

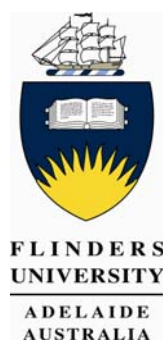


Water for a Healthy Country

Element and nutrient mass-balances in a large semi-arid riverine lake system (the Lower Lakes, South Australia)

Perran L.M. Cook, Kane T. Aldridge, Sébastien Lamontagne, Justin D. Brookes

June 2008



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Perran Cook^{1,*}, Kane T. Aldridge², Sébastien
Lamontagne³, Justin D. Brookes²

¹CSIRO Land and Water, 120 Meiers Road, Indooroopilly QLD 4068, Australia

²School of Earth and Environmental Sciences, The University of Adelaide, Adelaide SA 5005, Australia

³CSIRO Land and Water, PMB 2, Glen Osmond SA 5064, Australia

**Current address:* Water Studies Centre, Monash University, Clayton Vic 3800, Australia

June 2008

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Foreword

The environmental assets of the Coorong, Lower Lakes and Murray Mouth (CLLAMM) region are currently under threat as a result of ongoing changes in the hydrological regime of the River Murray. While a number of initiatives are underway to halt or reverse this environmental decline, such as the Murray-Darling Basin Commission's "Living Murray", rehabilitation efforts are hampered by the lack of knowledge about the links between flows and ecological responses in the system.

The CLLAMM program is a collaborative research effort which aims to produce a decision-support framework for environmental flow management for the CLLAMM region. The framework will attempt to evaluate the social, economic and environmental trade-offs for different scenarios of manipulation of management levers, as well as different future climate scenarios for the Murray-Darling Basin.

The ecology of the Lower Lakes (Lake Albert and Lake Alexandrina) and their role in controlling nutrient and organic matter inputs to the Coorong and Murray Mouth region are not well understood. The future status of the Lower Lakes is also unclear due to ongoing low inflows from the Murray-Darling River.

Land & Water Australia is co-sponsoring a series of projects on the Lower Lakes in partnership with CSIRO's Coorong, Lower Lakes and Murray Mouth program and the CLLAMMecology Research Cluster.

CLLAMMecology is a partnership between the University of Adelaide, Flinders University and SARDI Aquatic Sciences to study ecological responses to environmental change in the CLLAMM region, supported by CSIRO's Flagship Collaboration Fund.

Other partner research and funding agencies involved in the Lower Lakes project include SA Water and the WA Centre for Water Research.

Additional reports relevant from the CLLAMM program and the CLLAMMecology Research Cluster can be found at

<http://www.csiro.au/partnerships/CLLAMMecologyCluster.html>

Executive Summary

We undertook an analysis of historical water quality data (including nutrients and major ions, pH and bicarbonate) for the River Murray, Australia, and its terminal lake system, Lake Albert and Lake Alexandrina (the Lower Lakes) spanning the period 1979 to 1997. This was undertaken in order to elucidate the role of the Lower Lakes in the retention, transformation, and delivery of salts and nutrients to the Coorong, and how this varies with flow regime. The partial pressure of CO₂ ($p\text{CO}_2$) was highest in the river and relatively low at a site in the Lower Lakes. Values of $p\text{CO}_2$ fluctuated above and below atmospheric values, indicating that the lakes alternated between periods of net autotrophy and heterotrophy, which was primarily determined by water column turbidity. The average $p\text{CO}_2$ in the Lower Lakes was 460 μatm , indicating that overall they were net heterotrophic, but to a lesser extent than other lakes with comparable Dissolved Organic Carbon (DOC) loading. We suggest the DOC entering the Lower Lakes is of a relatively refractory nature owing to long water residence times within the highly controlled river system.

The Lower Lakes were consistently a sink for Filterable Reactive P (FRP), Total P (TP), nitrate+nitrite (NO_x) and Si, and an overall source of Total Kjeldahl N (TKN). Measured rates of P retention agreed well with a mass balance derived from previous measurements of sedimentation rate and sediment P content for the lakes. Rates of P retention within the Lower Lakes could be described well by a model and parameters used for North American and European systems under flow conditions representing the upper 75% of river discharge. Under low flow conditions, the retention of P was variable and difficult to predict accurately. Input and output of total N were in close balance. However, there was a substantial loss of N to the sediments, suggesting that N₂ fixation by cyanobacteria within the lakes made up the deficit. The Lower Lakes serve as a significant modulator of material entering the Murray Estuary, converting inorganic nutrients into an organic form and substantially increasing the N:P ratio of material entering the lakes (from ~12 to ~30 on a molar basis).

Given that the material exported from the Lower Lakes was predominantly in an organic form, one would expect the initial metabolic response of the receiving coastal and estuarine waters to be heterotrophic. Thus, rather than a rapid algal bloom being associated with waters released from the Lower Lakes, one would expect an initial response in zooplankton and bacterial growth, followed by a reassimilation of the released nutrients into algal biomass. The relative enrichment in N over P that occurs in the Lower Lakes is also fortuitous because coastal waters are generally considered to be limited by N rather than P. In this context we note that the volume of water released from the Lower Lakes over the past decade has been very low owing to drought and high rates of water extraction from the river system. This has most likely resulted in substantially reduced loads of organic material entering the adjacent lagoonal system (the 'Coorong') and coastal waters. The impact of reduced loads on the local food-webs remains to be determined.

There was a considerable input of salts to the Lower Lakes from an unknown source, amounting to 42% of the total input from the Lower Murray for Na⁺. We suggest this salt either originates from saline groundwater, or possibly leakage from the ocean through the barrages. In general the ratio of the major ions to chloride in the Lower Murray is slightly more elevated than in seawater. This is also reflected in the Lower Lakes, possibly supporting the hypothesis that the dominant supply of salts to the Lower Lakes is from the Lower Murray and its associated groundwater, rather than from seawater leakage.

Further work is required to follow up the observations and hypotheses made here and we make the following suggestions for future research:

- To improve the hydrological flux estimates for the Lower Lakes, especially during low flow conditions;
- To measure the bioavailability and composition of dissolved organic carbon entering and leaving the Lower Lakes, and how this changes over flow regime and water source;

- To measure internal nutrient cycling processes such as nitrogen fixation and denitrification to help constrain the nitrogen budget for the Lower Lakes;
- To identify the sources of salt, and to understand salt cycling between the Lower Lakes and surrounding floodplain and lacustrine wetland systems.

Acknowledgements

We thank the support of Land & Water Australia, SA Water and the CSIRO Flagship Collaboration Fund.

We also acknowledge the contribution of several other funding agencies to other aspects of the CLLAMM program and the CLLAMMecology Research Cluster, including the Fisheries Research and Development Corporation, the Murray-Darling Basin Commission's Living Murray program and the SA Murray-Darling Basin NRM Board. Other research partners include Geoscience Australia and the Flinders Research Centre for Coastal and Catchment Environments. The objectives of this program have been endorsed by the SA Department of Environment and Heritage, SA Department of Water, Land and Biodiversity Conservation, SA Murray-Darling Basin NRM Board and Murray-Darling Basin Commission. We also thank Caroline Fazekas and Phil Thomas from the Australian Water Quality Centre for providing the water quality data and advice on them, as well as Joe Davis from the MDBC for supplying the flow data.

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1. Introduction

Rivers may transport large quantities of nutrients, salts and organic matter through the landscape and ultimately into the coastal zone. Where rivers encounter large open water bodies such as lakes (including artificial impoundments) and estuaries, substantial material transformation and retention may occur (Dillon 1975, Straskraba et al. 1995, Eyre 1998). Nutrient retention within lakes and estuaries may help prevent coastal eutrophication when there is an oversupply of nutrients from the catchment (Straskraba et al. 1995, Nixon et al. 1996). On the other hand, in many semi-arid and subtropical estuaries, extensive diversions of freshwater flows and associated nutrients within catchments threaten long-term estuarine and coastal productivity (Gillanders & Kingsford 2002). In addition to nutrient transformations, terminal lakes and estuaries actively process organic matter inputs from the catchment and are generally considered to be net heterotrophic and therefore a source of CO₂ to the atmosphere (Heip et al. 1995, Sobek et al. 2005). An understanding of the balance between net organic carbon production and consumption is critical because it determines whether a system is likely to be a net source or sink of inorganic nutrients (Smith et al. 1989, Smith et al. 1991).

The bulk of studies of river systems and the transport of material into the coastal zone have focused on temperate river systems with relatively high, continuous discharges. While there have been a number of studies on nutrient budgets of Australian lakes (Walker & Hillman 1982, Royle & King 1992, Lamontagne 2002, Linden et al. 2004) and estuaries (Eyre & Mc Kee 2002), it is somewhat surprising that only two studies (Walker & Hillman 1982, Geddes 1988) have undertaken a nutrient budget within Australia's largest river system, the semi-arid River Murray. Only one study (Geddes 1988) has attempted to quantify retention of nutrients at the land-sea interface of the River Murray. This study was, however, limited to a period of three years and did not look at nutrient speciation in detail.

Here we present a long term record of nutrients, major ions, pH, and bicarbonate for Lake Albert and Lake Alexandrina (hereafter referred to as the Lower Lakes). We also used this record to calculate nutrient and major ion budgets and to estimate the CO₂ balance for the River Murray and a site in the Lower Lakes. This work builds on previous conceptual understanding (Geddes 1984, 1988) and elucidates how the Lower Lakes modify material fluxes from the Murray-Darling Basin into the Murray Estuary and coastal zone.

2. Methods

2.1. Study site

The Murray-Darling Basin is Australia's largest drainage basin (1,063,000 km²) and one of the world's longest rivers. As for many rivers in semi-arid regions, most of the runoff originates well upstream from a small proportion of the catchment with a more humid climate. The basin can be subdivided into three broad regions: the Upper Murray, the Darling, and the Lower Murray (that is, the section of the river basin below the junction with the Darling). The original flow regime of the River Murray at the Lower Lakes was characterized by spring floods and summer low flows, but the magnitude of both was variable from year-to-year (Jolly 1996). The flow regime of the River Murray was gradually modified following European settlement by a complex system of reservoirs, weirs and a set of barrages separating Lake Alexandrina from the Coorong (a coastal lagoon) and the Murray Mouth. Due to diversions for irrigation, annual runoff from the river is now <27% of that pre-European settlement, peak runoff is in early summer (when peak demands for irrigation occur) and the frequency and duration of small and medium floods has decreased significantly (Jolly 1996). The Upper Murray carries the largest and most constant flow of water, sourced from the western side of the southern Great Dividing Range in southern New South Wales and Victoria. The Darling River tributary has a lower and more variable flow, with its waters originating from the western side of the central Great Dividing

Range in northern New South Wales and southern Queensland. The waters of the Darling River carry high loads of fine particles, resulting in extremely high turbidity (often >400 NTU) in the Darling and the Lower Murray.

The Lower Lakes are large (over 75 000 ha; Sims & Muller 2004), shallow lakes (maximum depth of 4.1 m; Geddes 1984) at the end of the Murray-Darling Basin (Fig. 1). Although several local streams discharge into Lake Alexandrina, their overall contribution to total annual flow are only considered to be significant during periods of low River Murray inputs (Anon 2007). While many have considered the lakes to have been estuarine prior to European settlement (Von Der Borch & Altman 1979, Geddes 1984), more recently it has been suggested that the lakes were fresh more than 95% of the time (Sims & Muller 2004). Nevertheless, following European settlement and the development of the irrigation industry upstream, more frequent intrusions of salt water occurred into the Lower Lakes (Sims & Muller 2004). To prevent these intrusions, the Lower Lakes barrages were constructed between 1935 and 1940 to maintain the lakes as a permanent freshwater supply for irrigation and human use (Fig. 1).

