Sources and fate of nutrients in a subtropical reservoir

Michele A. Burford¹, Susanne A. Green¹,
Andrew J. Cook², Suzanne A. Johnson³,
Jason G. Kerr⁴, Katherine R. O'Brien⁵

¹Australian Rivers Institute, Griffith University, Nathan, Queensland 4111, Australia

²EDAW AECOM, Level 6/171 George Street, Brisbane, Queensland, 4000, Australia

³seqwater, 240 Ann St, Brisbane, Queensland 4002, Australia

⁴Department of Geography, Trent University, Peterborough, Ontario, Canada

⁵School of Chemical Engineering, the University of Queensland, St Lucia,
Queensland 4072, Australia

Running head: Nutrient source and fate in reservoirs

Corresponding author:

¹Michele Burford

Australian Rivers Institute

Griffith University, Nathan 4111, Australia

Email: m.burford@griffith.edu.au

Phone: +61 7 3735 6723, Fax: +61 7 3735 7615

Keywords: N, P, reservoir, river, nutrient budget

ABSTRACT

This study examined the sources and fate of nutrient inputs from two principal tributaries to the eutrophic subtropical Wivenhoe reservoir: an unregulated river and a dammed river with regular releases, during a period of declining reservoir water levels. Nutrient budgets were constructed over a period of 6 years, and combined with short-term data on nutrient concentrations and forms, and $\delta^{15}\text{N}$ stable isotope data. Our study found that over a 6 year period, there was net retention of phosphorus (P) in the reservoir, with 60% of inputs retained. Most of the P input load came from the unregulated river, with an agricultural catchment, during periods of high flow. During one event half of the total TP load from the unregulated river in the study period was delivered in only 12 days. Much of the P was dissolved inorganic P (DIP) and was derived from high P concentrations in soils and sediments. This highlights the importance of appropriate catchment management practices to reduce P losses from terrestrial systems because retention of P in reservoir sediments reduces the availability of this nutrient for agricultural production. In contrast, there was negligible retention of nitrogen (N). The unregulated river was an important source of N derived from N fixation in the river and adjacent soils, while the source from the dammed river was mostly reprocessed N. The high retention of P relative to N is consistent with relatively higher accumulation of P in sediments.

Introduction

Almost 3% of the world's land surface area is covered by artificial lakes and reservoirs (Friedl and Wüest 2002). This has increased the residence time of river waters by a factor of three. In regions such as tropical southeast Asia where rainfall is high, and there is a high density of human population, artificial lakes and reservoirs comprise by far the greatest area of inland waters. The damming of rivers to create water storages or reservoirs results in considerable modifications in nutrient dynamics, as well as plant and animal species composition (Bosch and Allan 2008). This is due to changes in geomorphology, water depth, water residence time and resulting vertical stratification.

Reservoirs are often sinks for phosphorus (P), and to a lesser extent nitrogen (N), due to higher residence times increasing sedimentation and burial rates compared with rivers (Sherman et al. 2001, Friedl and Wüest 2002, Bosch and Allan 2008). Indeed, a global study of N removal found that reservoirs play a major role in N removal per unit area per year (Harrison et al. 2009). In terms of P, there is increasingly a global shortage of P fertilizer reserves worldwide for agricultural purposes (Vaccari 2009). Hence the accumulation of P in reservoirs reduces P availability for agricultural production, as well as fuelling excessive algal production in lentic systems (Schindler 1977).

Determining the fate of nutrients in lentic systems is a challenging task. Studies may use short-term flux measurements, e.g. ^{15}N - and ^{32}P - uptake experiments, at limited spatial scales to make inferences about how whole systems, such as reservoirs and rivers, function at greater spatial and temporal scales (e.g. Burford et al. 2006).

Another approach is to combine nutrient concentrations, loads, and ratios, flow and

biomarker data, e.g. stable isotopes, with greater spatial and temporal resolution to provide multiple lines of evidence to determine the sources and fate of nutrients.

Stable isotopes of N, for example, have been used to infer the dominance of processes such as N fixation and internal N recycling (Fry 2006), while N:P ratios can infer nutrient limitation (Redfield 1958, Sterner et al. 2008).

Insights into how damming of rivers has modified nutrient processes are mostly based on temperate systems, which have cold, wet winters and warm, dry summers. In contrast, tropical and subtropical areas have high rainfall that falls mostly in the summer months. To accommodate the high inflows and minimize flooding downstream, reservoirs in the tropics and subtropics are typically larger with longer water residence times (Jones and Poplawski 1998). This has the potential to increase the retention of nutrients within reservoirs (Yeasted and Morel 1978), increasing algal blooms in the system.

