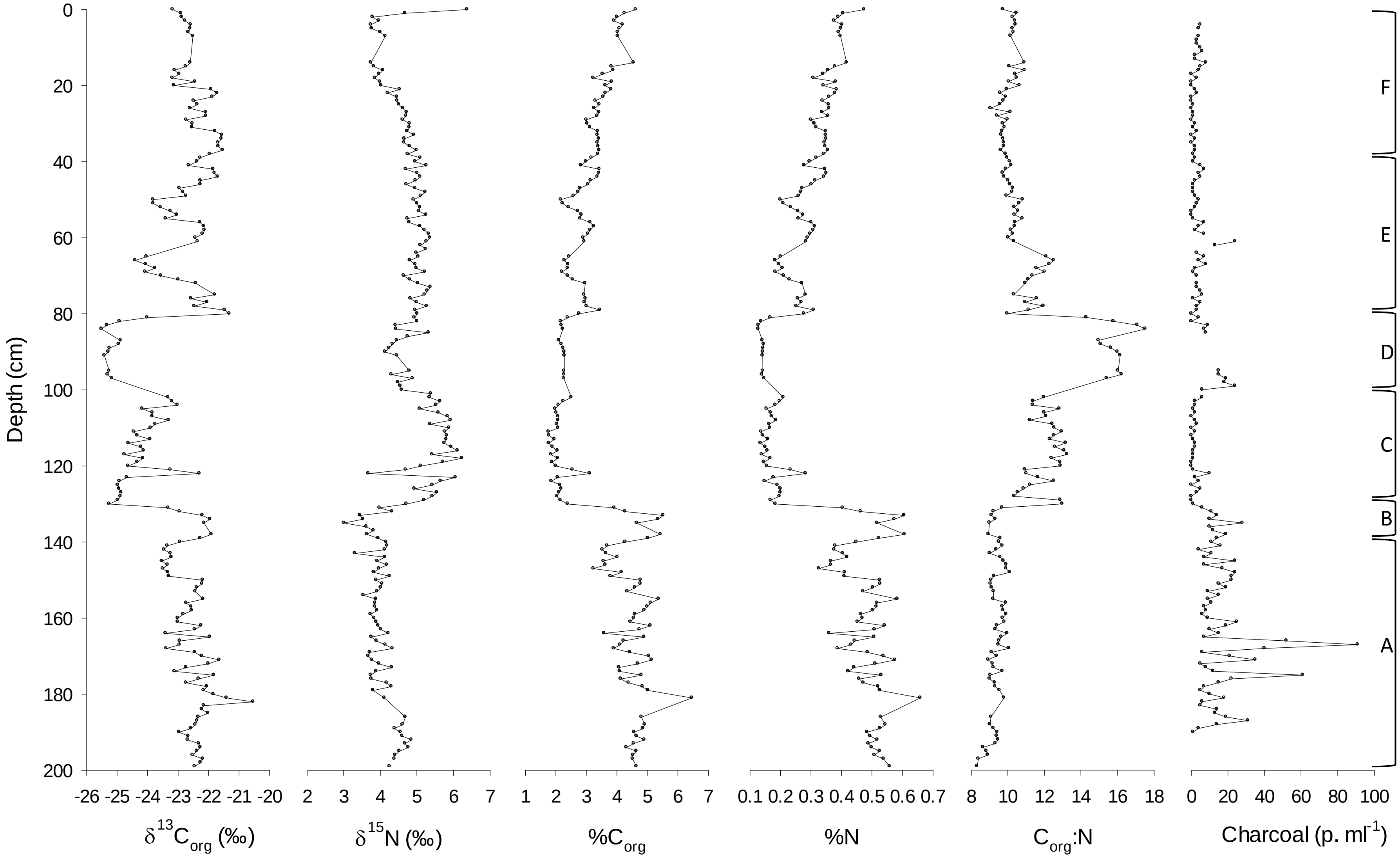

Figure 4: LKN2. sediment $\delta^{13}C_{org}$, $\delta^{15}N$, $\%C_{org}$, %N, C_{org}:N and charcoal concentration plotted against depth.

