

Effect of a flood event on the dynamics of phytoplankton and biogeochemistry in a large temperate Australian lagoon

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Abstract

In episodically driven estuaries, nutrient delivery is typically confined to sporadic flow events, followed by intense biogeochemical recycling of nutrients. We document the response of a temperate lagoon system with episodic winter- or spring-dominated catchment inflows (Gippsland Lakes, southeast Australia) to a flood event. High winter inflows resulted in high surface-water concentrations of inorganic nitrogen (IN; $\text{NO}_2^- + \text{NO}_3^- + \text{NH}_4^+$) relative to reactive phosphorus (RP) with an IN:RP ratio > 100 . This resulted in a rapid diatom and dinoflagellate bloom, which collapsed as water column nutrients were exhausted. Increased carbon delivery to the sediment stimulated benthic respiration and depleted bottom-water oxygen, which led to a large release of RP from the sediments, decreasing the IN:RP ratio in the bottom water to ~ 6 . Strong stratification of the water column allowed the accumulation of RP in the bottom water over spring and into summer. Mixing of RP from the bottom water over summer triggered the development of a *Nodularia spumigena* Mertens bloom. As such, the nutrient supply for the *Nodularia* bloom was through a biogeochemical filter that strongly favored N_2 -fixing cyanobacterial blooms by reducing IN:RP ratios through a combination of sediment denitrification and release of stored phosphorus from within the sediment. These observations lead us to the paradoxical conclusion that high nitrogen loading over winter contributed to severe nitrogen limitation over summer, and highlight the importance of controlling both nitrogen and phosphorus loading to estuaries.

Eutrophication of estuaries is a significant global problem. Our conceptual understanding of coastal eutrophication is evolving rapidly, and it is now recognized that the effects of anthropogenic stressors such as nutrient loads will vary greatly between estuaries (Cloern 2001). Examples of factors that alter estuarine responses to nutrient loading include tidal amplitude, residence time, and the grazing of phytoplankton. Detailed information on the manifestation of eutrophication is, therefore, required from a broad range of estuaries.

One factor known to influence estuarine function and response to eutrophication is the degree to which catchment inputs are dominated by episodic events (Eyre 1998; Webster and Harris 2004). Episodically dominated estuaries receive most of their catchment-derived nutrient inputs over a very short time interval following flow events. This nutrient input typically results in a rapid phytoplankton bloom that quickly consumes the catchment-derived nutrients (Ferguson et al. 2004). Upon the exhaustion of bioavailable nutrients, this initial bloom collapses and is internally recycled through sediment biogeochemical processes (Eyre and Ferguson 2006), which may then lead to a second algal bloom (Lukatelich and McComb 1986). Sediment biogeochemical processes are, therefore, likely to exert a critical control over nutrient and phytoplankton dynamics, particularly in episodically dominated estuaries with high residence times (low flushing) such as coastal lagoons. An understanding of the interaction between eutrophication and flow frequency is also particularly important within the context of climate

change, which is expected to increase rainfall and runoff variability (Lehner et al. 2006).

Estuarine and marine sediments are often found to recycle phosphorus (P) more efficiently than nitrogen (N), resulting in a decrease in the N:P ratio in those waters compared to freshwaters (Caraco et al. 1990). The preferential recycling of P over N in estuarine sediments is fundamentally driven by the fact that a significant amount of N processed within the sediment is denitrified and, thus, permanently lost. P, by contrast, has no stable gaseous form, and burial is the primary mechanism by which it is lost. Over the short term, a large fraction of the P that is mineralized within the sediment is adsorbed onto Fe(III) oxyhydroxides at the sediment surface (Howarth et al. 1995). Reduction and dissolution of this Fe(III) oxyhydroxide phase can lead to periodic high release rates of P from the sediment that are strongly decoupled from N release, potentially driving N:P ratios down to very low levels. The most commonly cited factor leading to spikes in P release from the sediment is water column hypoxia (Conley et al. 2002; Kemp et al. 2005). It is also recognized that sulfide production (i.e., sulfate reduction) rates within the sediment play an important role in controlling P storage within the sediment, primarily because sulfide leads to the reductive dissolution of Fe(III) oxyhydroxides (Jensen et al. 1995). The corollary of this is that episodically driven estuaries are likely to have internal N:P ratios well below the land-derived loading rate during periods of low flow.

Australian estuaries have highly episodic inflows (Eyre 1998), and a conspicuous feature of several temperate Australian estuaries is recurring noxious blooms of *Nodularia spumigena* Mertens (Francis 1878; Davis and Koop 2006). Such blooms are rarely observed in other

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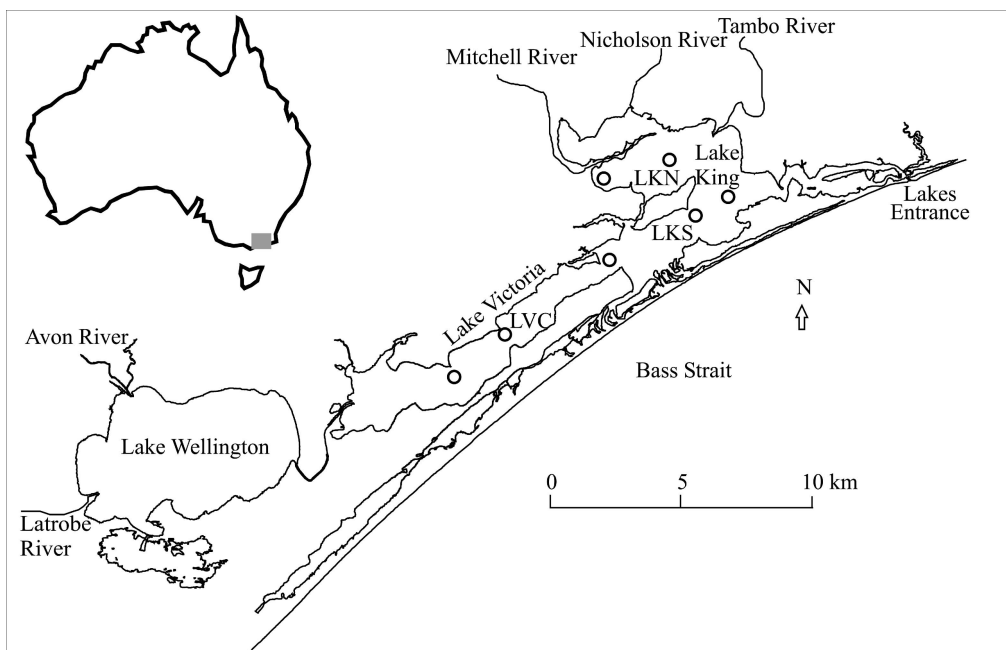