The purpose of this study was to assess the importance of a subtropical reservoir in modifying nutrient processes in a river system, through determining the sources and fate of N and P in a large subtropical reservoir and its two main tributaries: an unregulated river and a dammed river with regular releases.

Methods

This study used a combination of diverse datasets on nutrient concentrations, forms and loads, and stable isotope ratios, in large reservoir and its two main tributaries to develop a 6 year monthly budget of N and P across the reservoir, and assess the source and form of those nutrients.

Study site

The study area was Wivenhoe reservoir (27.39219°S, 152.61062°E), and two of its principal tributaries: the upstream Upper Brisbane River (UBR) and the Stanley River which is impounded, i.e. Somerset reservoir. They are located in subtropical, southeast Queensland, Australia (Fig. 1). Wivenhoe reservoir is a major source of drinking water to the city of Brisbane, with water continuously discharged for treatment downstream. Wivenhoe Reservoir holds 1,165,000 ML at capacity, has a mean depth of 10.8 m, and covers an area of 109 km². It is characterized as eutrophic and monomictic, i.e. stratified in the warmer summer months with an autumn overturn and well-mixed during the winter months (Burford and O'Donohue 2006). Wivenhoe reservoir also receives water, via the Stanley River, from controlled releases from Somerset reservoir (380,000 ML at capacity). The catchment for Somerset reservoir is 1330 km². The UBR has a catchment of 5554 km² and has been classified as a river with highly unpredictable and intermittent flow typically in summer (Kennard et al. 2010).

Long-term water quality in reservoir

Water samples were collected monthly at the surface and bottom (1 m from the sediment) at the dam wall (Site 1) in Wivenhoe reservoir, and upstream at the dam wall in Somerset reservoir from January 2002 to December 2008. Subsamples were stored on ice for total N (TN) and P (TP) analysis. Subsamples were also filtered through 0.45 µm membrane filters before being frozen for nitrite + nitrate (NO₂ + NO₃), ammonium (NH₄⁺) and dissolved inorganic P (DIP) analyses. Dissolved oxygen concentrations were also determined in the bottom waters using a datalogger (YSI 6920 Sonde).

Low flow sampling

Sampling transects were conducted at 7 sites in transect down the UBR and one tributary, Cressbrook Creek in the austral summer. One was in November/December 2005 and the other in March 2006 after a 4-year drought (mean rainfall of 633 mm p.a. compared with 790 mm p.a. for previous 20 years, www.bom.gov.au) (Fig. 1). The drought resulted in very low flow in the UBR (Fig. 2b, <http://www.nrw.qld.gov.au/water/>). All sites had shallow pools with little or no flow.

Triplicate surface water samples were collected at each UBR site using 1-L sample bottles, sampling just below the surface. Subsamples were taken for nutrients, total suspended solids (TSS), $\delta^{15}\text{N}$ values (particulate organic matter (POM), total dissolved N (TDN), and chlorophyll *a* analyses. At each site, light profiles through the water column were measured using a 4 pi sensor (Licor) and physical and chemical parameters (temperature and conductivity) were recorded using a profiler (YSI 6920 Sonde) at the surface and bottom of the water column. The euphotic depth was calculated as 1% of surface light based on the light profiles.

Two sampling transects were also conducted at 6 sites (Sites 1, 2, 3, 4, 5, 6) down the length of Wivenhoe reservoir (15% full supply) during the drought (December 2005 and March 2006) (Fig. 1). Triplicate surface (just below water surface) and bottom (1 m from sediment surface) water samples were collected at each site using a Van Dorn (3.2 L Vertical Beta Plus) water sampler for the same range of parameters as the river sites. At each site, light profiles, and physical and chemical variables were measured as per the river sites.

In November 2005 and March 2006, sediment samples were taken for TN and TP concentrations, and $\delta^{15}\text{N}$ values in the river and reservoir. Triplicate cores were taken at each sampling site and 2-cm deep undisturbed surface sediment retained. Triplicate dry surface soil samples were also taken on the slopes above the river channel. To gain greater insights into the P binding in the sediments, six replicate sediment grabs (2-cm surface slices) were also taken at sites 1, 1a, 2, 2a, 3, 4 (Fig. 1) in February 2008 for sequential extractions and determination of aluminium (Al) and iron (Fe) concentrations. All samples were kept frozen until analyzed.