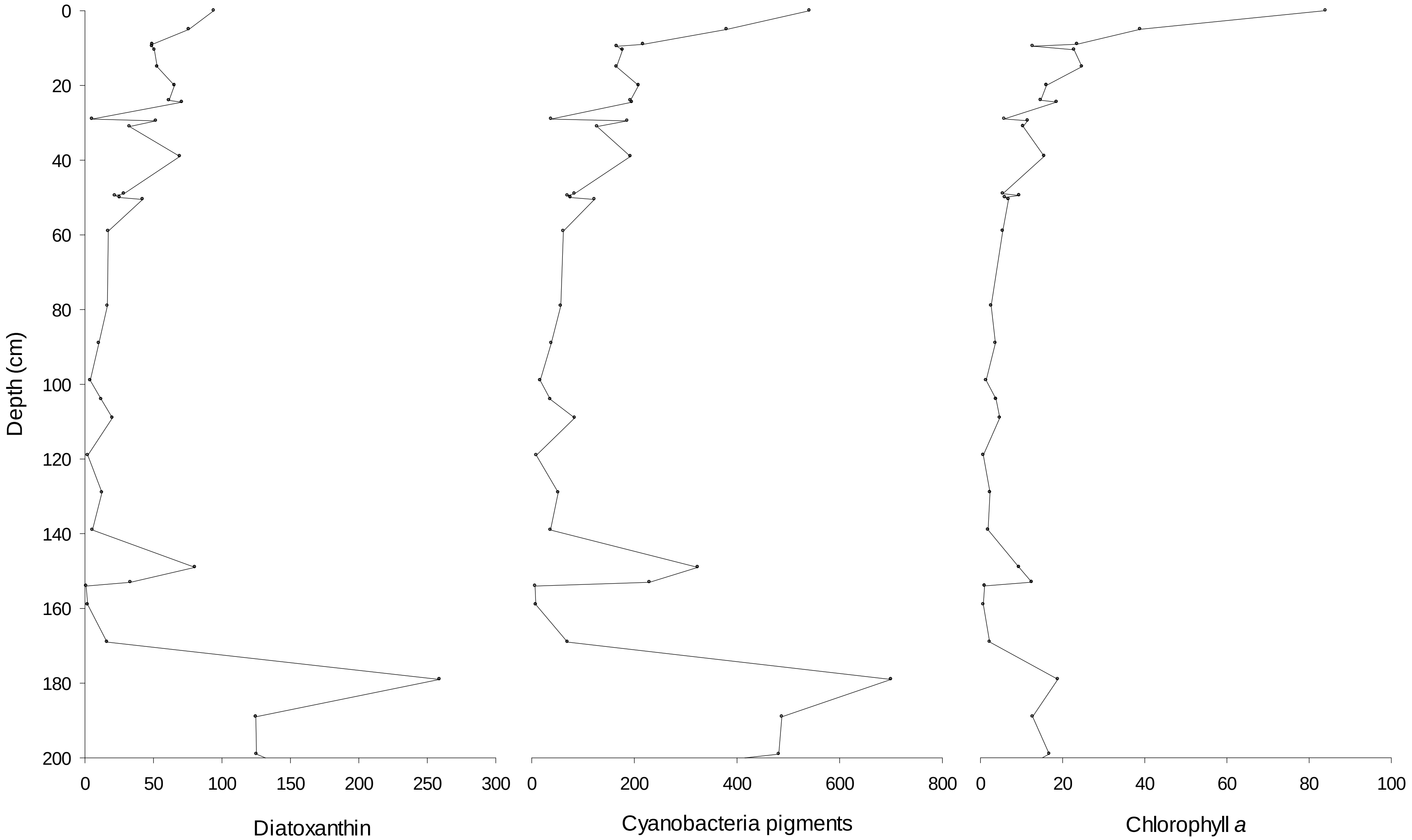

Figure 5: Pigment concentrations from core LKN2 (μmol g^{-1}). Diatoxanthin is a pigment of diatoms, while blue-green algae are represented by the total combined zeaxanthin, canthaxanthin and echinenone. Chlorophyll *a* is found in all phytoplankton and plants.