Fig. 1. The Gippsland Lakes, southeast Australia. The open circles show the location of benthic flux measuring sites. All water quality data presented in this paper are from site Lake King South (LKS). Detailed time series data for water quality and benthic flux parameters were also collected from sites Lake Victoria Central (LVC) and Lake King North (LKN); these are not presented, but are referred to in the text.

estuaries globally, with the exception of the Baltic Sea (Sellner 1997; Howarth and Marino 2006). A number of factors are known to be conducive to the formation of *Nodularia* blooms in estuaries, including low inorganic N (IN), high P, low salinity, high irradiance, warm temperatures, strong vertical stratification, and grazing (Sellner 1997; Chan et al. 2006; Marino et al. 2006). Given that the relative availability of N and P is a critical factor in the development of *Nodularia* blooms, internal nutrient recycling dynamics are likely to play an important role in their occurrence (Lukatelich and McComb 1986; Vahtera et al. 2007).

Aside from the Baltic Sea and the Peel-Harvey Estuary, there are no detailed published studies of estuarine N_2 -fixing cyanobacterial blooms that have simultaneously considered the biogeochemical controls over estuarine nutrient dynamics and how these contribute to bloom formation. Here, we present a set of data that details nutrient biogeochemistry and phytoplankton biomass following a large flow event in a temperate Australian lagoon, the Gippsland Lakes. The initial input of nutrients with a high N:P ratio triggered a bloom of diatoms and dinoflagellates. Subsequent recycling of this bloom increased benthic respiration, driving down the N:P ratio of the benthic fluxes and hence the water column, which was a critical factor in triggering a subsequent *N. spumigena* bloom. To our knowledge, this is the first comprehensive data set that includes water column nutrient and chlorophyll *a* (Chl *a*) measurements plus in situ benthic flux measurements to simultaneously document this sequence of events within an estuarine context.

Methods

Site description—The Gippsland Lakes form a large coastal lagoon system in southeastern Australia (Fig. 1). The main body of the lakes occupies 354 km², although there are additional ephemeral areas, such as Lake Reeve, south of Lake Victoria. Lake Wellington in the west is connected to Lake Victoria via the narrow McLennan's Strait, and Lakes Victoria and King are part of the same water body and share similar limnological characteristics. Lake Wellington is shallow with an average depth of 2.6 m, and is well mixed. The salinity varies from predominantly fresh in wet years up to salinities > 20 in drought years. Prior to 1968, Lake Wellington was dominated by macrophytes; increased salinities caused by a drought in that year killed these plants and the lake has since been dominated by phytoplankton. Lakes Victoria and King are deeper basins with average depths of 4.8 and 5.4 m, respectively, and are generally highly stratified, particularly in high-flow years, leading to periodic hypoxia of the bottom waters (Bek and Bruton 1979; Webster et al. 2001). The lakes have undergone significant ecological change since an artificial sea entrance was constructed in 1889, largely because of increased salinity from tidal inflows of seawater. Increases in catchment nutrient inputs over the same period have caused the lakes to become eutrophic, and blooms of the toxic, N-fixing cyanobacterium *N. spumigena* are a recurring problem (Stephens et al. 2004), with eight blooms being recorded since 1986. Detailed data on the physicochemical conditions preceding these blooms are lacking, but they tend to occur following conditions of

elevated winter and spring river flow that lead to surface salinities < 20 , concentrations of IN ($\text{NH}_4^+ + \text{NO}_3^-$) $< 0.4 \mu\text{mol L}^{-1}$, reactive P (RP) concentrations $> 0.1 \mu\text{mol L}^{-1}$, and elevated concentrations of Chl *a* in winter or spring. *Nodularia* blooms most commonly occur in Lakes King and Victoria, and this area is therefore the focus of this study.

Seven major rivers drain into the Gippsland Lakes, which has a total catchment size of 20,500 km². The Latrobe River (4900-km² catchment), which is joined near its downstream end by the Thomson and Macalister Rivers (3660-km²), and the Avon River (2000-km²) flow into Lake Wellington from the west, whereas the Mitchell (5500-km²), Nicholson (600-km²), and Tambo (3700-km²) Rivers flow into the north of Lake King (Fig. 1). A number of smaller creeks, rivers, and drains also flow into the lakes, but those mentioned above provide the majority of water and nutrient inputs into the lakes (Grayson et al. 2001). The lakes drain into Bass Strait via the artificial opening at Lakes Entrance. The average flushing time of the lakes (defined as the volume of the lakes divided by the net freshwater input) was estimated to be an average of 206 d between 1975 and 1999 (Webster et al. 2001). Tidal flushing is minimal owing to the relatively low tidal amplitude of the region and a single narrow entrance. The dominant mechanism of seawater exchange with Lakes King and Victoria is seasonal changes in the sea level on the order of 30 cm.

The climate of this region is temperate, and there is large year-to-year variation in rainfall; long periods of drought and high-intensity rainfall events are both common (flow coefficient of variation = 0.55). High-flow events tend to occur in winter or spring, whereas baseline flows are typical in summer. On average, 75% of the total annual flow occurs between the start of June and the end of November (austral winter and spring).

Sampling and analysis—We conducted frequent (1–2 weekly) water quality sampling between September 1998 and August 1999. Data from outside of this period come from the Victorian Environmental Protection Authority's long-term monitoring program, and were obtained from the Victorian Water Resources Data Warehouse (www.vicwaterdata.net). Although there is sporadic monitoring data (4–10 field trips per year) spanning the period 1986 to the present, we consider only this short sequence of high-frequency water column data that captured a drought and subsequent flood event.