Flow event sampling

A substantial flow event occurred in the UBR in early February 2008 (Fig. 2b). Additionally, at this time there were large water releases from Somerset reservoir into the Stanley River which entered Wivenhoe reservoir. This increased the reservoir supply level from 15 to 25% over the month of February 2008. Three sites (Crossing 12, Arababy and Gregors) on the UBR were sampled on 12 February 2008 (Fig. 1) during a substantial flow event in the river (Fig. 2b). Sampling protocols were the same as for the low flow sampling, but light profiles were not taken. At one of these sites, Gregors, 5 water samples were also automatically collected using a refrigerated autosampler triggered by the change in height of the depth gauge at the height of the flow event (5 February 2008) for TN, TP and TSS. Water flow rates were measured at a gauging station at Gregors.

On 15 February 2008, a transect was sampled from just above the confluence of the Stanley River (which receives discharges from Somerset reservoir) and the UBR

(UBR confluence) downstream to sites 5, 4 and 2a (adjacent to site 2) in Wivenhoe reservoir (Fig. 1). The same sampling design was used for the water column as for the drought sampling, however $\delta^{15}\text{N}$ values were only measured in the POM samples.

Analyses

Water samples for TN and TP were stored at -20°C until analyzed using a persulfate digestion process and standard colorimetric methods (American Public Health Association, 1995). Water samples for NH_4^+ , $\text{NO}_3 + \text{NO}_2$ and DIP were filtered through $0.45\text{-}\mu\text{m}$ cellulose NO_3 filters, and frozen until analyzed using standard colorimetric methods (American Public Health Association, 1995).

For total suspended solids (TSS), known volumes of water were filtered through pre-weighed, pre-combusted Whatman GF/F glass fibre filters, dried at 60°C , and reweighed. These filters were retained for stable isotope analysis. The filtrate was also collected and freeze dried to a powder, then analyzed for $\delta^{15}\text{N}$ of TDN and percentage N on a mass spectrometer (GV Isoprime, Manchester UK). Filters were also analyzed for $\delta^{15}\text{N}$ on a mass spectrometer.

For chlorophyll *a* concentrations, known volumes of water were filtered through glass fibre filters (Avantec GF75). The filters were stored at -80°C until analyzed. Samples were extracted by sonicating filters for 1 min in cold 100% acetone, and measured either spectrophotometrically or spectrofluorometrically (Jeffrey and Welshmeyer 1997).

Sediment and soil material were oven dried at 60⁰C for 24 h then ground to a fine powder then analyzed for $\delta^{15}\text{N}$, and percentage N on a mass spectrometer (GV Isoprime, Manchester UK).

Sediment P, Al, Fe

Al and Fe concentrations were determined on Wivenhoe sediment samples after sequentially extracting P fractions (Psenner et al. 1988). Prior to extraction, sediment and soil samples were first sieved through a 63- μm sieve. The sequential extractions involved using NH_4^+ chloride, followed by sodium bicarbonate-sodium dithionite (BD-P), followed by sodium hydroxide (NaOH). Al and Fe concentrations were determined on the sodium hydroxide (Al_{NaOH}) and BD-P fractions (Fe_{BD}), respectively, using flame atomic adsorption spectrophotometry (GBC Avanta Sigma, Melbourne) (Kopáček et al. 2005). Sediment TP was also determined on the fractions using an autoanalyzer.

N and P budget calculations

Monthly discharge of TN and TP from the UBR and Wivenhoe and Somerset reservoirs were calculated for the period January 2002 to July 2008 from the product of monthly water discharge (ML), and concentrations of TN and TP ($\text{mg L}^{-1} = \text{kg ML}^{-1}$) at the dam wall sites. The monthly discharge of TN and TP from the UBR were determined by adding the daily TN and TP loads, which were calculated from the daily flow-rate, using the relationships developed by Kerr (2009) for data from Gregor's Crossing (UBR) over the period 2003-2004:

$$\log_{10}\text{TP load} = 1.090 \pm (0.066 \text{ SE}) * \log_{10}\text{flow} - 1.004 \pm (0.178 \text{ SE}) \quad R^2 = 0.86 \quad (1)$$

$$\log_{10} TN \text{ load} = 1.048 \pm (0.037 \text{ SE}) * \log_{10} flow - 0.064 \pm (0.100 \text{ SE}) \quad R^2 = 0.95 \quad (2)$$

where *flow* is daily flow rate (ML/day), *TP* is the load of P (kg d⁻¹), and *TN* is the N load (kg d⁻¹). Equations 1-2 can be re-written in the form:

$$TP = A_1 flow^{B_1} \quad (3)$$

$$TN = A_2 flow^{B_2} \quad (4)$$

where $A_1 = 10^{-1.004 \pm 0.178} = 0.0991$ [0.066-0.15], $B_1 = 1.09 \pm 0.066$, $A_2 = 10^{-0.064 \pm 0.100} = 0.863$ [0.69-1.1], $B_2 = 1.048 \pm 0.037$, and the units and other symbols are defined as before.