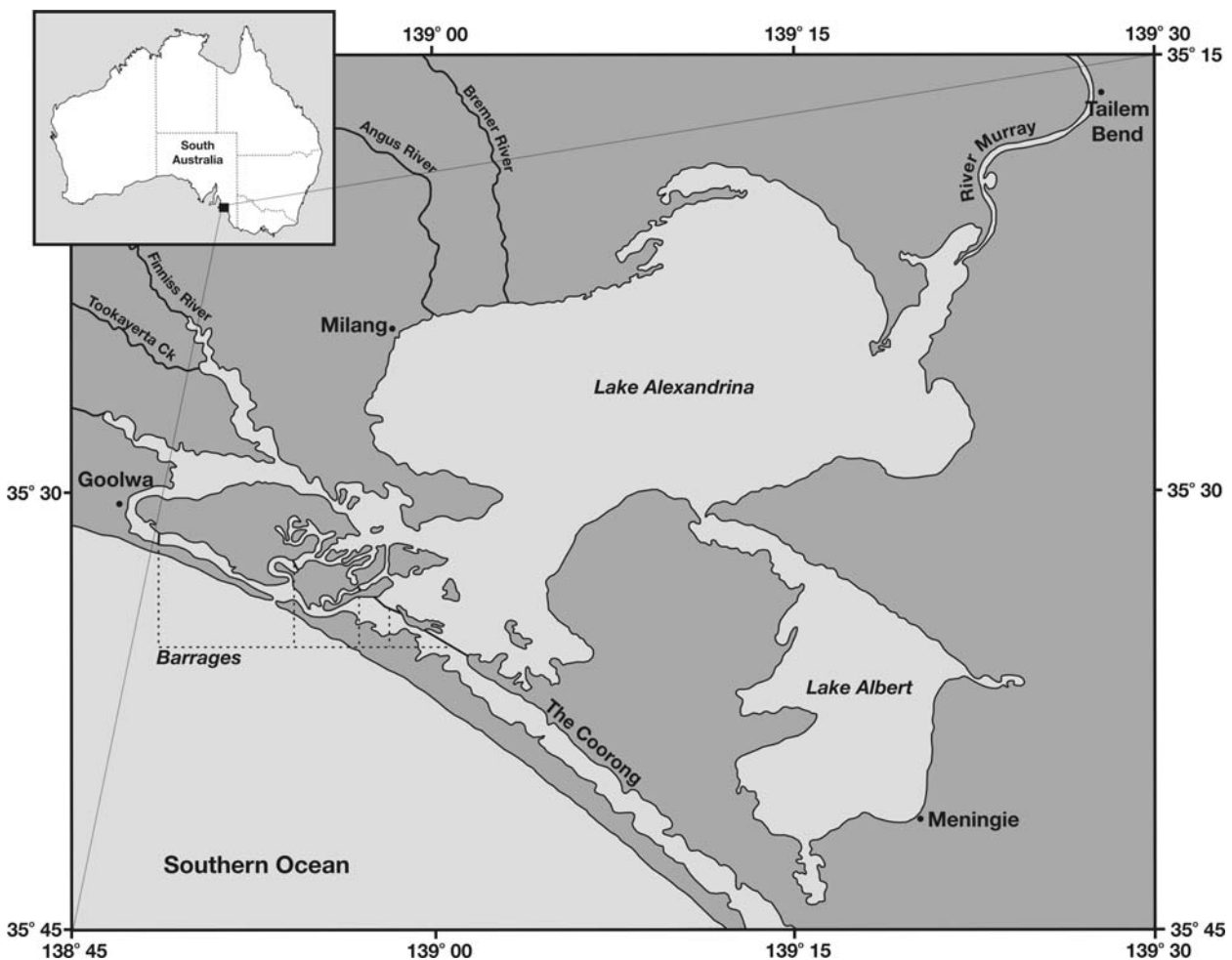


Figure 1. Location on the Lower Lakes and associated localities where samples were collected.

Current management of the barrages maintains an average water level of 0.75 m Australian Height Datum (AHD, approximately mean sea level; Anon 2007). As river flow increases, barrage gates are opened to maintain this level. The lakes are surcharged to 0.85 m AHD at the beginning of summer to insure that evaporation and irrigation demand during summer does not lower the water level below 0.6 m AHD by autumn. Overall, the net effect of flow regulation on the Lower Lakes is to have reduced the size (magnitude and duration) of peak flow, to have extended the frequency and duration of no outflow events, to have brought forward the timing of

peak flow, and to have increased the average lake water residence time. In addition, the lake level has been permanently raised and has a lower range in annual fluctuations. While the lakes are a discharge zone for local and regional aquifers, the groundwater flux is not known (Lamontagne et al. 2005a). Groundwater discharge could be a significant source of salt to the lakes even if a small flux of water, as is the case for much of the Lower Murray (Allison et al. 1990, Jolly 1996),. Some seawater leakage above or through the barrages occasionally occurs when high tides and onshore winds result in water levels on the downstream side of the barrages to be higher than in the Lower Lakes. Some seawater leakage also occurs when small boats pass through locks at the barrages.

Although there have been investigations of nutrient dynamics and primary production in Lake Alexandrina (Geddes 1984, 1988), there have been no detailed reports on the interannual delivery to and retention and transformation of nutrients within the lakes. A previous study (Geddes 1984) concluded that Total P (TP) and Total Kjeldahl N (TKN) levels placed Lake Alexandrina in the eutrophic-hypereutrophic category (Vollenweider 1968). In addition, it places Lake Alexandrina in the eutrophic category for Australian waters (Walker & Hillman 1977), but the shallow water depth and moderate water renewal rate enhances its trophic status with surface loadings 10-40 times the 'dangerous' phosphorus loading limits of eutrophy (Geddes 1984).

Despite the eutrophic status, it has previously been concluded that Lake Alexandrina was a marginal environment for phytoplankton growth (Geddes 1984) primarily because of its highly turbid environment (mean value of 93 NTU in 1963-1978, owing to high levels of sediment resuspension). Thus, it is likely that primary production is light-limited.

Lake Alexandrina and Lake Albert have suffered from the regular occurrence of algal blooms, particularly during periods of low flow and low turbidity (P. Baker, Australian Water Quality Centre, *personal communication*). In fact, it was the site of the first record of a toxic bloom of blue-green algae (*Nodularia spumigena*) in Australia (Francis 1878). Furthermore, picocyanobacterial (eg *Aphanocapsa*, *Planktolyngbya*) blooms now occur annually, blooms of *Nodularia spumigena*, *Anabaena circinalis* *Aphanizomenon*/*Anabaena* are common and the first recorded bloom of *Cylindrospermopsis raciborskii* occurred in the lakes in 2006 (P. Baker, *personal communication*).

2.2. Sample collection analysis and budgets

Water samples from the Lower Lakes and the Lower Murray were collected by the Australian Water Quality Centre (AWQC) and water samples from ephemeral tributaries to the Lower Lakes in the Eastern Mount Lofty Ranges were collected by the Environment Protection Authority (EPA, South Australia) and the South Australian Department of Water, Land and Biodiversity Conservation (DWLBC). All water samples were analysed by the AWQC, a NATA (National Association of Testing Authorities) accredited laboratory using standard methods. The parameters considered in this study were HCO_3^- , K^+ , Mg^{2+} , Na^+ , SO_4^{2-} , Ca^{2+} , Cl^- , NO_3^- , pH, Si (molybdenum reactive fraction), TKN, Total N (TN; defined as TKN + NO_3^-), Filterable Reactive P (FRP) and TP because they were the parameters consistently covered at all sites of interest over long periods of time. Only the years 1979–1996 were considered, as this was the most comprehensive period of water quality data collection. Where monthly data were missing (particularly at Milang in the years 1979–81 for the parameters HCO_3^- , K^+ , Mg^{2+} , Na^+ , SO_4^{2-} , Ca^{2+} , Cl^- , NO_3^-) the concentration for the missing months was taken as an average of the month preceding and subsequent to the missing months. This was justified on the basis that there was little variability in the analytes up to and subsequent to the missing data. Analytes below their detection limits (NO_x , FRP, and Si) were assumed to have half the concentration of the detection limit for budgeting purposes. Detection limits for nutrients were NO_x ($\text{NO}_3^- + \text{NO}_2^-$) $0.4\mu\text{M}$, FRP $0.1\mu\text{M}$, TP (total phosphorus), $0.1\mu\text{M}$, TKN $3.5\mu\text{M}$ and Si (silica) $35\mu\text{M}$. We note that samples for HCO_3^- were not filtered prior to determination, which means that particulate carbonates may have lead to a slight overestimate of dissolved HCO_3^- , although this is thought to be negligible in the waters considered here (P. Thomas, AWQC, pers. comm.).

Estimates of flows into the lakes at Wellington, and out of the lakes at the barrages were obtained from the Murray-Darling Basin Commission (MDBC) using the Murray-Darling Basin hydrological model BIGMOD (J. Davis, MDBC, *personal communication*). Concentrations for the inflow to the Lower Lakes were taken from data collected at Taillem Bend, the sampling site on the Lower Murray closest to the inflow to the Lower Lakes. Concentrations for the outflow were taken from Milang on the shoreline of Lake Alexandrina, which is the closest site to the barrages for which water quality data are available. Whilst this site is ~20 km from the barrages, a comparison of simultaneously collected data (monthly) for TKN and NO_x (the only nutrients available at Goolwa barrage) taken during 1999–2006 showed that these analytes were not significantly different between the two sites (*t*-test, *P*>0.05). It was assumed this observation applied to all nutrients considered here. We note that salinity was consistently higher at Goolwa than at Milang and on average the salinity at Milang was 40% of that at Goolwa. This is most likely a consequence of the observed leakage of seawater through the barrages, described earlier. Therefore our estimates of salt export can be considered a minimum.

For the purposes of this work, Lake Alexandrina and neighbouring Lake Albert were considered as one water body. Whilst this is justified for the budgets of the whole water body, we note that the site specific concentration data presented here are not representative of the whole lake system.

Monthly loads were obtained at the inflow and outflow points by multiplying the average monthly concentrations of each analyte (*n* = 1–4) by the monthly flow at that point. Monthly loads were added to obtain annual loads.

Annual element retention in the Lower Lakes was calculated as

$$M_{ret} = M_{in} - M_{bar} - M_{sto} - M_{irr} - M_{atm} \quad (1),$$

where M_{ret} is annual retention, M_{in} is the annual load into the lakes from the Lower Murray, M_{bar} is the annual flow over the barrages, M_{sto} is the annual change in storage due to changes in lake level (+ denotes increased storage, – denotes decreased storage), M_{irr} is the annual load withdrawn by irrigation and M_{atm} is annual atmospheric deposition. Lake volumes at the start of each month were calculated from a regression of lake volume versus lake level (DWLBC, unpublished) over the range of 0.3–1 m AHD, which was within the range of lake levels observed over the period of interest. The change in storage of analytes over each month was then calculated by multiplying the change in volume over each month by the monthly average concentration of the analyte of interest. Annual changes in storage were obtained from the sum of the monthly storage changes. Only annual data were available for irrigation withdrawals from the Lower Lakes spanning the years 1994–2004. Irrigation withdrawals were therefore estimated by taking the average of the annual withdrawals for the years 1994–2004, which was 31000 ML year⁻¹ (1 ML=1000 m³) with a standard deviation of 9000 ML year⁻¹ (DWLBC, unpublished). Irrigation withdrawal loads were calculated by multiplying the mean annual concentration of the analyte at Milang by the estimated annual volume of water withdrawn for irrigation. Wet atmospheric deposition of Na⁺, Ca²⁺, Mg²⁺, K⁺, Cl⁻, SO₄²⁻ and HCO₃⁻ were estimated from the deposition rates measured at Mt Gambier (Blackburn & McLeod 1983). Wet atmospheric concentrations of NO_x, TKN, FRP and TP were estimated from those measured in rainwater at Adelaide airport (Wilkinson et al. 2006), scaled to annual rainfall at Meningie. It was assumed atmospheric wet deposition was constant irrespective of rainfall. This was justified on the basis that there was a strong dependence of nutrient deposition on times between rainfall events (i.e., more nutrients were deposited in rainfall events after a long dry period; (Wilkinson et al. 2006). Rates of dry deposition are not known and were not included for budgeting purposes. Inputs from the Eastern Mt Lofty ranges via Currency Creek and the Bremer River were calculated for TKN, TP and Cl⁻ using measured river discharge and load-discharge relationships derived from water quality data spanning the years 1973 until 2003. Using this approach it was found that these ephemeral streams contributed a maximum of 4% and generally <1% of the annual load of TKN, TP and Cl⁻ to the Lower Lakes. Thus, element

loads from the Eastern Mt Lofty ranges were deemed insignificant and not included in the budgets. Inputs to the Lower Lakes from groundwater and leakage through the barrages were ignored for the purposes of this budget since no relevant data exists for these potential inputs. The implications of not including these potential sources will be discussed later.

Bicarbonate and pH data were used to calculate TCO_2 ($\text{CO}_2 + \text{H}_2\text{CO}_3 + \text{HCO}_3^- + \text{CO}_3^{2-}$) and the partial pressure was calculated from pH and TCO_2 using a spreadsheet routine (Lewis & Wallace 1998). The likely range of CO_2 fluxes across the air water interface were calculated from $p\text{CO}_2$ using gas transfer velocities of 3 and 7 cm h^{-1} (Raymond & Cole 2001).

3. Results

3.1. Analyte concentrations in the Lower Murray and the Lower Lakes

As is typical of Murray-Darling Basin waters (Herczeg et al. 2001), Na^+ and Cl^- were the main ions in the Lower Murray and the Lower Lakes, with smaller contributions from Ca^{2+} , Mg^{2+} , SO_4^{2-} and HCO_3^- . Inorganic nutrient (NO_x , FRP and Si) concentrations were generally highest in the Lower Murray and decreased markedly within the Lower Lakes, particularly for NO_x and FRP (Fig. 2). Silica concentrations showed a similar pattern, although this was less marked. A drought-breaking inflow in late 1983 through to 1984 resulted in some of the highest consistently observed concentrations of all inorganic nutrients in the Lower Murray, which was also reflected in the Lower Lakes. Indeed, concentrations of Si and FRP remained elevated in the Lower Lakes for several years after this inflow event. NO_x , by contrast, was rapidly removed from the water column, becoming undetectable within ~ 1 year. The years 1989 to 1993 had consistently high flows, but elevated inorganic nutrient concentrations within the lake were only observed in 1990. NH_4^+ was not determined on a routine basis, however, the limited data set available suggests it was always below the detection limit in the Lower Lakes and comprised a variable fraction (generally insignificant, but up to 50%) of inorganic N ($\text{NO}_x + \text{NH}_4^+$).

Total phosphorus concentrations were consistently highest in the Lower Murray and the highest concentrations in both the river and the Lower Lakes were associated with the drought-breaking inflow event of 1983, as for the inorganic nutrients (Fig. 3). In contrast to TP and the inorganic nutrients, TKN concentrations were consistently highest in the Lower Lakes. Turbidity in both the Lower Murray and the Lower Lakes was highly variable, but generally higher in the Lower Lakes than the Lower Murray. As was observed for the nutrients, the highest turbidity in the Lower Lakes was strongly associated with inflow events. For example, the highest turbidity measurements in the Lower Murray and the Lower Lakes were associated with the drought-breaking inflow event of 1983. The periods of lowest turbidity were always associated with periods of low flow.