Salinity and dissolved O₂ were measured in situ using calibrated water quality probes. Samples for total N (TN) and total P (TP) were stored on ice until return to the laboratory or frozen in the field. Samples for $\text{NO}_3^- + \text{NO}_2^-$, NH_4^+ , molybdenum-reactive silica (Si), and RP were frozen in the field, unfiltered. Nutrient samples were analyzed using standard colorimetric methods (Grasshoff 1983). Samples for Chl *a* were filtered onto glass-fiber filters (Whatman GF/C), frozen in the field, and analyzed spectrophotometrically according to Strickland and Parsons (1972), using the equations of Jeffrey and Humphrey (1975). The dominant phytoplankton taxa during blooms

were identified by microscopic examination of water samples by the Victorian Environment Protection Authority or the Regional Water Quality Officer from the Victorian Department of Natural Resources and Environment. River flows for the major rivers previously mentioned were obtained from the Victorian Water Data Warehouse (www.vicwaterdata.net). Wind speed was recorded at Bairnsdale Airport by the Australian Bureau of Meteorology.

Benthic fluxes were measured between September 1997 and July 1999 and between May 2002 and March 2003, using benthic chambers deployed in situ (Fig. 1). The chamber design has been previously described in detail (Nicholson et al. 1999). Briefly, each chamber enclosed 7–10 liters of water over an area of 0.09 m². The chambers were stirred with a paddle stirrer at a rate sufficient to create a diffusive boundary layer thickness of 0.3–0.4 mm. The volume of the chamber was calculated from the dilution of cesium injected into the chamber at the start of deployment. Between two and four benthic chambers were deployed at each site, and benthic fluxes were estimated by the change in concentration of metabolites within the chambers over time. Replicate transparent and opaque chambers were used to account for the effect of benthic primary production on metabolite fluxes. Chambers were deployed for 6–24 h. All nutrient samples ($\text{NO}_2^- + \text{NO}_3^-$, NH_4^+ , RP, and Si) were filtered through 0.45- μm filters, frozen in the field, and analyzed as previously described. Samples for pH were analyzed in the field using a high-precision electrode and meter. Alkalinity was measured by Gran titration of samples with dilute standardized HCl. Alkalinity and pH were then used to calculate total carbon dioxide (TCO₂). Cesium concentrations were measured using flame atomic absorption analysis. Benthic fluxes were calculated by linear least-squares regression of metabolite concentration over time; only linear portions of the concentration vs. time plots were used to estimate fluxes. A positive sign indicates flux out of the sediment.

Results

A detailed time series of water quality parameters and benthic fluxes was taken at three sites: Lake King North, Lake King South, and Lake Victoria Central (Fig. 1). For brevity and clarity, we have chosen to present the data collected from site Lake King South, which is the most central site sampled and most clearly illustrates the interplay between phytoplankton dynamics and nutrient biogeochemistry that is the focus of this work. The year 1997 was a drought year, with low flows into the lakes. In June 1998, a small flow event occurred, followed by a large flood event, peaking at $\sim 200 \text{ GL d}^{-1}$. These were then followed by a number of smaller flow events throughout the rest of the year (Fig. 2a). Water temperature varied between $\sim 10^\circ\text{C}$ during the austral winter and $\sim 20^\circ\text{C}$ during the summer. Wind speed generally varied between 10 and 20 km h⁻¹, with periodic storm events gusting $> 30 \text{ km h}^{-1}$ (Fig. 2b). Bottom-water salinities remained relatively stable at ~ 30 throughout the study period. Surface-water salinities dropped markedly after the flood