Equations 1-4 are non-linear in flow; hence using discharge data on shorter or longer time-scales than the daily time step used to develop these equations will result in errors.

Discharge data were available from January 2002 to July 2008, with the exception of the period June 2006-August 2007 when the gauge was malfunctioning. There was no or low flow through that period except for one small event. Data were recorded every two hours for very low or no flow, every four hours for low flow, increasing to every 20 min for very high flow. Daily flow-rate was integrated from sub-daily discharge data, assuming constant flow between the mid-points between each measurement.

Uncertainty analysis

Since the off-take depth for reservoir discharge was typically mid-depth, surface and bottom concentrations of TP and TN, were used to provide an upper and lower bound for the mass of nutrients discharged from the reservoirs. Uncertainty in monthly discharge volume from the reservoirs was neglected.

The uncertainty in the TN and TP predicted from Equations 3-4 was determined using sum of squares of errors, i.e.

$$\delta y^2 = \left(\frac{\partial y}{\partial x_1} \right)^2 \delta x_1^2 + \left(\frac{\partial y}{\partial x_2} \right)^2 \delta x_2^2 + \dots + \left(\frac{\partial y}{\partial x_n} \right)^2 \delta x_n^2 \quad (5)$$

where y is the dependent variable (i.e. TP or TN), x_1-x_n are the independent variables or parameters, and δ indicates absolute error. Hence the absolute error in TP or TN will depend on the how much the discharge rate ($flow$) and the constants affect the nutrient load ($\partial y / \partial x_i$), and that absolute error in that variable (δx_i). Application of the error relation in Equation 5 to Equations 3-4 yields the following relationship for TP, and a corresponding relationship for TN calculated from the discharge:

$$\frac{\delta TP}{TP} = \sqrt{\left(\frac{\delta A_1}{A_1} \right)^2 + B_1^2 \left(\frac{\delta flow}{flow} \right)^2 + (\ln(flow))^2 \delta B_1^2} \quad (6)$$

Replacing the A_1 , B_1 with A_2 , B_2 in Eqn 6 yields the uncertainty for TN. Equation 6 indicates that the uncertainty in nutrient loads increases at higher flow-rates. The relative uncertainty in the flow rate of the UBR ($\delta flow / flow$) was assumed to be 5%.

RESULTS

Hydrology

Wivenhoe reservoir water volume decreased from full supply in the beginning of the study (2002) until 2007 (16% of full supply), with the exception of a minor increase in 2004 (Fig. 2a). In 2008, the reservoir volume increased again. The increases in volume were largely the result of water flow in the UBR (Fig. 2b). In other years, there was little flow in the UBR. Water releases from Somerset reservoir decreased until 2007, when it increased spasmodically (Fig. 2c). Releases from Wivenhoe decreased consistently over the study, but was always higher than releases from Somerset reservoir.

Long-term nutrient concentrations and nutrient budgets

Monthly TN and TP input loads from UBR to Wivenhoe reservoir were less than those from Somerset reservoir over much of the 6 year study, corresponding with extended periods when the flow rates in UBR were low (Fig. 3 a, b). However, during flow events, the proportion of TN and TP input loads from UBR was substantially higher. Indeed, half of the total TP delivered by UBR to Wivenhoe reservoir occurred on days where the flow rate was greater than 3000 ML d^{-1} , which corresponds to only 12 days out of the 2374 day study period (Fig. 4a). This reflects the episodic nature of flow in the river, and drought conditions that dominated the study period; almost 8 % of the total rainfall over the 6 years was delivered on a single day, 6 March 2004. Because the coefficients relating TN load to flow in Eqns 2, 4 were lower than those for TP in Eqns 1, 3, the delivery of TN was slightly less biased towards large flow events. However, half of the TN was delivered for flows above 2000 ML d^{-1} , i.e. over only 17 days of the study.