Figure 6: Gippsland Lakes sediment stable isotope survey. The size of the circle indicates $\delta^{15}N$. The smallest circles are >6.5 ‰ and the largest circles are <4 ‰. The shade of the circles indicates δ^{13}Corg (‰), and ranges from <-23 (white) to >-15 (black). Sites strongly influenced by *Nodularia* have large, grey circles, e.g. Bunga Arm.

Discussion

The history of algal blooms in the Gippsland Lakes

The biogeochemical proxies analysed here provide clear evidence for two periods of eutrophication and blue-green algae blooms in the Gippsland Lakes – 1. The recent period after the Second World War and 2. Prior to the opening of the artificial entrance in 1889. The latter part of the most recent period has been well monitored and so provides an excellent means to calibrate the biogeochemical proxies. The first piece of evidence for the recent period of eutrophication comes from the steady increase in sediment organic carbon content after the 1940s, consistent with a previous paleolimnological study (Saunders *et al.* 2008). The $\delta^{13}C_{org}$ of this organic matter is typically ~-23 ‰, consistent with organic matter inputs derived from phytoplankton. In 1987, the first of the recent series of severe *Nodularia* blooms occurred and this was reflected in the sediment record as a marked dip in $\delta^{15}N$ from ~5 to 3.5 ‰ followed by a lower baseline $\delta^{15}N$ of ~4 ‰ to the top of the core. This period also coincided with a marked jump in the sum of the blue-green algae pigments zeaxanthin, echinenone and canthaxanthin from a baseline of ~10 up to 500 µmol g^{-1} at the top of the core. The close agreement between these blue-green algae markers and recent recorded blooms gives us confidence that they are appropriate markers of blue-green algae blooms within the Gippsland Lakes.

The biogeochemical proxies for the period before the opening of the entrance likewise suggest a period of eutrophication and intense cyanobacteria blooms. The sediment organic content was high, the $\delta^{15}N$ was low, the $\delta^{13}C_{org}$ was in the range typical of phytoplankton and the cyanobacteria pigments were high. With no permanent entrance, the inflow of seawater was greatly reduced, and at this time the lakes were considerably fresher (Harris *et al.* 1988). *Nodularia* grows best at salinities from about 5 to 20 (Cook *et al.* 2009) (ref??). When the salinity was below 5, it is likely that other nitrogen fixing blue-green algae, such as *Anabaena* would instead dominate. *Anabaena*, another potentially toxic blue-green algae species, mostly occurs in freshwater, and occasionally blooms in Lake Wellington, and may therefore be the source of blue-green algae in Lake King prior to 1889. The lack of flushing combined with low surface salinity would lead to enhanced stratification of the water column, which would isolate the bottom waters, inducing anoxia and phosphorus release, a phenomenon that recent research in the lakes shows leads to *Nodularia* blooms (Cook *et al.* 2010).

Ascertaining a specific reason for the re-eutrophication of the Gippsland Lakes in modern times is difficult, but we can speculate that a combination of changing land practices, particularly the high fertiliser irrigation, and changing climate, which is a likely cause of more frequent droughts, floods and fires is involved. We know that sediment phosphorus is a key driver of *Nodularia* blooms.

Impact of the permanent entrance (1889-1985)

The opening of the entrance in 1889 led to an increase in $\delta^{15}N$ and C_{org}:N, and a decrease in $\delta^{13}C_{org}$, %N and %C. Combined, these indicate of a drop in nitrogen fixating blue-green algae ($\delta^{15}N$) and a drop in the overall productivity of the lakes (%N, %C), as well as an increase in the relative influence of catchment inputs (C_{org}:N, $\delta^{13}C_{org}$).

A marked drop in $\delta^{15}N$ around the turn of the century (122 cm) is suggestive of a large blue-green algae bloom or blooms. This coincides with the Federation Drought, which led to massive bushfires in Gippsland in 1898 (there is only a small pulse in charcoal at 122 cm, which shows that the size and intensity of a bushfire might not be well reflected in the charcoal record). In 1899 there are reports of at least minor flooding in the catchment (The Maffra Spectator, April 10, 1899), and so it is possible that a bushfire followed by a flood led to a bloom. It may be that conditions then were not dissimilar to what was experienced in Gippsland over the past five years. We have, however, found no specific mention of a bloom around 1900 in the historic records.