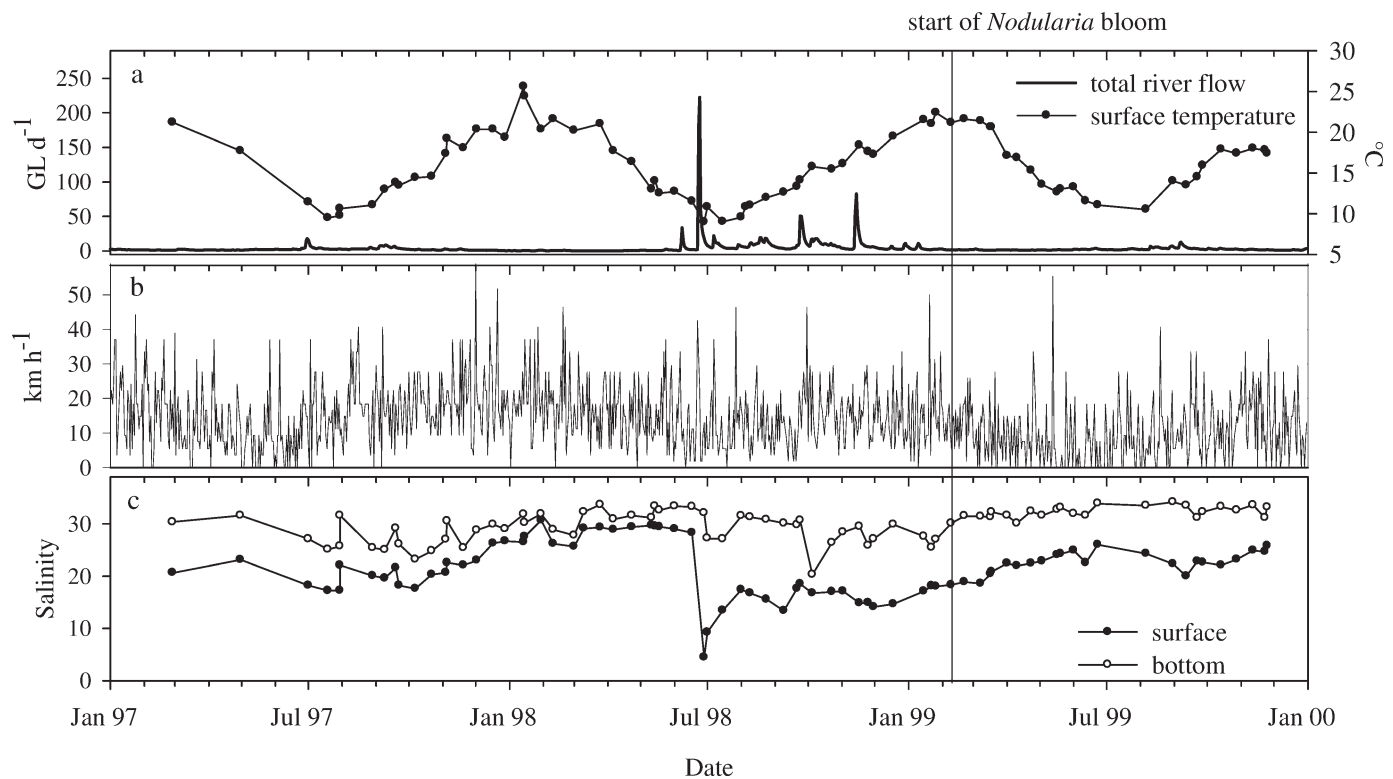


Fig. 2. A time series of physical water quality parameters including (a) total river flow and surface-water temperature; (b) wind speed; and (c) salinity in the surface and bottom waters from 1997 to 2000 at site Lake King South (LKS) in the Gippsland Lakes.

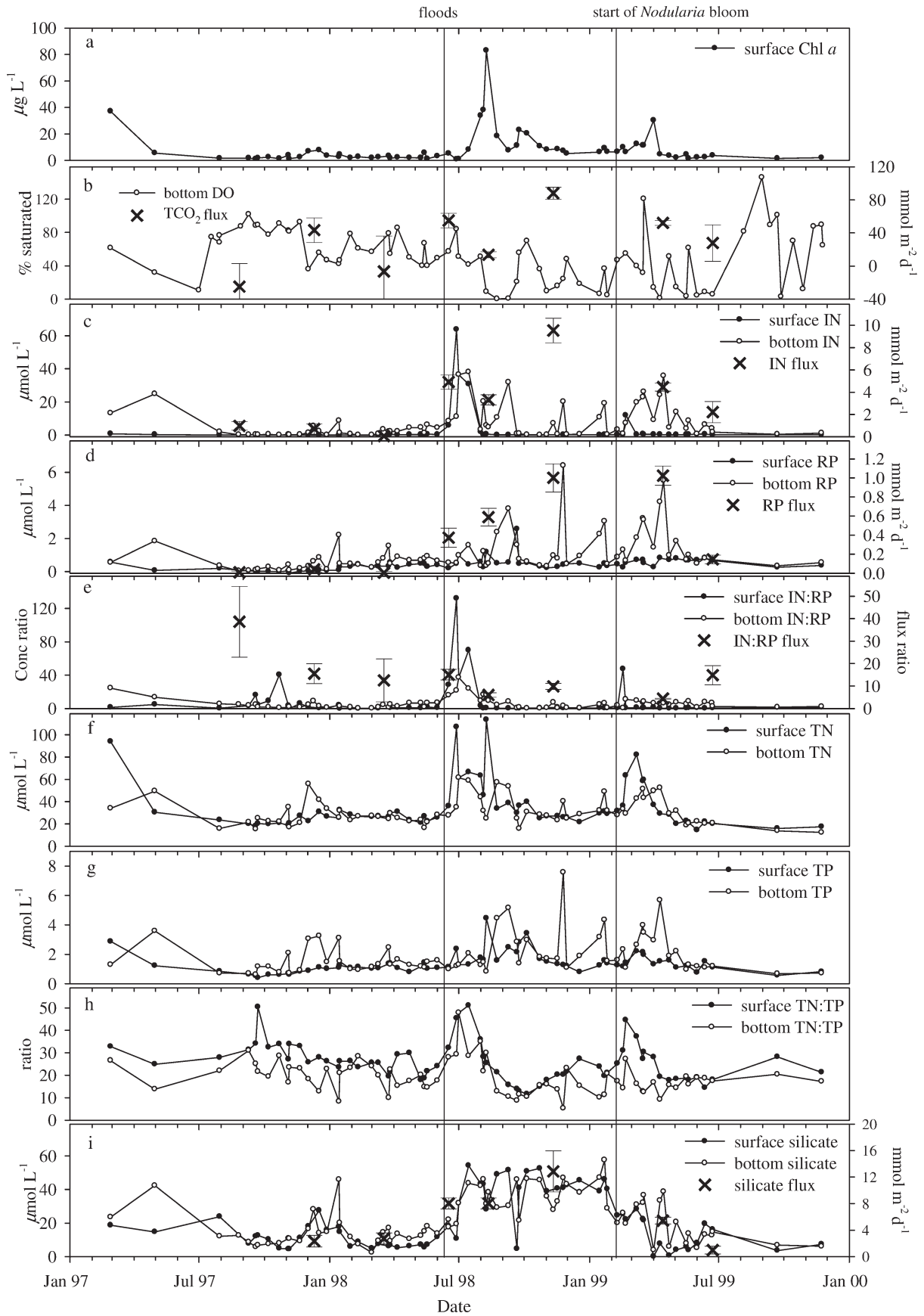
event (to ~ 3), then slowly rose to ~ 25 over the subsequent 6–8 months (Fig. 2c).

Phytoplankton biomass (specifically Chl *a* concentration) was high in the summer of 1997 because of a *Nodularia* bloom, but then remained low throughout 1997 and early 1998. It then increased markedly, up to $80 \mu\text{g L}^{-1}$, following the flood event (Fig. 3a). These high Chl *a* concentrations were associated with a dinoflagellate (*Heterocapsa triquetra*) and to a lesser extent *Gymnodinium cf. aureolum* and diatom (*Skeletonema costatum*) bloom initially (05 August), which then transitioned to dinoflagellate (*H. triquetra*) dominance by 20 August (Stephens et al. 2004). This bloom was observed throughout Lake Victoria and Lake King, but was most intense in Lake Victoria and Southern Lake King (Stephens et al. 2004). Chl *a* concentrations then dropped to $\sim 10 \mu\text{g L}^{-1}$ before increasing again in February 1999 because of a *N. spumigena* bloom, which was first recorded in Lake King on 06 February 1999 (Fig. 3a). This bloom was present throughout most of Lake Victoria and Lake King, but was patchy in distribution, and mainly concentrated in the east