The pH was consistently highest in the waters of the Lower Lakes compared to the Lower Murray (Fig. 4). In the Lower Lakes, conspicuously high pH was generally associated with low inflow, whilst in the Lower Murray, low pH was associated with increased flow. Bicarbonate concentrations were generally similar in the Lower Murray and the Lower Lakes, with the highest concentrations being observed between floods. Partial pressures for CO_2 within the Lower Murray were generally in the range of 1000–2500 μatm and consistently elevated above atmospheric $p\text{CO}_2$, indicating that the river was consistently a net source of CO_2 . High flow events in the river were generally associated with slightly depressed $p\text{CO}_2$ values and were often followed by a spike in the $p\text{CO}_2$, presumably reflecting the mineralisation of material washed into the river channel during floods. In the Lower Lakes, $p\text{CO}_2$ generally ranged between 100 and 750 μatm , indicating that the lake alternated between as source and a sink for CO_2 . The lowest values of $p\text{CO}_2$ generally occurred between inflow events. The estimated fluxes of CO_2 across the air-water interface generally ranged between 20–100 $\text{mmol m}^{-2} \text{d}^{-1}$ for

the Lower Murray and between a net source of 20 to a net sink of 20 $\text{mmol m}^{-2} \text{d}^{-1}$ in the Lower Lakes.

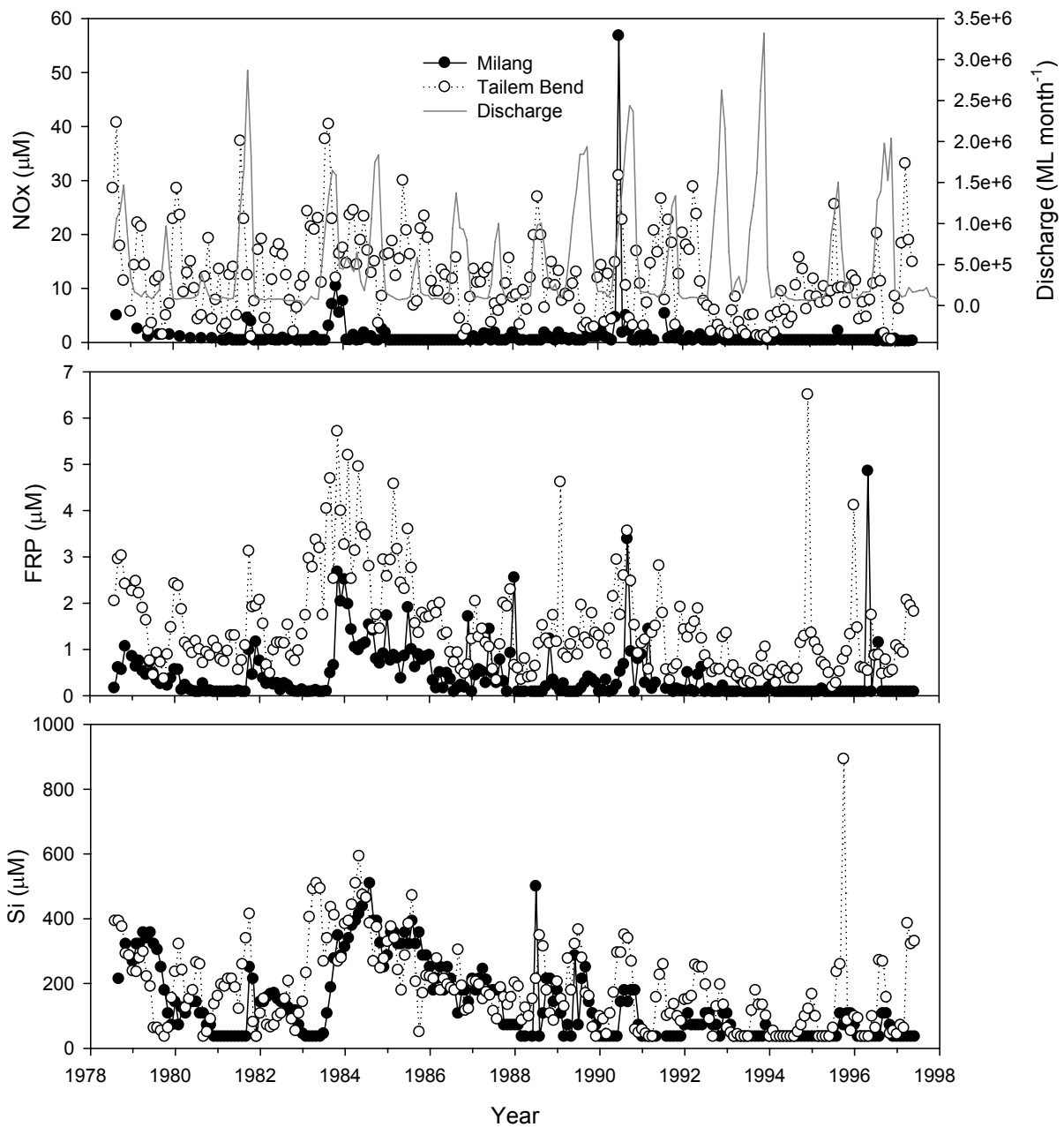


Figure 2. Average monthly concentrations of NO_x (top panel), FRP (middle panel) and Si (bottom panel) at Tailm Bend on the Lower Murray and Milang in the Lower Lakes. River discharge is also shown on the top panel, units are in megalitres (1 ML=1000 m³) per month.

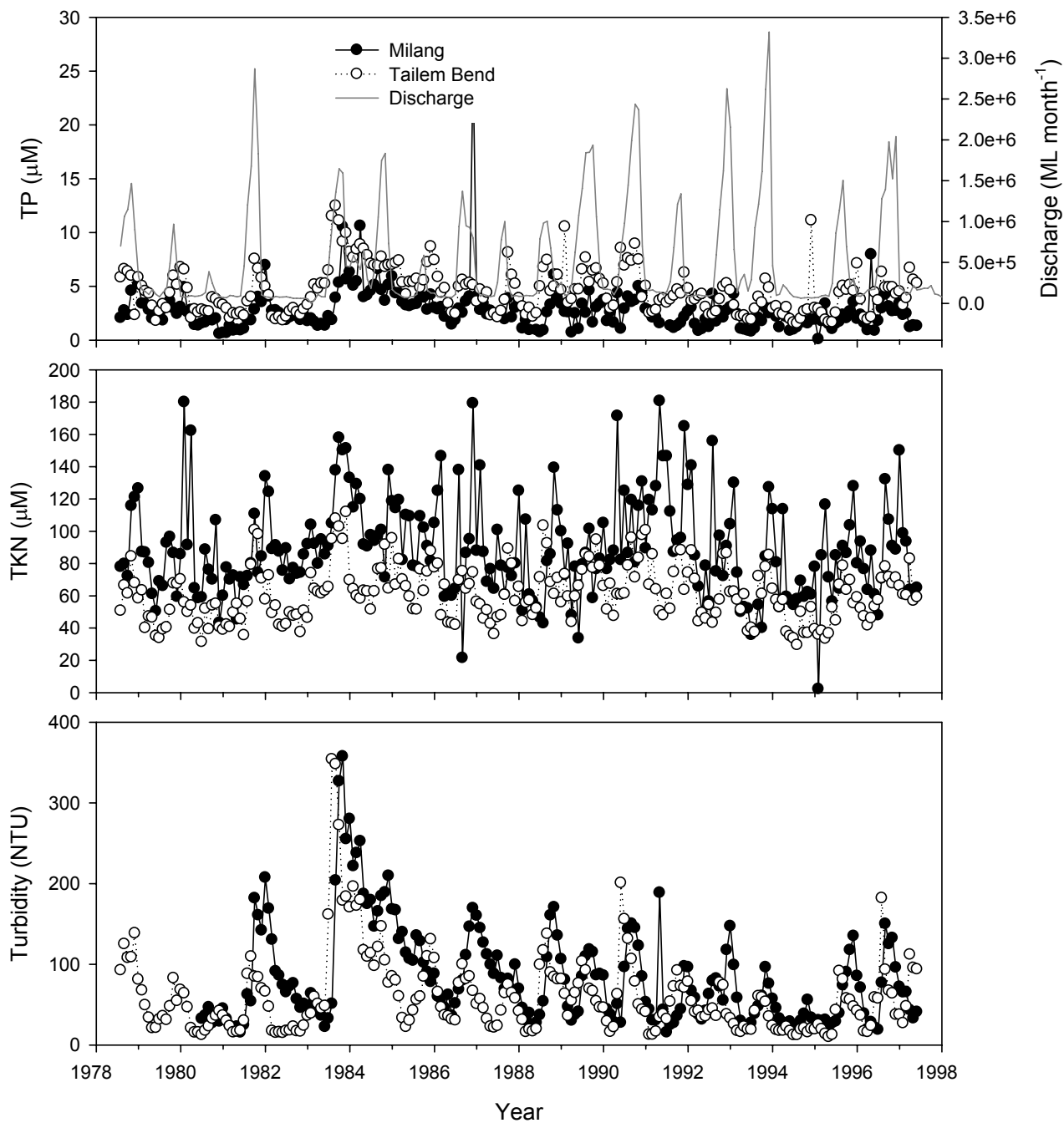


Figure 3. Average monthly concentrations of TP (top panel), TKN (middle panel) and turbidity (bottom panel) at Tailem Bend on the Lower Murray and Milang in the Lower Lakes. River discharge is also shown on the top panel, units are in megalitres ($1 \text{ ML} = 1000 \text{ m}^3$) per month.

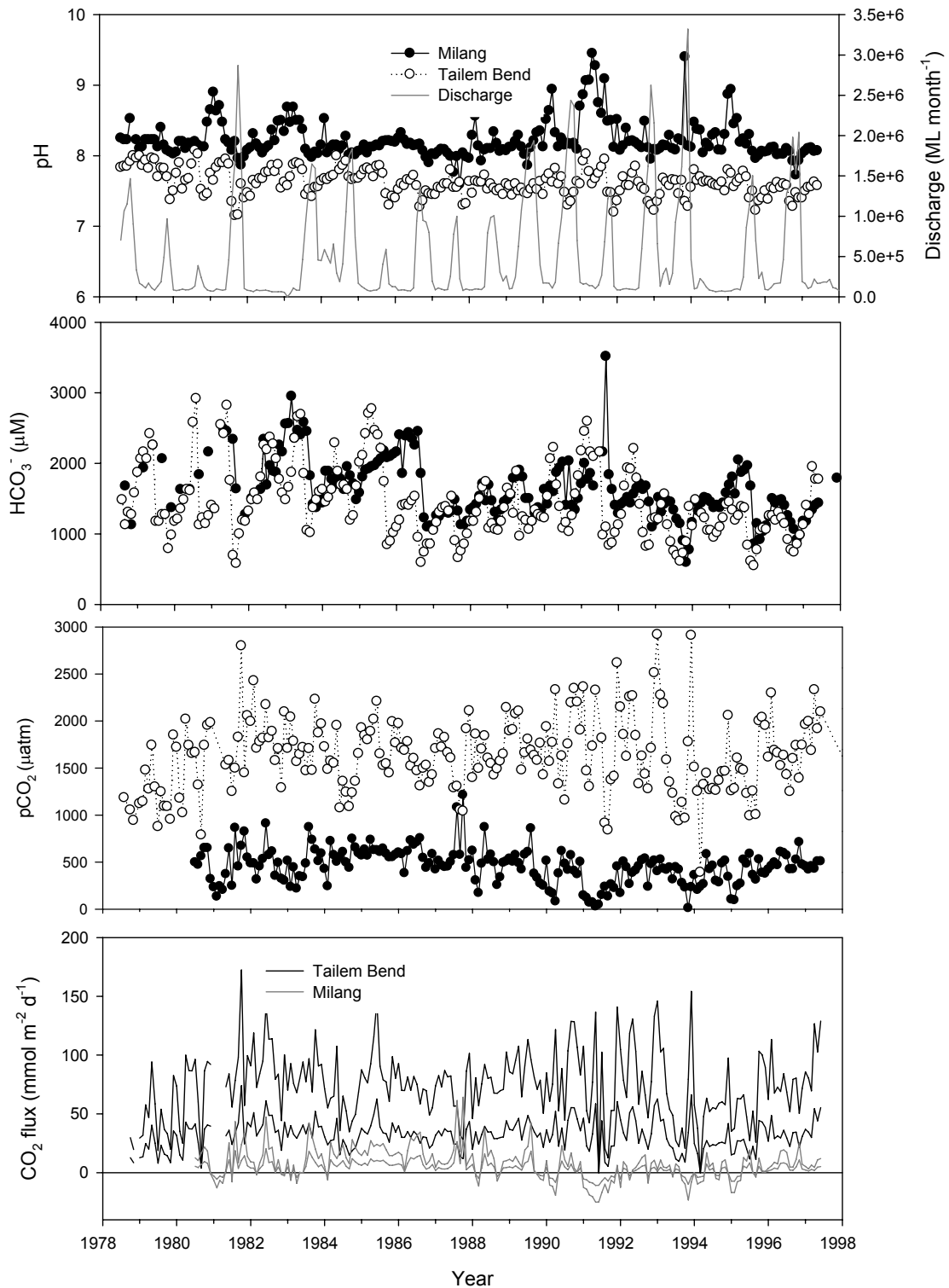


Figure 4. Average monthly pH (top panel), HCO₃⁻ (upper middle panel), pCO₂ (lower middle panel) and estimated CO₂ flux (bottom panel) at Taillem Bend on the Lower Murray and Milang in the Lower Lakes. For the CO₂ flux, an upper and a lower estimate are given for each site using a lower and an upper gas transfer coefficient of 3 and 7 cm h⁻¹. River discharge is also shown on the top panel, units are in megalitres (1 ML=1000 m³) per month.