The net TN and TP monthly load retention in Wivenhoe was determined based on inputs from UBR and Somerset minus discharge from Wivenhoe (Fig. 5 a, b). Retention of TP was close to zero over much of the study, but increased substantially during the two periods of higher flow in the UBR (Fig 2a). There was typically negative retention of TN over the low flow conditions that characterised much of the study period, with the exception of the two periods of higher flow in the UBR. The uncertainty in the load data was higher for TN than for TP due to higher variability in TN concentrations between the surface and bottom in the two reservoirs than TP (Fig. 5a,b, Table 1). Over the 6 years of the study, net retention of TP was positive (58%), but TN retention was less than the uncertainty in the data (Table 1).

The TN:TP ratios in inflow water from UBR were consistently lower than that of Somerset reservoir (Fig. 6). The discharge ratio from Wivenhoe was highly variable but typically higher than inputs from Somerset.

There were annual summer peaks in NH_4^+ and DIP in bottom waters at the dam wall in Wivenhoe reservoir from 2002 to 2008 (Fig. 7). This coincided with low dissolved oxygen concentrations in bottom waters. NH_4^+ and DIP concentrations decreased substantially in bottom waters after the autumn water overturn, while concentrations in surface waters were typically near detection limits ($0.002 \mu\text{g L}^{-1}$). In contrast, $\text{NO}_2 + \text{NO}_3$ concentrations in bottom waters fluctuated throughout the year, while in surface waters, concentrations were typically highest in the winter months. The mean molar DIN:DIP ratios in bottom waters were 65:1.

Water quality transects in low flow conditions

During low flow conditions, transect sampling occurred in both November 2005 and March 2006. Sampling sites on the UBR varied in depth from 0.5 to 1.5 m with light penetration to the sediment surface (Table 2). Wivenhoe reservoir sites ranged in depth from 3.5 m at the upstream site to 23.0 m at the dam wall site with a euphotic depth ranging from 1.8 to 4.9 m (Table 2). Specific conductivity was $1.83 \pm 0.71 \text{ ms cm}^{-1}$ in the river and $0.37 \pm 0.5 \text{ ms cm}^{-1}$ in the reservoir. Concentrations of other variables, i.e. nutrients, chlorophyll *a* and TSS, were similar between the UBR and Wivenhoe reservoir. TN and TP concentrations were typically higher at the bottom than the surface at sites 1 to 4, with less difference between surface and bottom at the upstream sites 5 and 6. TSS and chlorophyll *a* concentrations were higher upstream than downstream. DIN (NH_4^+ and $\text{NO}_2 + \text{NO}_3$) concentrations were typically higher but highly variable in the bottom waters in Wivenhoe reservoir than in the UBR (Table 2). DIP concentrations fluctuated between sites with no obvious trends between depths or sites.

TP concentrations were higher in the adjacent catchment soils than in the sediment at upstream river sites but became more similar further down the UBR (Table 3). TN concentrations were highly variable in both the soil and sediment in the UBR. The molar N:P ratios in the UBR and reservoir sediment, and adjacent soil, were always relatively low. The $\text{Al}_{\text{NaOH}}:\text{Fe}_{\text{BD}}$ molar ratios in the sediments of Wivenhoe reservoir were 1.1 to 2.1 in the upstream sites and 0.5 at the dam wall (Table 3). In contrast, $\text{Al}_{\text{NaOH}}:\text{P}_{(\text{H}_2\text{O}+\text{BD})}$ molar ratios were variable between sites.

$\delta^{15}\text{N}$ values in the adjacent soil were higher than in the sediment in the UBR, although values were highly variable among sites (Fig. 8). $\delta^{15}\text{N}$ values in the sediment in

Wivenhoe reservoir were higher than those in the UBR. The $\delta^{15}\text{N}$ values for TDN and POM were lower in the UBR sites than in surface waters of the reservoir.

Water quality during high flow event in 2008

During the flow event in early February 2008 (Fig. 2b), specific conductivity in the UBR was lower (0.47 to 0.51 mS cm^{-1}) than during low flow conditions (0.98 to 3.03 mS cm^{-1}) (Table 4). A mean TN concentration of the samples collected automatically at Gregors Crossing at the peak of the flow was 2.38 mg L^{-1} , with a mean of $0.83 \pm 0.20 \text{ mg L}^{-1}$ at the three sites during the event, higher than during low flow (Table 4). It was similar at the UBR confluence. The percentage DIN, relative to TN, also increased during the flow event.