of Lake King, where the Victorian Environmental Protection Authority recorded Chl *a* as high as $400 \mu\text{g L}^{-1}$. Bottom-water dissolved oxygen (DO) generally remained in excess of 40% saturation prior to the flood event, but frequently dropped below 20% thereafter (Fig. 3b), a trend that was observed at all study sites. Average daily TCO₂ fluxes varied from $-25 \text{ mmol m}^{-2} \text{ d}^{-1}$ during August 1997 up to $88 \text{ mmol m}^{-2} \text{ d}^{-1}$ in November 1998 (Fig. 3b). Concentrations of dissolved IN ($\text{NO}_2^- + \text{NO}_3^- + \text{NH}_4^+$) generally remained low ($< 5 \mu\text{mol L}^{-1}$) prior to the June 1998 flow event, but increased rapidly thereafter to $\sim 60 \mu\text{mol L}^{-1}$ in the surface water before decreasing rapidly (Fig. 3c). Bottom-water IN concentrations showed sporadic spikes of up to $\sim 40 \mu\text{mol L}^{-1}$ following the June 1998 flow event. Benthic IN fluxes were low ($1 \text{ mmol m}^{-2} \text{ d}^{-1}$) prior to the June 1998 flow event, and increased immediately thereafter to $4\text{--}8 \text{ mmol m}^{-2} \text{ d}^{-1}$ (Fig. 3c). RP concentrations and benthic fluxes showed a very similar pattern to IN, with low fluxes ($< 0.2 \text{ mmol m}^{-2} \text{ d}^{-1}$) and concentrations (generally $< 1 \mu\text{mol L}^{-1}$) before the June 1998 flood event, followed by a rapid increase in benthic

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Fig. 3. A time series of water quality parameters and sediment biogeochemistry including (a) Chl *a* in the surface waters; (b) bottom-water dissolved oxygen (DO) and sediment TCO₂ fluxes; (c) benthic fluxes and water column concentrations of inorganic nitrogen (IN = $\text{NO}_2^- + \text{NO}_3^- + \text{NH}_4^+$); (d) benthic fluxes and water column concentrations of reactive phosphorus (RP); (e) the ratios of IN:RP of the benthic fluxes and in the water column; water column concentrations of (f) TN and (g) TP; (h) the ratios of total nitrogen (TN) to total phosphorus (TP) in the water column; and (i) the benthic fluxes and water column concentrations of silicate from 1997 to 2000 at site Lake King South (LKS) in the Gippsland Lakes. Error bars show the standard error of benthic flux measurements.



fluxes ($0.6\text{--}1\text{ mmol m}^{-2}\text{ d}^{-1}$) and concentrations ($1\text{--}6\text{ }\mu\text{mol L}^{-1}$) in the bottom waters thereafter (Fig. 3d). In contrast to IN, RP in the surface waters did not show any marked increase in concentration during the flood event, with concentrations generally being elevated in the bottom waters compared to the surface waters (Fig. 3d). In general, the ratio of IN:RP dissolved in the water column was very low (< 5), except during the June 1998 flow event, when the IN:RP ratio increased dramatically in the surface water to > 50 , and, briefly, following the onset of the *N. spumigena* bloom (Fig. 3e). Concentrations of TN in the surface waters were generally in the range of $20\text{--}30\text{ }\mu\text{mol L}^{-1}$, but increased markedly following the June 1998 flood event ($\sim 100\text{ }\mu\text{mol L}^{-1}$) and the *N. spumigena* bloom ($80\text{ }\mu\text{mol L}^{-1}$; Fig. 3f). Concentrations of TP generally closely mirrored RP in both concentrations and variability, indicating that RP constituted the majority of TP (Fig. 3g). TN:TP ratios were generally in the range of $20\text{--}40$ in the surface waters, increasing during the June 1998 flow event (~ 50) and the *Nodularia* bloom (~ 40); this increase has also been observed in other systems during *Nodularia* blooms, most likely reflecting N_2 fixation (Moisander et al. 2003; Cook et al. in press). TN:TP ratios were consistently lower in the bottom waters (Fig. 3h). Concentrations of Si were relatively low ($5\text{--}20\text{ }\mu\text{mol L}^{-1}$) prior to the 1998 flow event, and increased markedly thereafter ($\sim 20\text{--}40\text{ }\mu\text{mol L}^{-1}$) before dropping to background levels between January and March 1999. Sediment fluxes of Si were lowest prior to the 1998 flow event ($< 2\text{ mmol m}^{-2}\text{ d}^{-1}$), increasing to $> 8\text{ mmol m}^{-2}\text{ d}^{-1}$ thereafter, before dropping again in early 1999 (Fig. 3i).

Benthic fluxes showed the same general increase at Central Lake Victoria following the flood and winter bloom (data not shown). No increase in benthic TCO_2 and nutrient fluxes was evident at Lake King North (data not shown), which we ascribe to the fact that the dinoflagellate and diatom bloom had a lower biomass ($< 50\%$) than Lake King South and Lake Victoria had. Water column nutrient concentrations also followed the same general trends at sites Lake Victoria Central and Lake King North (data not shown). High IN concentrations were observed immediately following the flood, which then rapidly decreased during the winter diatom and dinoflagellate bloom. Sporadically elevated concentrations of IN and RP were observed in the bottom water throughout spring and into summer, with an IN:RP ratio < 10 .

Discussion

The role of catchment inputs in driving algal blooms in coastal lagoons is now well established. Few studies have, however, documented the role of internal nutrient cycling in triggering subsequent blooms as well as influencing their taxonomic composition. This study clearly documents an initial dinoflagellate and diatom bloom triggered by catchment inputs followed by a summer *N. spumigena* bloom driven by benthic P release. We now discuss in detail the critical factors controlling this sequence of events.