The major ion concentrations were highly correlated and we only show examples of concentrations for Na^+ and SO_4^{2-} (Fig. 5). The highest concentrations of salts in the Lower Murray and the Lower Lakes were observed after the 1983 drought. A consistent pattern of increasing ion concentration during low flow periods followed by a decrease in concentration during higher flow periods was also observed. In general, the ratios of the major ions to chloride in both the Lower Murray and in the Lower Lakes were slightly elevated relative to seawater. This was with the exception of HCO_3^- and Ca^{2+} , which were highly elevated relative to chloride concentrations in seawater (Fig. 6). This observation is consistent with previous studies (Herczeg et al. 1993). A period of elevated Ca^{2+} concentrations relative to Cl^- was associated with drought-breaking inflows following the 1994 drought. We note that there are no Cl^- data available for the 1984 drought-breaking flows.

Major ion concentrations all showed a strong negative relationship with flow, as represented by Na^+ in Figure 7, with minimum concentrations being reached above monthly inflows of 1.5×10^6 Megalitres (ML, 1 ML=1000 m³) month⁻¹. There were no strong relationships between nutrient concentrations and discharge into the Lower Lakes. TKN concentration had the strongest relationship to flow, with an r^2 of 0.3 (Fig. 7). Major ion concentrations increased markedly below 0.2×10^6 ML month⁻¹, as illustrated for Na^+ in Figure 7. There was also a slight difference in the relationship between the falling and rising stages of the hydrograph, with generally higher salt concentrations being observed at intermediate flows on the rising compared to the falling stage. This may reflect the washout of salts accumulated in surrounding floodplains after prolonged dry periods.

Flow relationships with annual elemental loads were much stronger than for concentrations, although the relationships for NO_x and FRP with flow were still relatively weak (Fig. 8). Strong relationships between total N and P, as well as the major ions were observed ($r^2 > 0.8$).

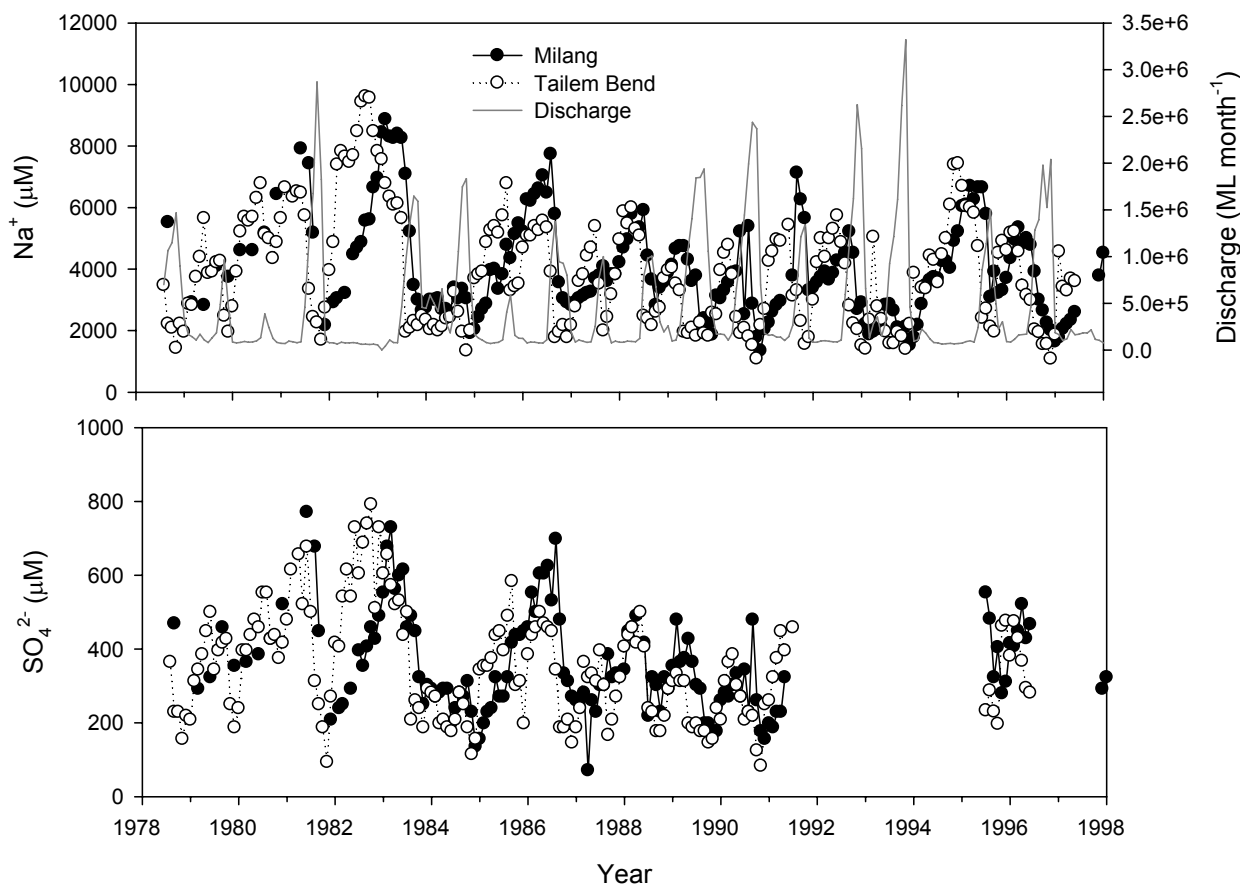


Figure 5. Average monthly concentrations of Na^+ (top panel) and SO_4^{2-} (bottom panel) at Tailem Bend on the Lower Murray and Milang in the Lower Lakes. River discharge is also shown on the top panel, units are in megalitres (1 ML=1000 m³) per month.

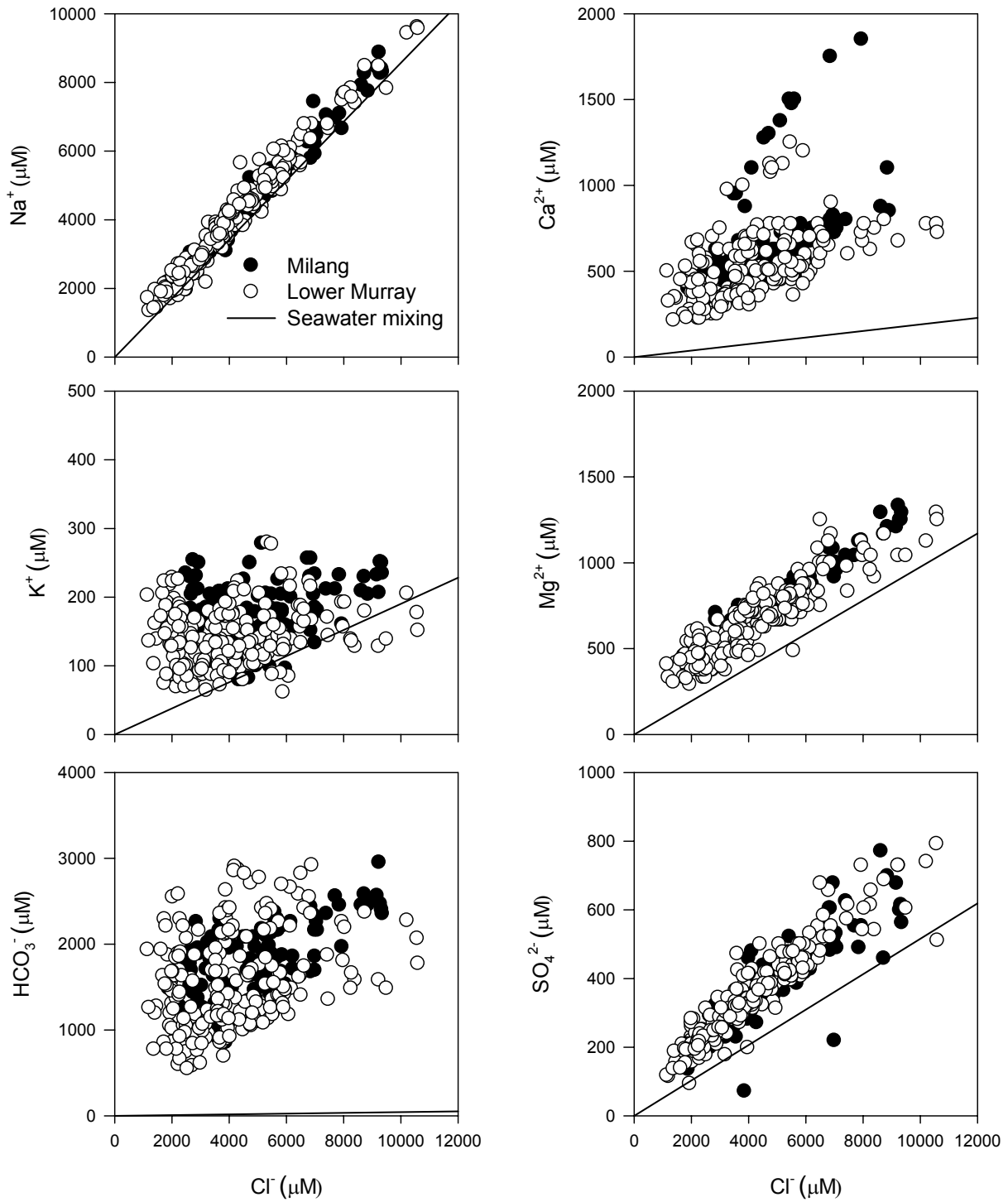


Figure 6. Plots of the major ions versus chloride concentrations in the Lower Murray at Tailern Bend and in the Lower Lakes at Milang. The relationship for seawater dilution is also shown (solid line).

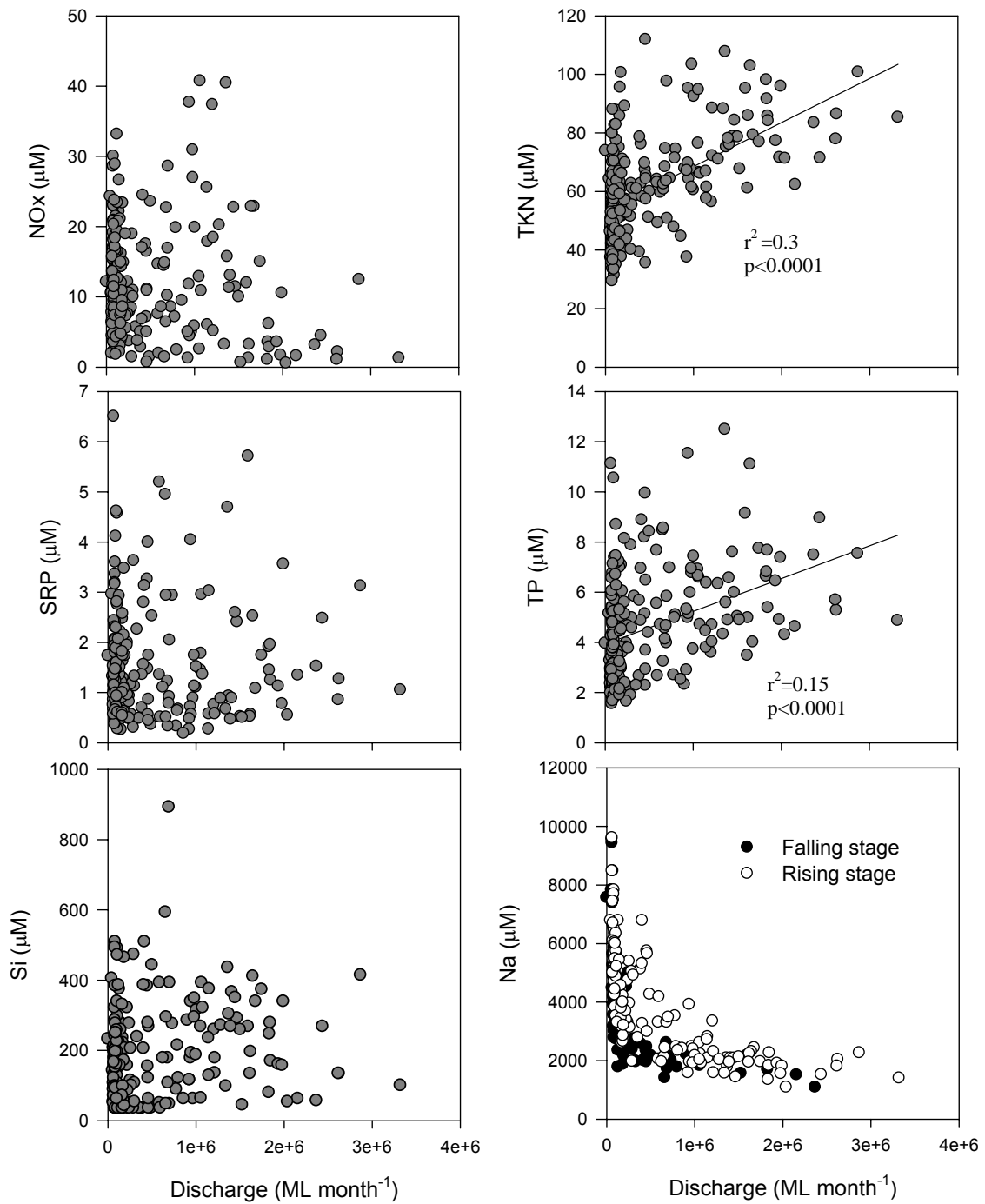


Figure 7. Plots of average monthly concentrations of NO_x, FRP, Si, TKN, TP and Na⁺ versus monthly discharge at Tailem Bend on the Lower Murray. For Na⁺, the relationship for the rising and falling stages are shown. Discharge is in megalitres (1 ML=1000 m³) per month.