The period from the mid 1910s until the late 1920s appears to show big influxes of material from the catchment, and may relate to wide-spread clearing in Gippsland, erosion from gold mining, and the loss of the *Phragmites* reeds fringing the lakes (Bird 1983).

The middle of the century was characterised by uniformly high $\delta^{15}N$, which suggests that *Nodularia* blooms were rare and isolated occurrences, and this is consistent with the historic record, apart from the two previously noted exceptions in 1965 and 1973.

The blooms that are reported from 1965 and 1973, however, show no $\delta^{15}N$ signal. The 1965 bloom was in Lake Wellington (Solly 1966) and we would not necessarily expect this to result in a measurable change in the sediments of Lake King North, given the distance and hydrology involved (Figure 1). The bloom in 1973 was present in Lake King, but may not have been intense enough to leave a $\delta^{15}N$ signal. Perhaps only major blooms, or a rapid series of blooms, are visible in the sediment $\delta^{15}N$ record.

The history of benthic vegetation in the deep basins of the Gippsland Lakes

If the organic material in the sediments of Lake King North were from macrophytes such as seagrass then we would expect a $\delta^{13}C_{org}$ of -10‰, such as was found in the sediment of Carstairs Bank (Table 1). The $\delta^{13}C_{org}$ was consistently below -20‰, indicating that the organic material was instead phytoplankton dominated. This suggests that in the past 200 years, the deep basins of the Gippsland Lakes have been unvegetated and dominated by phytoplankton.

Fire History

Charcoal is a poor indicator of fires in the catchment of the Gippsland Lakes. The biggest fires of the past century, the intense, catchment-wide fires in 2007 and 1939, are barely perceptible in the sediment charcoal. It appears that very little ash is transported into the lakes from fires in the upper parts of the catchment.

There is evidence of frequent fires in the charcoal record in the deepest part of the cores, a period which probably includes both pre-European and early settlement periods. As mentioned, the size of the charcoal signal may not represent the size of the fire, and instead these peaks might better represent local burning (rather than catchment wide burning), either through land clearing by European settlers, or through Aboriginal burning practices, particularly the burning of the *Phragmites* reeds fringing the lakes.

Current δ15N distribution

The area of the lakes where the 2011-2012 *Nodularia* bloom was most intense – Ocean Grange and up Bunga Arm in particular and Lake King more generally – had a distinctly lower $\delta^{15}N$ than surrounding areas, whilst having relatively high $\delta^{13}C_{org}$. This combination of stable isotope measures appears, therefore, to be a good indicator of bloom activity spatially as well as temporally.

Conclusion

Toxic blue-green algae blooms are not a purely recent occurrence in the Gippsland Lakes. Three distinct periods of blue-green algae activity can be established. A period of frequent, intense algal blooms prior to the opening of the entrance, followed by a period of low blue-green algae activity until the mid 1980s, after which *Nodularia* blooms became a regular occurrence. There are enough similarities in the data between the pre-entrance and the post 1985 periods to suggest that, even though the lakes were physically and hydrologically very different, high nutrients and frequent algal blooms occurred at both times.

We hypothesis from these observations that the Gippsland Lakes were eutrophic (highly nutrient enriched) prior to the opening of the entrance, and this was probably due to low flushing and stagnant water, combined with nutrient inputs from localised burning and land clearing, potentially from both Aboriginal burning practices and European land clearing. The opening of the entrance increased flushing and increased the salinity in the lakes, leading to a clearer water column and fewer blooms. Recent land practices (further land clearing and high intensity agriculture) have contributed to the re-eutrophication of the system and the re-occurrence of blue-green algal blooms.

Acknowledgements

Funding was provided through the Gippsland Lakes Environment Fund, and this report was prepared for the Gippsland Lakes Ministerial Advisory Committee. Further funding was provided by an award from the Australian Institute of Nuclear Science and Engineering (AINSE grant 12139) for dating work at the Australian Nuclear Science and Technology Organisation (ANSTO).