Phytoplankton bloom dynamics—The initial June flow event was rapidly followed by a dinoflagellate and diatom

bloom, which then transitioned to dinoflagellate dominance. A detailed study of a phytoplankton bloom in the Gippsland Lakes in December 1988 showed a transition from a mixed diatom and dinoflagellate population at the start of the bloom to a population dominated by dinoflagellates as the bloom progressed (Longmore 1994), and this is likely to be a typical sequence. The most likely explanation for the rapid transition to dinoflagellate dominance is strong stratification of the water column (Fig. 2c). Dinoflagellates are known to dominate algal blooms under stable stratified conditions such as those observed here (Smayda 1997). One of the critical reasons for this is their motility, which allows them to migrate between light-rich surface and nutrient-rich subsurface waters, giving them a distinct advantage over other algal taxa, such as diatoms, which require regular mixing of the water column to keep them supplied with nutrients and prevent them from permanently sinking out of the euphotic zone (Smayda 1997). This hypothesis is supported by the time-series observations from Lake King that show that N and P are rapidly depleted in the surface waters, but remain high in the bottom waters owing to benthic recycling (Fig. 3c).

Si limitation can also be a factor controlling the succession of diatoms to dinoflagellates (Turner 2002). This is unlikely to be the case in this system because the IN:Si ratio was nearly always in excess of the 1:1 ratio requirement of diatoms and in the two instances that it was not, the Si concentration remained above $20\text{ }\mu\text{mol L}^{-1}$ (Fig. 3i), which is well above the limiting concentration of $2\text{ }\mu\text{mol L}^{-1}$ identified by Egge and Aksnes (1992). The dinoflagellate bloom declined during September when IN concentrations in the surface and subsurface waters dropped below $3\text{ }\mu\text{mol L}^{-1}$ (Fig. 3c), which is below or close to the half saturation constants for IN that have been reported for dinoflagellates (Smayda 1997).

Phytoplankton biomass then remained low until the following February, when the *N. spumigena* bloom occurred (Fig. 3a), although high Chl *a* concentrations were not immediately apparent. Two factors could explain why the bloom was not immediately apparent in the Chl *a* readings: surface samples were typically collected from 0.5 m into the water column, while *Nodularia* filaments are buoyant and on a calm day will accumulate in the top few centimeters; and the bloom was patchy in distribution and likely aggregated in nearshore areas through wind and wave action. *Nodularia* blooms typically occur under calm, stratified conditions, high irradiance, warm temperatures, and low N:P (Sellner 1997; Marino et al. 2006). Temperature, irradiance, and stratification were all high over the summer period, and, as discussed below, recycling processes within the Gippsland Lakes sediments led to a high accumulation of RP relative to IN in the bottom waters (IN:RP ~ 6). The ultimate trigger for the *Nodularia* bloom is unclear; we speculate, however, that a short period of strong easterly winds of up to 50 km h^{-1} , blowing along the axis of the Gippsland Lakes in late January (Fig. 2b), led to a slight mixing of P-rich bottom water with surface water. Other observations to support the mixing hypothesis include a slight increase in surface-water TP, a

big decrease in bottom-water TP (Fig. 3g), and a slight decrease in bottom-water salinity (Fig. 2c). We did not observe an increase in surface-water RP and we suggest this was because it was rapidly assimilated by the developing bloom. The following period of relative calm (Fig. 2b) then provided ideal growing conditions for *Nodularia*. This scenario bears a close resemblance to outbreaks of *Nodularia* blooms in the Baltic Sea, which occur when low N:P bottom water mixes with surface water during warm, calm periods (Stipa 2002; Kanoshina et al. 2003).

Salinity has also been identified as an important factor influencing the development of N-fixing cyanobacterial blooms, with blooms generally commencing at salinities of < 12 (Lukatelich and McComb 1986; Kanoshina et al. 2003), although culture studies have shown growth rates to be unaffected up to salinities of ~ 20, including strains from the Gippsland Lakes (Moisander et al. 2002; Myers 2008). In this instance, the *Nodularia* bloom commenced at a salinity of 18 (Fig. 2c), which is significantly above the threshold of 12 generally considered conducive to such blooms in estuaries (Howarth and Marino 2006). The exact mechanism of salinity control over *Nodularia* blooms (as well as heterocystous cyanobacterial blooms in general) remains to be fully elucidated; however, recent work has shown that *Nodularia* are capable of growing, albeit slowly, at salinities of ~ 30, at reduced grazing pressures (Marino et al. 2006). Reduced growth rates render the cyanobacteria more susceptible to grazing pressure, which severely curtails the growth of large filaments, thus preventing bloom formation (Chan et al. 2006). We have no data on the abundance of grazers or grazing rates in the Gippsland Lakes over the study period, but the unusually high salinity at which the bloom developed and persisted suggests that unusually low grazing rates may have been a factor in the development of this *Nodularia* bloom.

The role of sediment biogeochemistry in the transition from P to N limitation—A high availability of RP relative to IN in the water column during the summer was a critical factor in the development of the *Nodularia* bloom observed here, yet the flood preceding this bloom introduced virtually no P into the lakes (Fig. 3g). This resulted in extremely high IN:RP and TN:TP ratios (> 100 and 50, respectively) immediately following the flood, and as a consequence, the initial bloom was most likely to have been P limited (Guildford and Hecky 2000). Following the flood there was a pronounced increase in the benthic flux of RP, and a reduction in the IN:RP sediment flux ratio to < 10 (Fig. 3d). This led to a reduction in the TN:TP ratio in the surface and subsurface waters to < 20 (Fig. 3h), resulting in N being the most likely limiting nutrient (Guildford and Hecky 2000). This shift from P to N limitation has significant management and ecological implications, and the biogeochemical mechanism driving this shift requires careful examination.

Stoichiometric approaches are commonly used to constrain nutrient fluxes relative to the mineralization of organic matter (Dollar et al. 1991). Here we have used plots of the benthic fluxes of IN and RP vs. benthic TCO₂ fluxes to gain insight into the sediment biogeochemical processes

taking place (Fig. 4). If we assume that the organic matter undergoing mineralization is derived predominantly from phytoplankton of Redfield stoichiometry, then one would expect the TCO₂:IN and TCO₂:RP flux ratios to be 106:16 and 106:1, respectively. In general, there was a deficit in the IN flux compared to that expected from stoichiometry (Fig. 4a) and this is, most likely, a consequence of coupled nitrification–denitrification, leading to the permanent loss of N from the sediment. Direct measurements of N₂ fluxes confirm that denitrification accounts for this observed stoichiometric discrepancy in measured IN fluxes and those expected from the mineralization of Redfield material (Roberts et al. 2003). The assumption that phytoplankton is the dominant source of carbon to the sediments is further justified on the basis of carbon stable-isotope measurements, lipid biomarkers, and sediment C:N ratios in Lakes Victoria and King (McGhie et al. 1998).