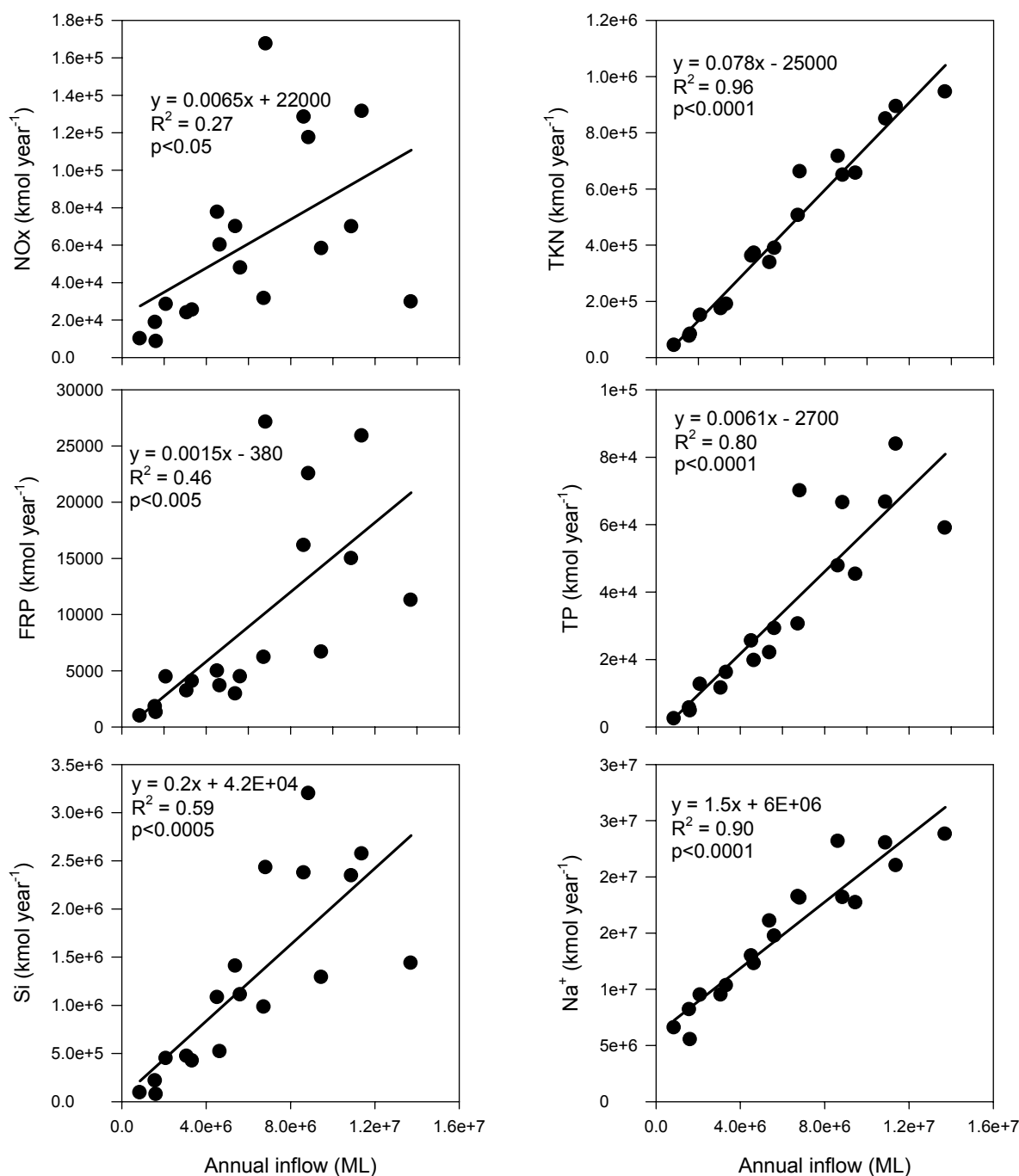


Figure 8. Plots of annual discharges of NO_x, FRP, Si, TKN, TP and Na⁺ versus annual flow at Taillem Bend on the Lower Murray. Annual flow is in megalitres (1 ML=1000 m³).

3.2. Element retention in the Lower Lakes

Inorganic nutrients were generally quite strongly retained in the Lower Lakes, with a net retention of NO_x, FRP and Si occurring virtually every year (Fig. 9). Highest absolute retention rates generally occurred in the highest flow years, whilst lowest absolute retention rates occurred in the lowest flow years. Retention of NO_x ranged between 2×10^4 and 1.6×10^5 kmol year⁻¹ and generally, 90–100% of the NO_x entering the Lower Lakes was retained. For FRP, retention rates varied between 1800 and 25,000 kmol year⁻¹, with between 60 and 100% of FRP entering the Lower Lakes retained. Silica retention in the Lower Lakes was more variable, ranging from a slight source, through to being a sink of 1.7×10^6 kmol year⁻¹. This represented

a release equivalent to 50% of the incoming load and a retention of up to 85% of the incoming load. Retention of TKN was more variable, ranging from a net release of up to 4.52×10^5 kmol year⁻¹ (141% of incoming load) through to a net retention of 1.7×10^5 kmol year⁻¹ (86% of incoming load; Fig. 10). There was a slight net release of TKN over the entire study period equivalent to 14% of the total inflow. Total nitrogen retention showed a very similar pattern to TKN, but there was a net balance in retention and release over the study period owing to the high retention efficiency of NO₃⁻. TP was always retained, ranging between 609 and 4.9×10^4 kmol year⁻¹, equating to 0.5 to 97% of incoming load. In general atmospheric deposition was <20% of the Lower Lakes nutrient load, with the exceptions of the drought years 1982 and 1994, when atmospheric deposition comprised up to 60-80% of the nutrient load.

The major ions all exhibited a very similar behaviour, with large net releases occurring in wet years and a retention occurring in dry years. The largest net release occurred in 1983, which was a wet year preceded by the 1982 drought (Fig. 11). In general the Lower Lakes were a source of the major ions (Table 1). Atmospheric deposition was generally <1% of the river-borne salt load to the Lower Lakes.

The water residence time had two distinct impacts on annual element retention in the Lower Lakes. Highest nutrient retention occurred during periods of lowest water residence time, with the exception of TKN which showed the opposite trend. Salts showed the highest retention during periods of highest water residence time, and the largest source during low water residence times (Fig. 12).

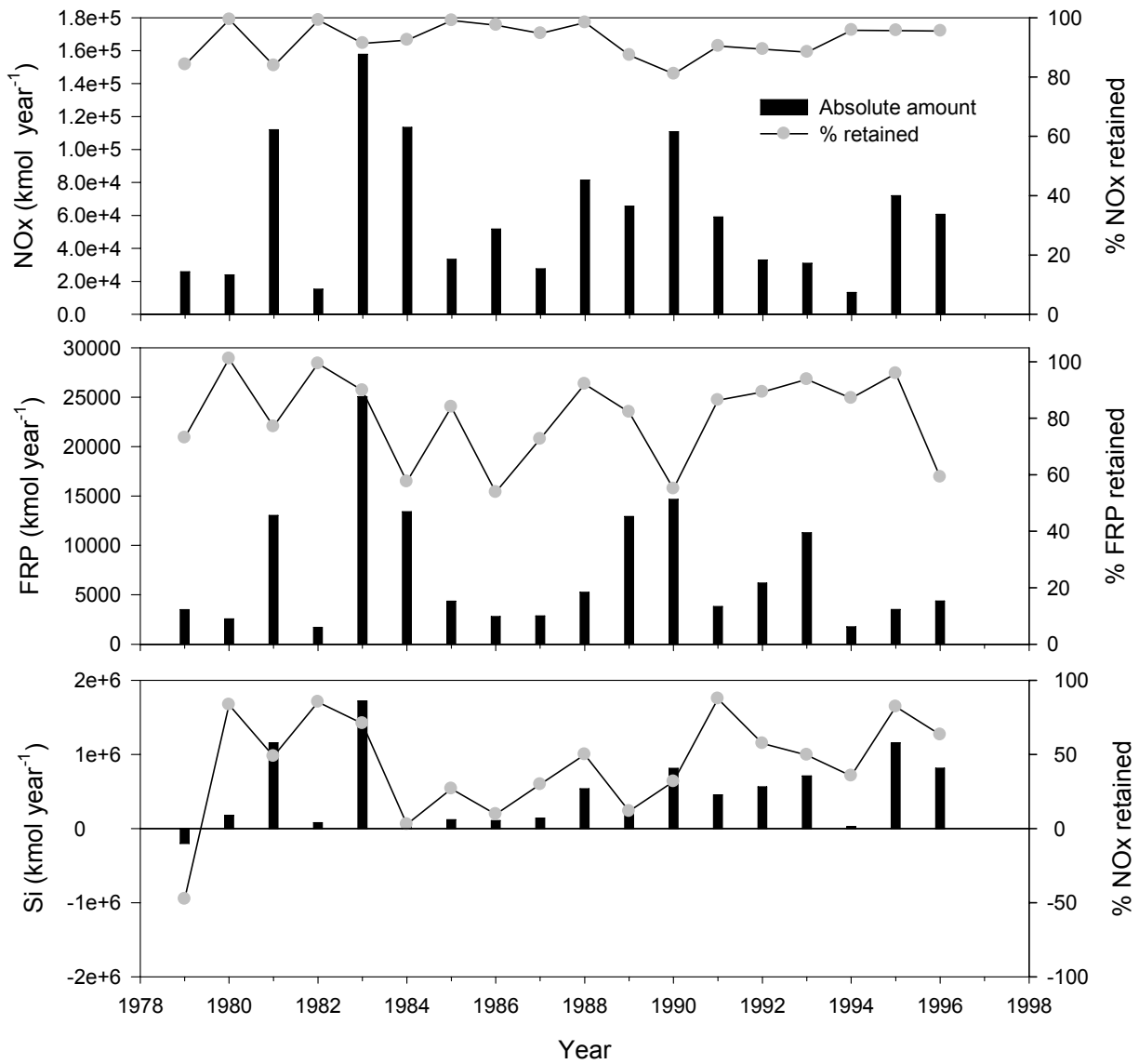


Figure 9. Annual retention of NO_x, FRP and Si shown of as both an absolute amount and as a proportion of incoming load to the Lower Lakes. Positive values denote net retention, negative value denote net release.

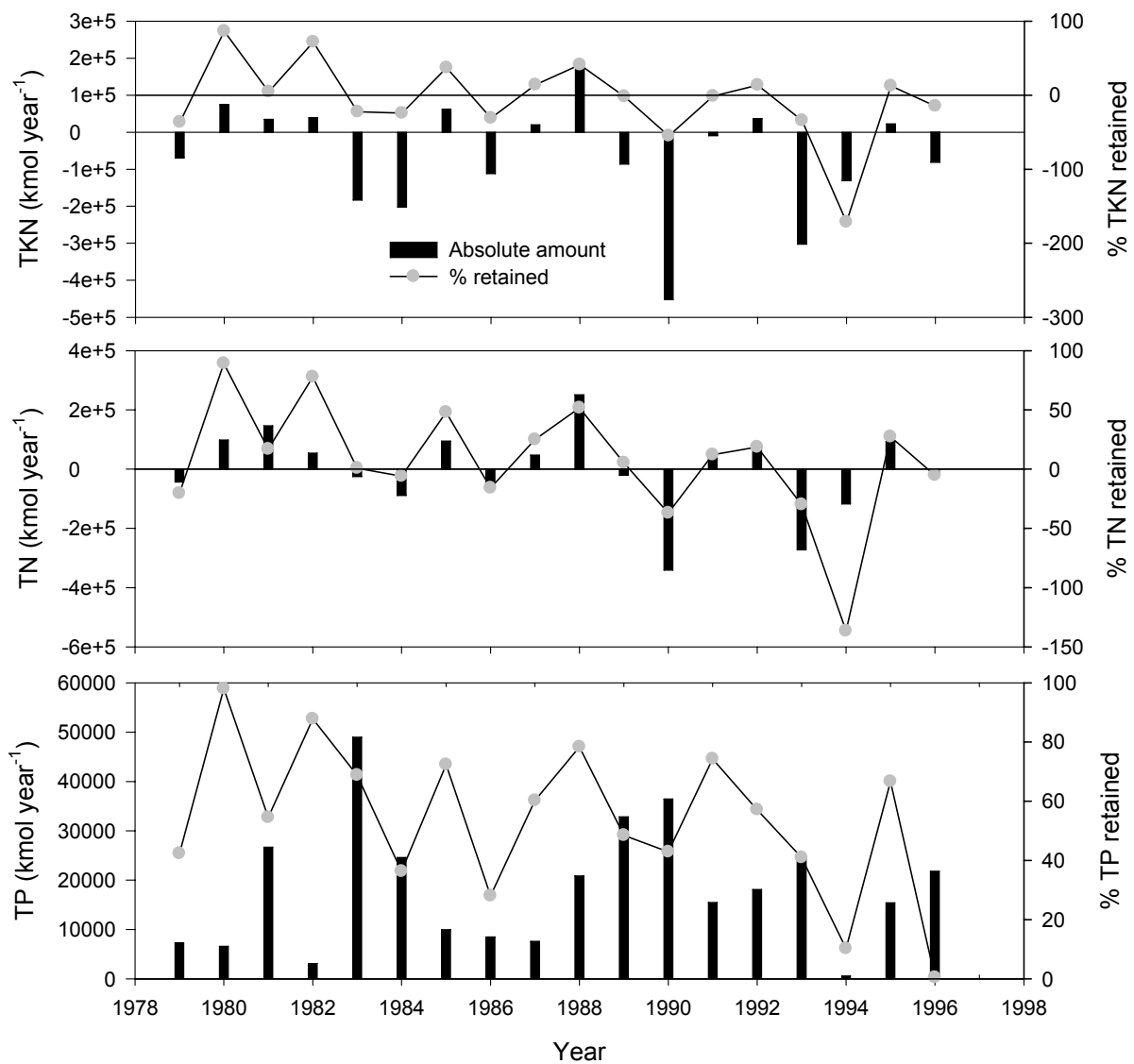


Figure 10. Annual retention of TKN, TN and TP shown of as both an absolute amount and as a proportion of incoming load to the Lower Lakes. Positive values denote net retention, negative value denote net release.