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Appendix A: Influences of the process affecting the $\delta^{13}C_{org}$ and $\delta^{15}N$ in estuary sediment

Basic concept	Stable isotopes are expressed in the delta notation ($\delta^{13}C_{org}$ and $\delta^{15}N$) relative to the stable isotopic ratio known standards. $\delta^{H}X = (R/Rstd - 1) \times 1000$, where X is C or N and, $R = {}^{H}X/{}^{L}X$, the heavy (H) and light (L) isotope ratio. The $\delta^{13}C_{org}$ and $\delta^{15}N$ of organic matter produced within a water body is influenced by the ${}^{H}X/{}^{L}X$ ratio of the dissolved portion in the water body. This, in turn, is controlled by a suite of physical, chemical and biological processes in and around the lake. Over time, the $\delta^{13}C_{org}$ and $\delta^{15}N$ of autochthonous organic matter may change as a consequence of a shift in one or more of these processes. It can also be altered due to the source of the material (i.e. terrestrial, phytoplankton, seagrass diagenesis). (Goericke, Montoya *et al.* 1994)
Biogeochemical processes	**$\delta^{13}C_{org}$and $\delta^{15}N$**
Aquatic primary production	Increased $\delta^{13}C_{org}$. During high aquatic primary production, there is accumulation of autochthonous organic matter and its associated ${}^{13}C/{}^{12}C$ isotopic ratio of the dissolved inorganic carbon (DIC) in lake water that is used for photosynthesis. Fractionation occurs due to the preferential uptake of the lighter isotope, ${}^{12}C$ becomes depleted, leading to an increased proportion of the heavier isotope ${}^{13}C$ in the organic matter. (Fogel, Cifuentes *et al.* 1992; Gu, Schelske *et al.* 1996; Hodell and Schelske 1998) Increased $\delta^{15}N$ (non-diazotrophic). Primary production is fuelled by nutrients, which are scavenged, leading to the depletion of the lighter isotope and enrichment of the heavier one. (Bratton, Colman *et al.* 2003; Savage, Leavitt *et al.* 2004; Teranes and Bernasconi 2000; Wada and Hattori 1978) Decreased $\delta^{15}N$ (diazotrophic). Input of nitrogen from the atmosphere ($\delta^{15}N = 0$) through nitrogen fixation into diazotrophic cyanobacteria. (Bianchi, Engelhaupt *et al.* 2000; Teranes and Bernasconi 2000)
Aquatic Plants	Increased $\delta^{13}C_{org}$. Aquatic Plants have a lower efficiency of assimilating carbon into the cell, which causes CO_2 limitation in the boundary layer at the plant surface, enriching the isotopic ratio in the cell due to increases in the

	input of HO_3^- (isotopically heavier). (France and Holmquist 1997; Haddad and Martens 1987)
Terrestrial (allochthonous) input	Decreased $\delta^{13}C_{org}$. Indicate inputs of terrestrial derived organic matter. Higher level plants fix carbon from the atmosphere which is lighter than the carbon in organic matter produced in lakes. (Goñi, Ruttenberg *et al.* 1997) Increased $\delta^{15}N$. Denitrification in soils is intensified by anthropogenic influences including sewage treatment and agricultural run-off. During denitrification, NO_3^- is converted into N_2 gas. At each stage of this process fractionation occurs, which is when the lighter isotope is preferentially used – due to lower energy requirements for breaking molecules – leading to a loss of the lighter isotope and enrichment in the heavier one. (Kellman 2005; Voß and Struck 1997)
Anoxic diagenesis	Increased $\delta^{13}C_{org}$. Methanogenesis is favoured under anoxic conditions and produces isotopically light CH_4 and isotopically heavy CO_2.^{13}C enrichment in the water column has been attributed to the input of CO_2 from methanogenesis. (Gu, Schelske *et al.* 1996; Stiller and Magaritz 1974) Decreased $\delta^{15}N$. Decay during anoxic bacterial growth adds $\delta^{15}N$ depleted biomass to the residual material. (Lehmann, Bernasconi *et al.* 2002)