In contrast to IN, there was considerable scatter in the ratio of TCO₂:RP released from within the sediment (Fig. 4b). Four data points (indicated in Fig. 4a,b) are excluded from subsequent analysis and discussion on the basis that they had high IN and RP fluxes relative to carbon mineralization and were all measured at the same site, during August 1998. The extreme anomalous behavior suggests that these nutrient fluxes may have originated from a source other than phytoplankton mineralization, and we justify excluding them on this basis. At TCO₂ fluxes < 80 mmol m⁻² d⁻¹, there was generally a slight deficit in the RP flux compared to that expected from the mineralization of Redfield material (as indicated by a moving average < the Redfield ratio in Fig. 4b), suggesting that there was a net storage of P within the sediment. At TCO₂ fluxes > 80 mmol m⁻² d⁻¹, there was generally an excess of RP released from the sediment compared to that expected from the mineralization of “Redfield material” (as indicated by a moving average > the Redfield ratio), suggesting that there was a remobilization of P stored within the sediment. Overall, these differences in IN and RP recycling led to fluxes with IN:RP ratios slightly above the N:P Redfield ratio of 16:1 at low mineralization rates, but dropping below this ratio at mineralization rates > 80 mmol m⁻² d⁻¹ (Fig. 4c). The rate of carbon mineralization within the sediment, therefore, played a critical role in controlling both the amount of RP as well as the ratio of IN:RP released from the sediments. A similar phenomenon has also been observed in Port Phillip Bay, Australia (Berelson et al. 1998), although this is not universal as no similar effect was observed in Tomales Bay, California (Dollar et al. 1991). The mechanistic explanation for this observation arises from the well-known fact that RP is strongly bound to Fe(III) oxyhydroxides at the sediment surface. In coastal sediments, the majority of carbon mineralization takes place through sulfate reduction (Canfield et al. 2005) leading to the production of sulfide. At elevated benthic mineralization (and hence sulfate reduction) rates, high rates of sulfide production will lead to the chemical reduction of Fe(III) to soluble Fe(II), which is subsequently trapped as FeS, leading to a release of stored P (Jensen et al. 1995). The

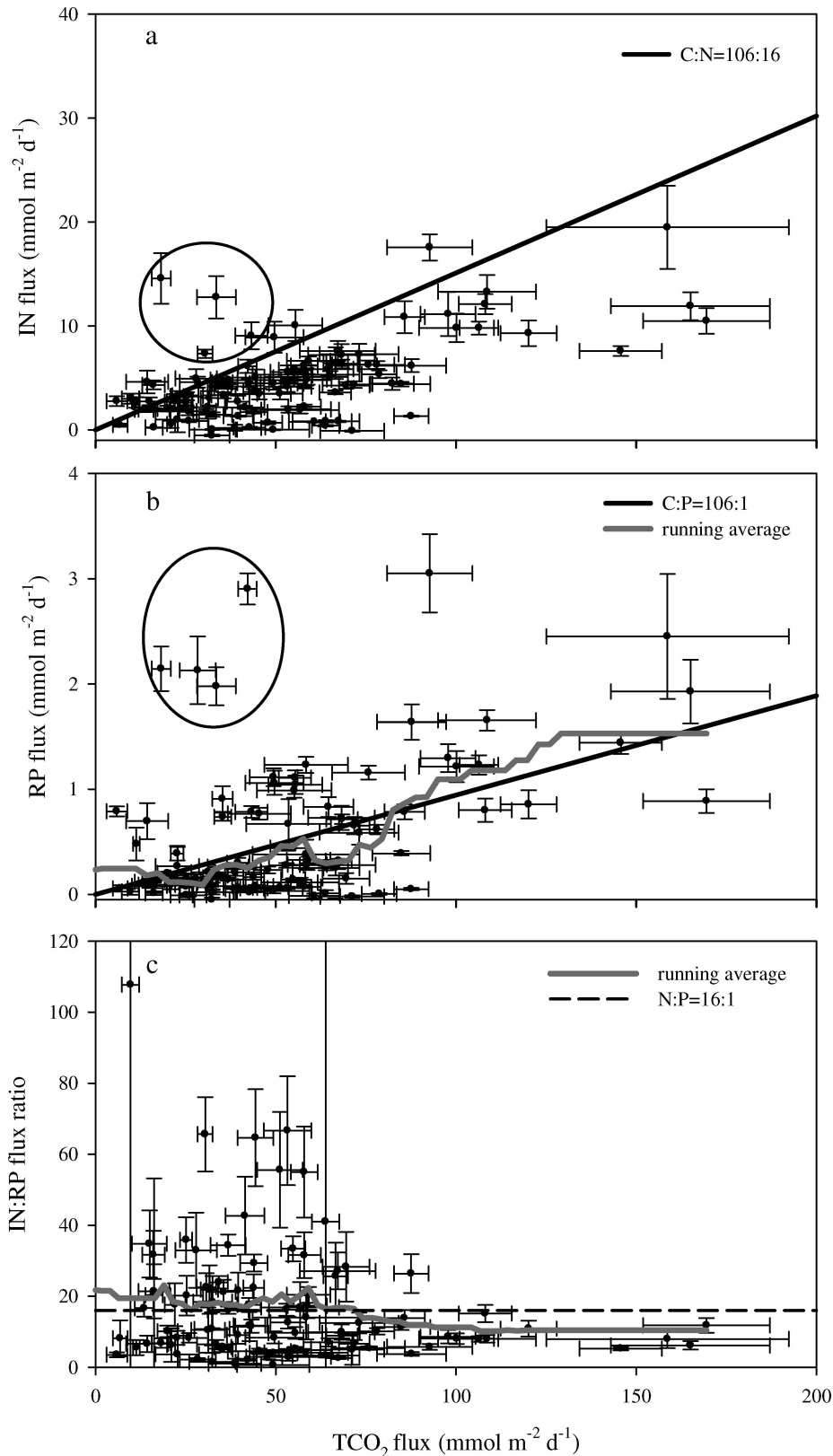


Fig. 4. (a) Dissolved inorganic nitrogen (IN) fluxes; (b) reactive phosphorus (RP) fluxes; and (c) the IN : RP flux ratio vs. TCO_2 observed in all chamber incubations undertaken within the Gippsland Lakes between 1997 and 2003. Error bars represent the standard error about the mean. The solid gray lines represent the running average, sampling 10% of the data. Marked outliers are omitted from the running average and are discussed in the text.