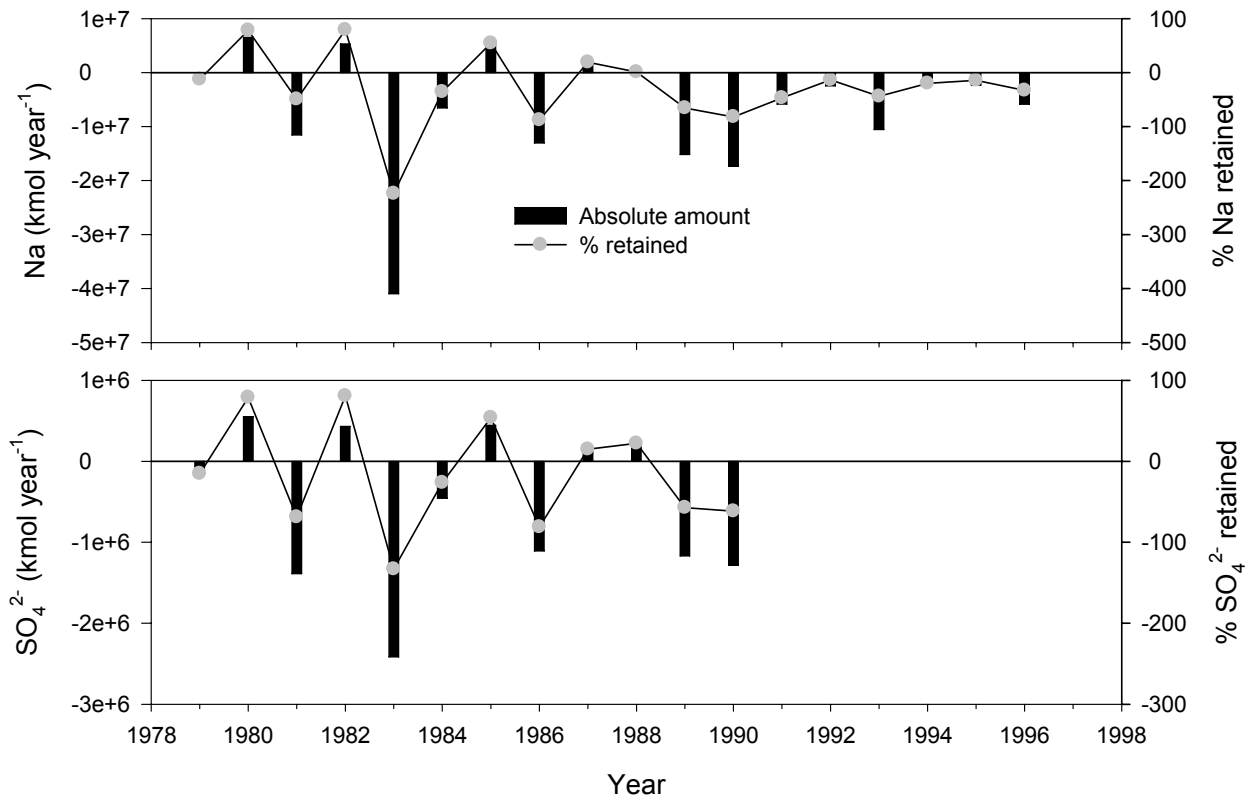


Figure 11. Annual retention of Na⁺ and SO₄²⁻, shown of as both an absolute amount and as a proportion of incoming load to the Lower Lakes. Positive values denote net retention, negative value denote net release.

Table 1. Annual retention of elements in the Lower Lakes during the years 1979 to 1996. Units are in Mmol per year. A negative sign denotes a net release from the lakes, – denotes no data available. Annual flows are in Gegalitres (10^6 m³).

Year	NOx	FRP	TKN	TP	Ca ²⁺	Cl ⁻	HCO ₃ ⁻	K ⁺	Mg ²⁺	Na ⁺	Si	SO ₄ ²⁻	Annual flow
1979	26	4	-69	7	-277	-1350	-994	-100	-394	-1331	-200	-160	2952
1980	24	3	75	7	609	6871	1757	165	952	6539	179	552	349
1981	112	13	35	27	-1496	-8066	-3699	-42	-1581	-11565	1156	-1389	7905
1982	15	2	39	3	454	5774	1150	111	687	5323	78	432	33
1983	158	25	-183	49	–	-46863	-9173	-798	-5446	-40956	1720	-2416	6402
1984	113	13	-203	25	–	-8756	-1415	-254	-677	-6557	91	-457	8394
1985	33	4	62	10	526	5461	1373	106	768	5243	120	444	910
1986	52	3	-112	9	-1727	-14543	-5422	-481	-1973	-13065	107	-1108	4494
1987	28	3	20	8	58	1856	180	29	303	1845	139	118	1910
1988	82	5	170	21	91	–	916	167	212	90	538	242	3059
1989	66	13	-86	33	-1730	–	-4688	-413	-2304	-15190	273	-1168	12556
1990	111	15	-452	36	-2182	–	-4813	-203	-2480	-17385	814	-1287	12516
1991	59	4	-10	15	-566	–	-1823	-158	-706	-5854	453	–	3514
1992	33	6	36	18	-242	–	-394	-91	-495	-2471	562	–	5610
1993	31	11	-303	25	-962	–	-1092	-245	-1779	-10555	712	–	14640
1994	13	2	-131	1	-451	–	-1726	-148	-375	-1125	26	–	2490
1995	72	4	23	15	-1621	–	-1110	-8	-516	-2324	1155	–	3959
1996	61	4	-81	22	-439	–	-376	-78	-668	-5903	815	–	8284

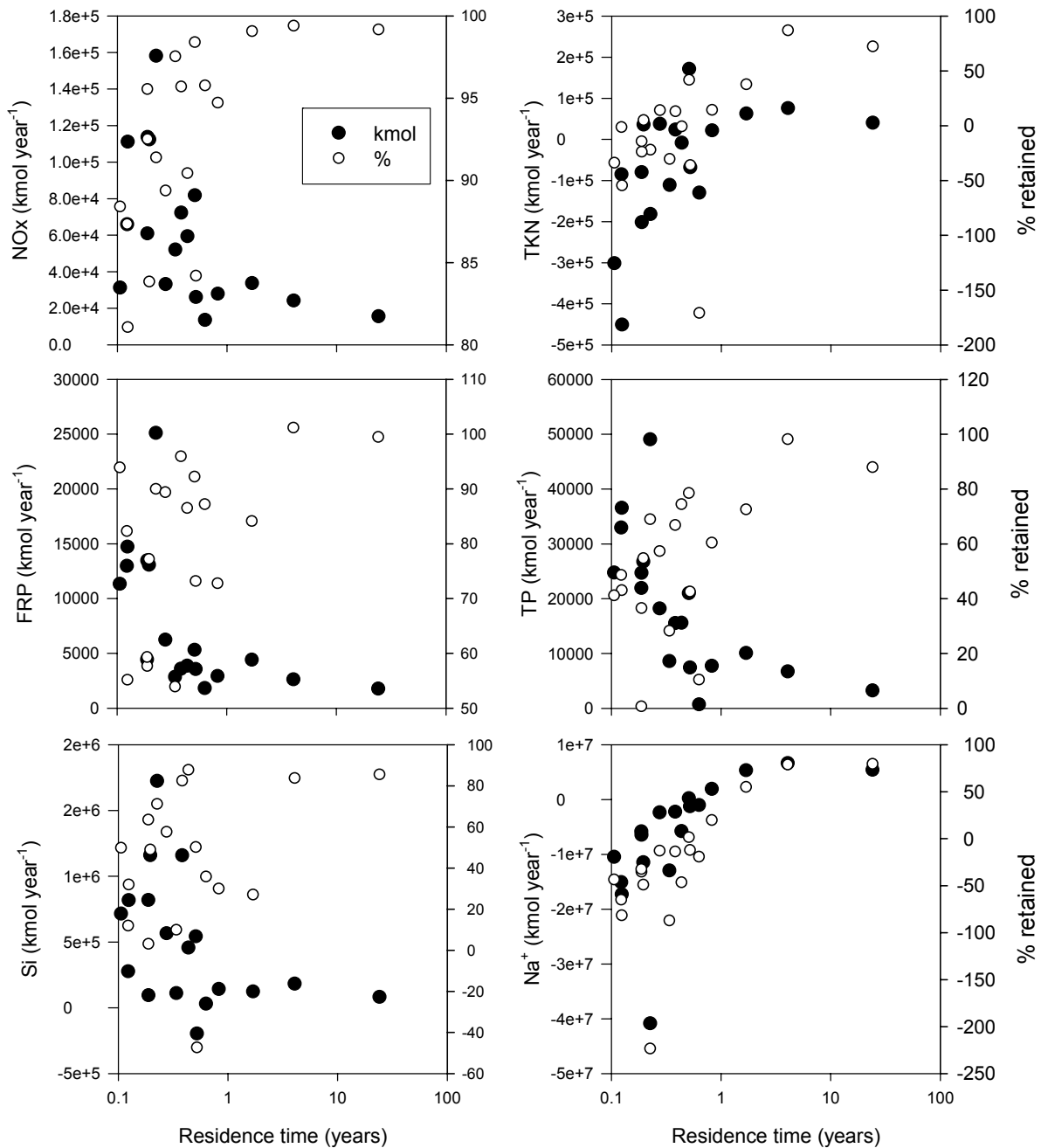


Figure 12. Annual retention of NO_x, FRP, Si, TKN, TP and Na⁺, shown as both absolute amounts and as a percent of the load entering the Lower Lakes, as a function of lake residence time.

4. Discussion

4.1. $p\text{CO}_2$

The range of $p\text{CO}_2$ values observed in the Lower Murray generally fell within the mid to lower range observed in other rivers studied throughout the world (Frankignoulle et al. 1998, Raymond et al. 2000, Zhai et al. 2005) and references therein. This oversaturation of CO_2 in rivers may be due to in-situ respiration, but may also be in part due to the import of CO_2 from other sources, such as groundwater or the floodplain wetlands along the margins of the Lower Murray. In a similar long term data set for the Hudson River, a seasonally distinct variation in $p\text{CO}_2$ was observed, with the highest values occurring in summer and the lowest in winter (Raymond et al. 1997). By contrast, season had no clear effect on $p\text{CO}_2$ in the Lower Murray, most likely reflecting the relatively mild climate (water temperature range 10–25°C). River discharge did have a marked impact on $p\text{CO}_2$ and bicarbonate, with distinct dips being observed in high flow events, an observation which has also been made in the Mississippi River (Cai 2003). Estimated CO_2 effluxes from the Lower Murray generally covered the range of sediment CO_2 effluxes observed in shallow riverine and coastal systems (Cook et al. 2004a, Cook et al. 2004b).

There was a distinct drop in the $p\text{CO}_2$ in the Lower Lakes compared to simultaneous measurements made in the Lower Murray, which we ascribe to several factors. Firstly, the Lower Lakes are a large, well-mixed, shallow water body with a relatively high water residence time relative to the river, suggesting a larger potential to attain gaseous equilibrium with the atmosphere. Secondly, considerable primary production takes place within the lakes (Geddes 1984, 1988), consuming CO_2 , which is reflected by the periodic drop in the $p\text{CO}_2$ below atmospheric levels. Indeed, we note that the net uptake of CO_2 observed in 1981 corresponded with a period of high production, which was ascribed to a period of low turbidity (Geddes 1984). Consistent with this, there was generally a clear correspondence between periods of net CO_2 uptake and low turbidity within the Lower Lakes (Figs. 3 and 4). It has been suggested that periods of low turbidity are most likely caused by an interaction between relatively low inflows from the Darling River (the more turbid tributary) and high salinity within the Lower Lakes (Geddes 1984). Our data broadly supports this hypothesis, with the periods of lowest turbidity generally coinciding with periods of highest salinity in the lake and low turbidity of the inflowing waters (Figs. 3 and 5). We note that no sustained periods of autotrophy were observed following the drought-breaking 1983 inflows which brought high loads of nutrients, but also high suspended solids. The increased turbidity would have restricted light availability and algal growth.

On average, the $p\text{CO}_2$ value in the Lower Lakes was 460 μatm , which is above atmospheric levels, suggesting the lake was a slight net source of CO_2 . This is in agreement with the emerging paradigm that lakes are generally a net source of CO_2 (Sobek et al. 2005). The observed $p\text{CO}_2$ values in the Lower Lakes were generally in the lower range of values of $p\text{CO}_2$ observed in lakes and estuaries from around the world (Frankignoulle et al. 1998, Sobek et al. 2005), including those from similar climate zones. It has been found that Dissolved Organic C (DOC) concentrations within lakes explain a significant proportion of the variation observed in $p\text{CO}_2$ (Sobek et al. 2005). The range of DOC concentrations observed for the Lower Lakes and the Lower Murray generally fell in the range of 500–1000 μM (AWQC, unpublished data), which was actually in the mid to upper range of DOC concentrations measured in the various lakes considered a previous study (Sobek et al. 2005). Very few of the lakes in that study with comparable DOC concentrations to the Lower Lakes had such low $p\text{CO}_2$ values. Furthermore, a similar regression ($n = 79$) of $p\text{CO}_2$ and DOC for the Lower Lakes showed no significant relationship between these two variables (including when they were sorted for flow), and indeed the slope of the regression was slightly negative. This would suggest that the DOC entering the Lower Lakes from the Lower Murray is of a relatively refractory nature compared to other river systems around the world.

A relatively large input of refractory DOC to the Lower Lakes is consistent with the changes in the hydrology of the Murray-Darling Basin since European settlement. In particular, water residence time in the basin has increased and the connectivity between floodplains and the main river channel has been significantly restricted. Under current conditions, water leaving areas of high rainfall is stored in deep reservoirs, before being released at controlled intervals during the summer agricultural growing season. Longer water residence times due to storage in reservoirs will tend to decrease the concentration of DOC (Curtis & Schindler 1997). Thus, upon reaching the Lower Lakes the labile fraction of DOC originating from the catchment has probably been partially metabolised, leaving a relatively larger fraction of refractory material. On the other hand, because of the semi-arid climate, longer water residence times would tend to increase the concentration of the remaining DOC by evapoconcentration (Curtis & Adams 1995). In addition to longer water residence times, the reduction of the annual flood-pulse of the River Murray now largely prevents the lateral transport of labile organic matter from floodplains to the river (Robertson et al. 1999). When floods do occur in the Upper Murray, sufficient labile DOC can be mobilised to generate deoxygenation events (“blackwaters”) in floodplain wetlands (Howitt et al. 2007). The changes in the quantity and quality of organic matter delivered to the River Murray are thought to have switched the system to one now dominated by algal production (Robertson et al. 1999).

4.2. Phosphorus

Freshwater lakes and reservoirs are well known to have a significant retention of total P and the Lower Lakes were no exception, with a net retention of TP occurring in all years studied. Our estimates of TP retention cover the range of those calculated by Geddes (1984), who estimated retention rates of $1.2\text{--}2.4 \times 10^4 \text{ kmol year}^{-1}$ in the years 1975-1978. A number of simple models have been devised to describe P retention within lakes and these usually express P retention as function of the total P mass in the water column, the total annual P loading, or the areal P content of the lake (Prairie 1989). It has also been suggested that net retention of P should be best viewed as the partial sedimentation of the load and the partial sedimentation of the mass of P in the water column. The general relationship for this two component model is:

$$R_p = (0.25 + 0.18\tau) / (1 + 0.18\tau) \quad (2),$$

where R_p is the fraction of TP retained and τ is the residence time of the lake in years (Prairie 1989). TP retention as a function of lake residence time is shown in Figure 13a in comparison to that expected based on a model (Prairie 1989). It can be seen that R_p was consistently higher in the Lower Lakes than predicted by the model. Given that the Lower Lakes are relatively shallow and have a very large surface area, a more applicable approach might be to express TP retention as a function of residence time normalised to the surface area of the lake using the relationship:

$$R_p = v / (v + q_s) \quad (3),$$

where R_p is the fraction of P retained, v is the apparent settling velocity and q_s is the areal loading defined as the flow through the lakes divided by their surface area (Chapra 1975, Dillon & Kirchner 1975). In general, an average settling velocity of $10\text{--}16 \text{ m year}^{-1}$ would be expected for North American and European lakes (Dillon & Kirchner 1975). A plot of R_p vs q_s for the Lower Lakes, with the expected settling velocities overlaid is shown in Figure 13b. It can be seen that there is a high degree of scatter in the data at lower areal loadings (river flows), suggesting that there is a high degree of variability in sedimentation velocities. At an areal loading above 7 m year^{-1} , there is a much better conformity to the model, reflecting more constant sedimentation velocities. The cumulative flows through the lake for all years with areal

loading rates above 7 m year^{-1} , amounts to $>75\%$ of the discharge occurring over the study period, and thus the model is applicable when the vast majority of the discharge (and hence TP loading) takes place. During these years, the average sedimentation velocity is 12 m year^{-1} , which is very close to the generally applicable value of 13.2 (Dillon & Kirchner 1975). We note the single data point with a substantially lower sedimentation velocity of 6 m year^{-1} corresponds to 1984. In this year, the Lower Lakes maintained extremely high turbidities (Fig. 3), reflecting high relative inflows from the turbid Darling River. Presumably, the fine particles responsible for the turbidity of the Darling would also tend to have relatively low settling velocities. As such, we suggest a good approximation of R_p can be obtained using this model for the Lower Lakes in moderate to high flow years, except when there is a major input from the Darling River.

The amount of TP retained within the lake between 1979 and 1996 amounted to $3.3 \times 10^5 \text{ kmol}$. Based on an average sediment TP content of 250 mg kg^{-1} dry weight (K. Aldridge, *unpublished data*) and a sediment porosity of 0.65 (K. Aldridge, *unpublished data*), this amounts to an average sedimentation rate of $\sim 3.3 \text{ mm year}^{-1}$ averaged over the lake. This is in excellent agreement with a sedimentation rate of 3 mm year^{-1} previously calculated in the Lower Lakes using ^{210}Pb (Herczeg et al. 2001). This gives us some degree of confidence in our estimates of P retention, as well as those estimated in another study (Geddes 1984). As well as sedimentation, another possible sink for P is removal in the form of fish biomass by the commercial fisheries on the Lower Lakes. Using total fish catch data from the years 1985 to 1996 (South Australian Research and Development Institute, *unpublished data*) and assuming that P comprises 25 g kg^{-1} dry fish biomass, we estimate that fish biomass removal as a proportion of TP retention ranges between 1 and 60%, with a proportion of 2% for the total retention over the entire period 1985 to 1996. The high proportion of 60% arose in the drought year 1994, when TP retention in the lake was negligible (due to the lack of input). This estimated rate of P removal in fish biomass is somewhat lower than a rate of 10% estimated for Lake Donghu in China (Tang & Ping 2000).

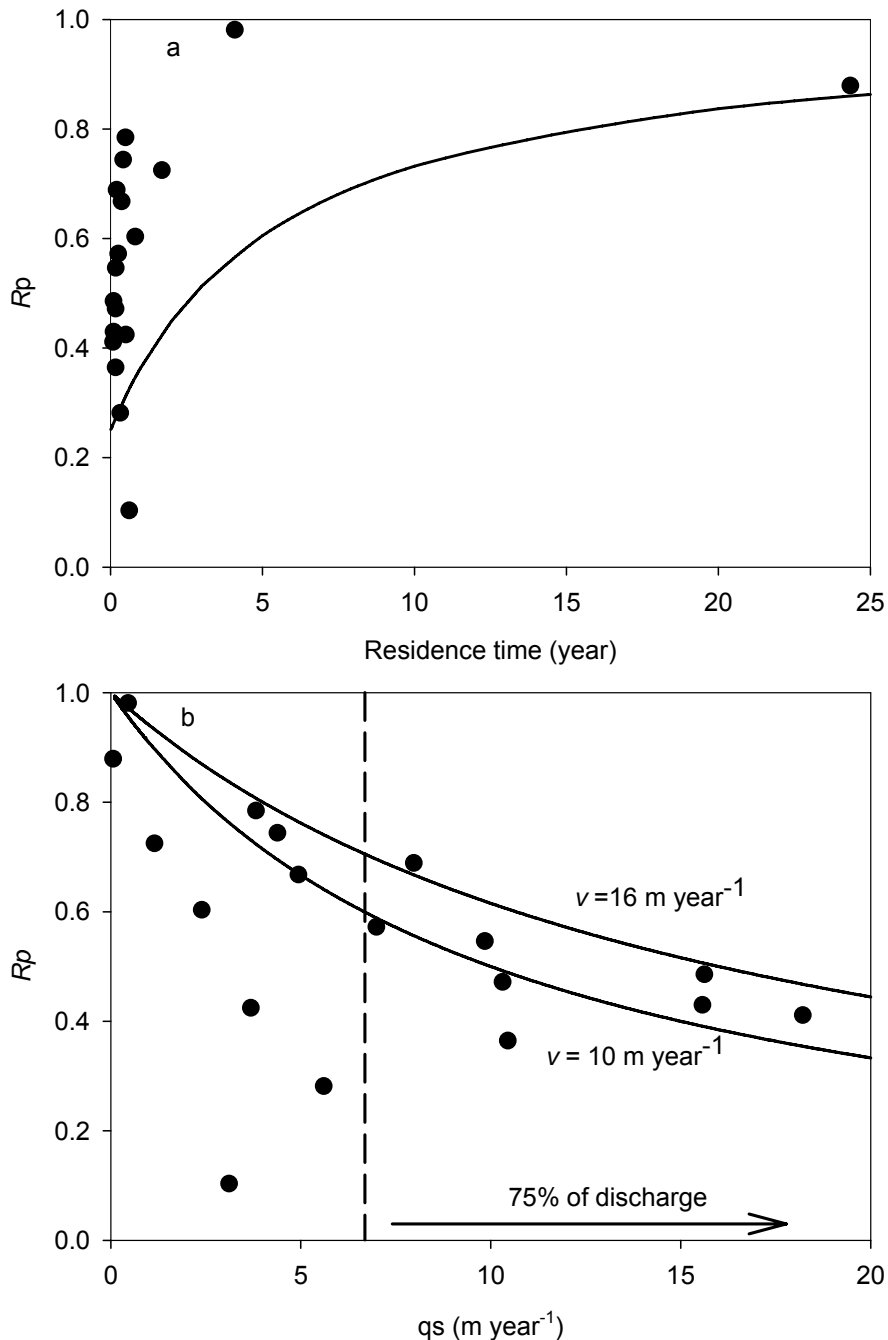


Figure 13. The proportion of TP entering the lakes retained (R_p) shown as a function of water residence time within the Lower Lakes (a) and the areal P loading rate of the Lower Lakes (b). The solid line in (a) shows the relationship according to a previously published model (Prairie 1989). The solid lines in (b) show the expected relationship according to another published model (Dillon & Kirchner 1975) assuming sedimentation velocities of 10 and 16 $m\ year^{-1}$. Also shown in (b) are the areal loading rates corresponding to the upper 75th percentile of river discharge.

4.3. Nitrogen

In contrast to TP, the TN budget showed that over the study period, the Lower Lakes were either neutral or a slight net source of TN (8.3×10^4 kmol), representing <1% of the incoming load to the Lake. Based on the previously estimated sedimentation rate and a sediment TN content of 0.25% dry mass (K. Aldridge, *unpublished data*, Herczeg et al. 2001), we calculate a TN loss of 7.5×10^6 kmol for the Lower Lakes over the entire study period, representing ~80% of

the total TN load into the lakes. This leaves a deficit of 7.6×10^6 kmol, suggesting a significant source of TN to the Lower Lakes other than from atmospheric deposition, the Lower Murray or the Eastern Mt Lofty Ranges. Dinitrogen fixation by cyanobacteria is a likely additional source of TN to the Lower Lakes as they have a long history of cyanobacterial blooms (Francis 1878, Codd et al. 1994). Strong evidence that cyanobacteria were fixing significant amounts of N comes from two sources. Firstly, there was often a strong drawdown of FRP in the Lower Lakes, even after NO_x had become depleted (Fig. 2). Secondly, the NO_x :FRP ratio in both the Lower Murray and the Lower Lakes were generally well below the Redfield ratio of 16, yet there was a substantial increase in the total N:P ratios in the Lower Lakes compared to the Lower Murray (Fig. 14). Given that there was no enrichment of P relative to N in the sediment we can rule out a preferential loss of P compared to N to the sediment as an explanation for the increased N:P ratios. This suggests that there is assimilation of N from a source other than dissolved fixed N and we suggest the TN deficit is filled by N_2 fixation, which on an annual basis normalised to the area of the lake is equal to $0.55 \text{ mol N m}^{-2} \text{ year}^{-1}$, and is in the upper range of $0.014\text{--}0.65 \text{ mol N m}^{-2} \text{ year}^{-1}$ observed for eutrophic lakes (Howarth et al. 1988). Groundwater remains another possible source of N and P. However, there are currently no data available for either the groundwater flux or the nutrient content of groundwater in the vicinity of the Lower Lakes. We note also that denitrification is likely to be a substantial sink for N, and therefore the rate of N fixation given here can only be considered a net rate, in reality the gross rates could be higher.