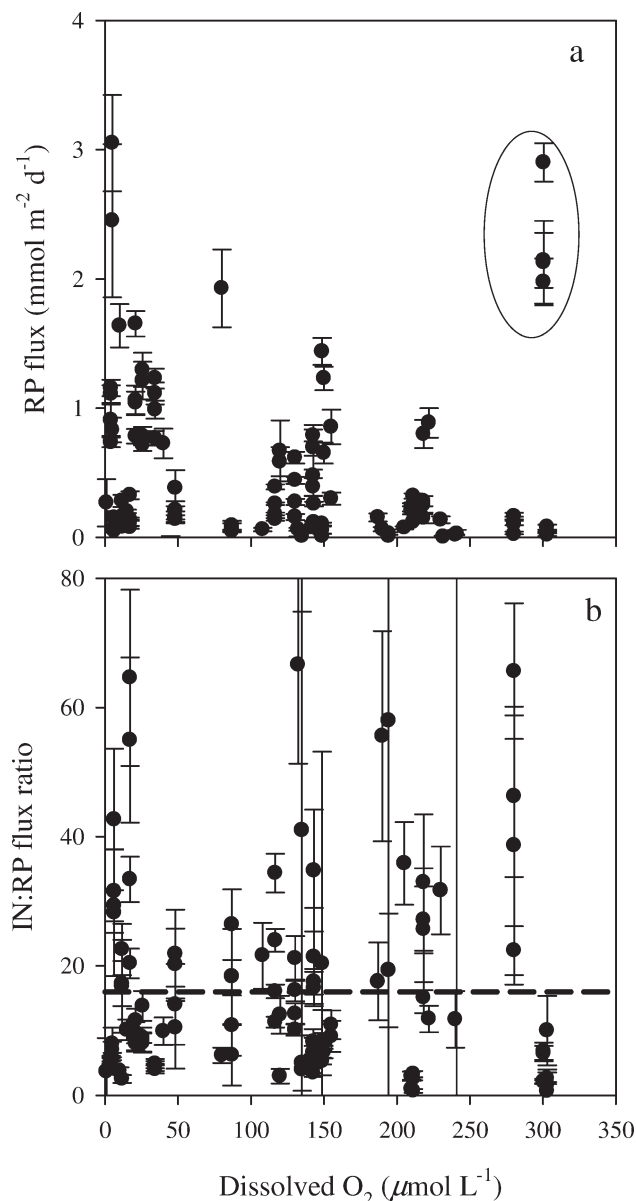


Fig. 5. (a) Reactive phosphorus (RP) fluxes and (b) the IN:RP flux ratio vs. the dissolved O₂ concentration in the bottom of the water column. Marked outliers are discussed in the text.

extent to which P is accumulated and released will, therefore, be highly dependent on the Fe content of the sediment.

DO concentrations are well known to exert a strong control over RP release from coastal sediments, with higher release being observed at low DO concentration (Ingall and Jahnke 1997; Kemp et al. 2005). In this study, DO also had an influence (albeit weaker than TCO₂ fluxes) on RP fluxes, if the outlying high RP fluxes (the same fluxes previously commented upon) at high DO are ignored (Fig. 5a). Surprisingly, though, DO concentration had no effect on the IN:RP flux ratio (Fig. 5b). Fundamentally, bottom-water DO will have a strong influence over RP release because it exerts a major control over the flux of O₂ into the sediment. In the absence of or at low DO, Fe(III)

oxyhydroxides will undergo reductive dissolution, releasing RP. The rate at which this occurs is strongly dependent on the carbon mineralization rate, so DO concentrations and mineralization rates will both exert a controlling influence over RP fluxes. We confirmed this by multiple regression analysis (MRA), which showed that DO concentrations and carbon mineralization rates could both significantly ($p < 0.001$) and independently contribute to a model (as indicated by good colinearity diagnostics, including a tolerance of 0.996 and a variance inflation factor of 1.004) that described 50% of the variance of the RP fluxes, when the aforementioned data points were excluded from the analysis. The following regression equation was obtained:

$$\text{RPflux} = 0.01\text{TCO}_2 - 0.002\text{DO} + 0.170$$

where RP flux is the flux in mmol m⁻² d⁻¹, TCO₂ is the TCO₂ flux in mmol m⁻² d⁻¹, and DO is the DO concentration in μmol L⁻¹. Similar attempts to describe the IN:RP flux ratios using MRA showed that only TCO₂ fluxes contributed significantly ($p < 0.05$) to the variance.

The finding that benthic mineralization plays a critical role in both the absolute amount of RP and its release relative to IN is significant because most studies on P release from coastal sediments to date have focused on either the role of bottom-water DO concentration (Ingall and Jahnke 1997; Kemp et al. 2005) or benthic mineralization rates (Dollar et al. 1991; Berelson et al. 1998) in isolation from each other. The results here clearly underscore the role of both low bottom-water DO and carbon delivery to the sediment in driving the release of RP from the sediments in the Gippsland Lakes.

This study comprehensively illustrates the importance of internal biogeochemical processes in shifting the Gippsland Lakes from P limitation following a flood to severe N limitation over several months. The underlying mechanism for this was the release of P stored within the sediment, induced by increased rates of organic matter mineralization within the sediment, along with bottom-water hypoxia, following a winter algal bloom. Severe N limitation combined with favorable physicochemical conditions resulted in an N₂-fixing bloom of *N. spumigena*. This leads to the paradoxical conclusion that large N inputs from the catchment during winter ultimately played a critical role in driving the Gippsland Lakes to severe N limitation the following summer. This study further underscores the need to control both N and P loading rates to estuaries (Conley et al. 2009) even when N₂-fixing cyanobacteria are present.

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