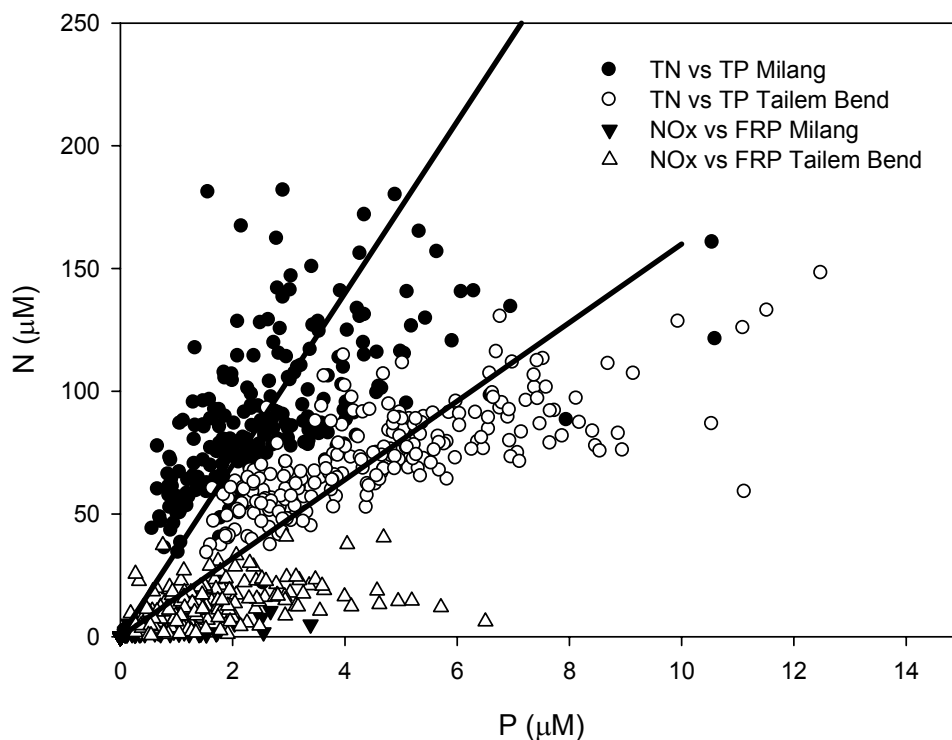


Figure 14. Plots of NO_x versus FRP and TN versus TP for Taillem Bend on the Lower Murray and Milang on the Lower Lakes. Solid lines denote N:P ratios of 16 and 35.

4.4. Silicon

There was a substantial retention of Si within the Lower Lakes over the study period, although the proportion of the incoming load retained was generally much lower than for FRP and NO_x . A strong retention of Si in reservoirs has been observed in Europe and there is concern that this

may be significantly reducing the export of Si relative to N and P. This has been suggested to lead to an increase in nuisance algal blooms at the expense of diatoms (which have a high Si requirement) in coastal waters (Humborg et al. 2000). Within the Lower Lakes, Si concentrations were generally well in excess of NO_x , which makes it very unlikely that Si approached limiting concentrations, given the Si:N growth requirement of ~ 1 for diatoms (Turner 2002). Similarly, the export of Si from the Lower Lakes was generally higher than N by a factor of at least 10. Despite extensive damming and water storage in the Murray-Darling Basin, there is still a relatively high export of Si compared to other nutrients, and it is unlikely to be limiting to diatom growth.

4.5. The Lower Lakes as a nutrient modulator

A budget of N and P for the 17 year study period is shown in Figure 15. It can be seen that the Lower Lakes acted as a strong modulator for both N and P in two respects. Firstly, the lakes assimilated inorganic nutrients (NO_x and FRP) and exported them in organic forms (such as TKN, which is predominantly organic nitrogen given that NH_4^+ was generally low). Secondly, there was a substantial increase in the TN:TP ratio from ~ 15 in the incoming waters up to ~ 30 in the waters leaving the lakes. The net assimilation of inorganic nutrients into an organic form suggests the system is generally net autotrophic (Smith et al. 1991). The inferred high N fixation rates also suggest a strong net autotrophic demand for nutrients.

The observation that the Lower Lakes are net importers of inorganic nutrients and exporters of organic forms contrasts with the generalised view of Australian reservoirs given by Harris (2001), who concluded that DON and TKN are consumed and NO_x is exported. We note that this conclusion was based on relatively deep storages compared to the Lower Lakes and suggest the discrepancy arises as a consequence of different reservoir geometry and also outlet mechanism. In deeper stratified reservoirs where the net heterotrophic bottom waters are released, one would indeed expect a consumption of organic forms of nutrients and a production of inorganic forms. In a large shallow system such as the Lower Lakes, there is a much greater potential for net autotrophic metabolism in the well mixed water column and hence conceptually one would expect a consumption of inorganic nutrient forms and a corresponding release of organic forms. Thus, any generalisation about the role of reservoirs in nutrient cycling should be tempered against their geometry and function.

Given that the material exported from the Lower Lakes was predominantly in an organic form, one would expect the initial metabolic response of the receiving coastal and estuarine waters to be heterotrophic. Thus, rather than a rapid algal bloom being associated with waters released from the Lower Lakes, one would expect an initial response in zooplankton and bacterial growth, followed by a reassimilation of the released nutrients into algal biomass. The relative enrichment in N over P that occurs in the Lower Lakes is also fortuitous because coastal waters are generally considered to be limited by N rather than P. Thus, the organic material released from the Lower Lakes is also likely to be of a high nutritional quality for marine food-webs. In this context we note that the volume of water released from the Lower Lakes over the past decade has been very low due to drought and high rates of water extraction from the river system. This has most likely resulted in substantially reduced loads of organic material entering the adjacent lagoonal system (the 'Coorong') and coastal waters. The impact of reduced loads on the local food-webs remains to be determined.

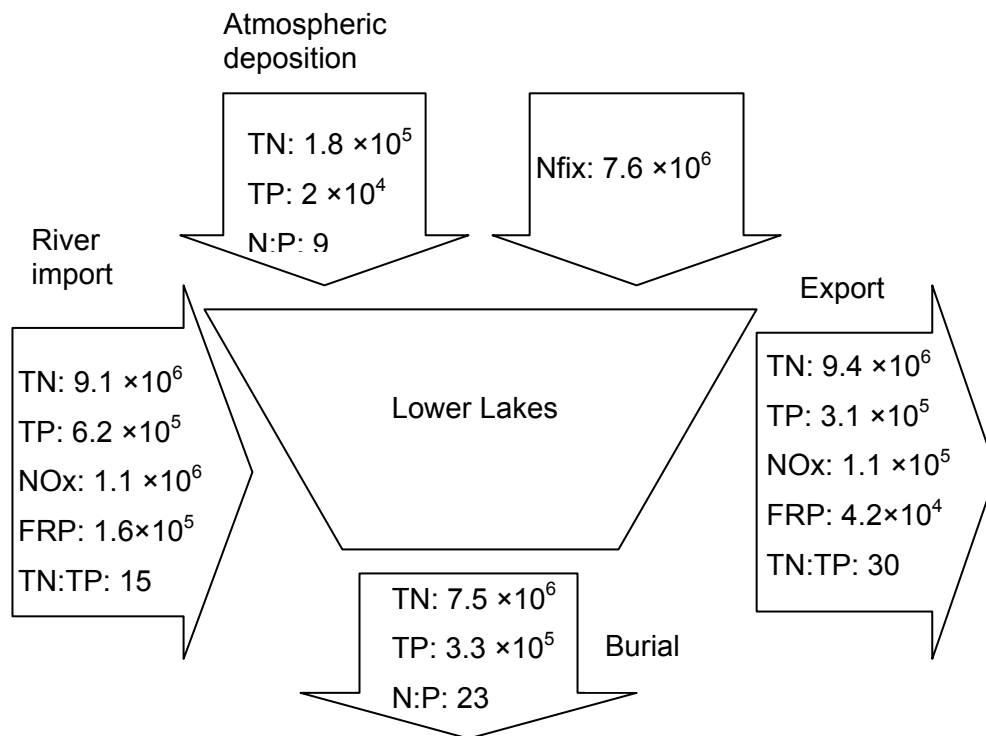


Figure 15. A budget for N and P in the Lower Lakes spanning the years 1979 to 1996. Quantities shown are total for the 17 year study period with units in kmol.

4.6. Salt export from the Lower Lakes

There was a considerable input of salts to the Lower Lakes from an unknown source, amounting to 42% of the total input from the Lower Murray for Na^+ . By far the largest export of salts from the Lower Lakes occurred in 1983 associated with the flood following one of the worst droughts on record. This dynamic nature of salt export from the Lower Lakes has some similarities to the one of the Lower Murray. As for the Lower Lakes, the peak salt export from the lower sections of the River Murray occurs in the months following floods (Jolly 1996). Changes in groundwater–surface water interactions between floodplains and the river appear to be the primary mechanism for the increased salt export following floods (Lamontagne et al. 2005b). Due to a combination of processes (see review in Jolly 1996), floodplains (as opposed to the river channel) are often the discharge zone for many regional and local groundwater systems along the Lower Murray. Much of the groundwater in the floodplains is also highly saline because of efficient groundwater use by phreatophytes and high evaporation rates due to shallow water tables (Jolly 1996). However, following floods, hydraulic gradients are temporarily reversed and discharge of floodplain groundwater to the river occurs. For example, at the Chowilla Floodplain, the salt load to the river remained elevated for 18 months following a medium flood. Because of the raised lake levels caused by the barrages, a high proportion of groundwater discharge also probably occurs in floodplains at the margins of the Lower Lakes rather than into the lakes themselves. This is consistent with the widespread occurrence of halophytic vegetation in the lakes' floodplain. Thus, wash-off of surface salts and the reversal of hydraulic gradients in floodplains during and following floods may increase the salt export from

the Lower Lakes. Groundwater–surface water interactions in the Lower Lakes region are not well known and require further investigation.

The trends in salt export to the Lower Lakes may have also been influenced by the commissioning of salt interception schemes upstream in the river basin during the study period. Due to concerns about rising salinity levels in the River Murray compromising the water supply from Adelaide (Murray-Darling Basin Commission 1999), a number of saline groundwater interception schemes were implemented during the study period (Murray-Darling Basin Commission 2003), which may have reduced the amount of salt exported to the Lower Lakes. However, there was no obvious declining trend in the concentration of major ions at Taillem Bend or in the Lower Lakes over the study period (Fig. 9), especially when compared to the variability in concentrations between flood and baseflow events.

Another possible source of salts is leakage from the ocean through the barrages. The water level of the Lower Lakes is only held ~0.5 m higher than sea level, and periodic tidal and storm surges result in the sea level occasionally being higher than the lake level. As such, a certain degree of seawater intrusion into the Lower Lakes is inevitable. An insight into the relative contributions of these sources of the salts into the Lower Lakes can be obtained from inspection of the ratios of the major ions in the Lower Lakes (Fig. 6). In general the ratio of the major ions to chloride in the Murray-Darling River is slightly more elevated than in seawater. This is also reflected in the Lower Lakes, possibly supporting the hypothesis that the dominant supply of salts to the Lower Lakes is from the Lower Murray and its associated groundwater, rather than from seawater leakage. Further work is, however, required to confirm this hypothesis.

Conclusion

The Lower Lakes altered between periods of net autotrophy and net heterotrophy, but were on average net heterotrophic. We suggest the dissolved organic carbon entering the Lower Lakes is relatively refractory owing to high residence times within reservoirs in the highly modified catchment. The Lower Lakes acted as a strong modulator of nutrients entering from the River Murray, retaining inorganic forms and releasing them in an organic form. Future studies should investigate the bioavailability of organic carbon entering and leaving the Lower Lakes under a range of flow conditions. The Lower Lakes were a large net source of nitrogen and we suggest high nitrogen fixation rates are occurring in the Lower Lakes. Further work is required to measure relative rates of nitrogen fixation rates and denitrification. The Lower Lakes were also a substantial source of salts and we suggest this most likely arose from saline groundwater entering the lakes. Further studies on the hydrology and geochemistry of the groundwater in the region are required to further investigate this hypothesis.

There are significant uncertainties in the budgets derived in this study because of:

- Modelled as opposed to measured in- and outflow from the lakes;
- A bias towards shoreline as opposed to offshore sampling stations.

The error on the hydrological fluxes is probably more significant during low flow conditions because of a greater uncertainty in Lower Murray inflow rates to the lakes, and the unknown contribution of groundwater discharge and leakage from the barrages. It is difficult to assess the bias caused by the lack of offshore monitoring station because there has been limited offshore sampling of the Lower Lakes historically. However, comparison of on- and offshore element and nutrient concentrations have been undertaken recently (K. Aldridge, unpublished data). Despite these shortcomings, the trends in element and nutrient export between high and low flow years were significant and repeatable and provided useful insights on the role of the Lower Lakes in nutrient export to downstream systems.

Further work is required to follow up the observations and hypotheses made here and we make the following suggestions for future research:

- To improve the hydrological flux estimates for the Lower Lakes, especially during low flow conditions;

- To measure the bioavailability and composition of dissolved organic carbon entering and leaving the Lower Lakes, and how this changes over flow regime and water source;
- To measure internal nutrient cycling processes such as nitrogen fixation and denitrification to help constrain the nitrogen budget for the Lower Lakes;
- To identify the sources of salt, and to understand salt cycling between the Lower Lakes and surrounding floodplain and lacustrine wetland systems.

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