Mean TP concentrations in the UBR increased from 0.018 to 0.098 mg L^{-1} during low flow to 0.120 to 0.150 mg L^{-1} during high flow (Tables 3,4). The mean TP concentration of samples collected automatically at the peak of the flow at Gregors was 0.560 mg L^{-1} (Table 4). The mean over the three sites after the peak was 0.137 mg L^{-1} , higher than during low flow. It was similar to the UBR confluence. DIP concentrations and the %DIP, relative to TP, also increased substantially during high flow conditions throughout the UBR.

The mean TSS concentration collected automatically at the peak of the flow at Gregors was 697 mg L^{-1} (Table 4). Chlorophyll *a* concentrations were $3.8 \pm 0.2 \text{ } \mu\text{g L}^{-1}$ during high flow compared with $14.11 \pm 18.27 \text{ } \mu\text{g L}^{-1}$ during low flow conditions, while $\delta^{15}\text{N}$ ratios in the river POM were similar to low flow conditions (Fig. 8, Table 4).

By comparing the nutrient and other parameters at UBR confluence with the Stanley River data, it is possible to differentiate the contribution of UBR and Somerset reservoir to Wivenhoe reservoir during the high flow event (Table 4). TN, TP, TSS and chlorophyll *a* concentrations were all higher in the UBR than the Stanley River at the confluence, with TN being 4 to 5 times higher, TP being double and chlorophyll *a* being more than 10 times higher.

During the high flow event, TP and DIP concentrations increased in Wivenhoe reservoir, particularly at the upstream sites, compared with the low flow period (Tables 3,4). TN concentrations were not substantially higher but the proportion of NH_4^+ and $\text{NO}_3 + \text{NO}_2$ increased. TSS concentrations were also higher throughout the reservoir. $\delta^{15}\text{N}$ values for POM at the upstream site in Wivenhoe reservoir were lower than during low flow conditions and were comparable with the UBR sites.

Discussion

Our study showed that the UBR was the main contributor of N and P to Wivenhoe reservoir under high flow conditions. In the absence of significant inflows from the UBR, our study suggests that the dominant external nutrient source to Wivenhoe was the upstream reservoir, Somerset. However, in contrast to the UBR, the N:P ratios were considerably higher. Therefore during dry periods the N:P ratio entering Wivenhoe is higher, while the opposite is true in wet periods,. Much of the N and P was in particulate form, however, with DIN and DIP 25% and 24%, respectively, of the inflow water from Somerset and 26% and 46%, respectively, of the inflow from UBR (Kerr 2009).

There was net P retention in the reservoir over the 6 years of the study. This was largely driven by inputs of TP from UBR during a few major inflow events. However, the study period was characterized by drought with few periods of high flow in the upstream river. In higher flow periods, TP loads from the UBR to the reservoir would be even higher. Furthermore, while the study quantified only removal of P from the system (discharge from the reservoir), it did not account for all inflows; P would also have been delivered from direct land runoff and minor creeks. Hence this study will underestimate P retention within the reservoir.

Reservoirs typically result in P retention (Jossette et al. 1999, Bosch and Allan 2008). In our study, DIP concentrations were typically high in bottom waters during summer stratification when dissolved oxygen concentrations were low, suggesting net effluxes of P from the sediment. The $Al_{NaOH}:Fe_{BD}$ and $Al_{NaOH}:P_{(H_2O+BD)}$ molar ratios were lower than 3 and 25, respectively, consistent with P desorption from sediments (Kopáček et al. 2005). The contribution of bacterial remineralization is not known. The high DIN:DIP ratios in the bottom water (molar mean of 111:1), and low TN:TP ratios in the sediment, suggest greater N release in the sediment relative to P. Jossette et al. (1999) in a study of French reservoirs, also found substantially higher NH_4^+ than DIP fluxes from sediments.

The main source of P in the catchment was derived from the catchment soils. Neara Volcanic soils, which have high P concentrations ($1052 \pm 345 \mu g g^{-1}$), have previously been shown to dominate soils in this catchment (Douglas et al. 2007). A high proportion of the TP from UBR was DIP (Kerr 2009). The soils in this

catchment have high rates of DIP release when wet (Kerr et al. 2010a). Indeed, extended periods of drought increase the potential for sediments to release P into overland flow (Kerr et al. 2010b). Other studies have also measured a high proportion of DIP (~65%) relative to TP in rivers (Bramley and Roth 2002, Sherman 2001). This contrasts with studies that have shown that TP in rivers is mostly associated with the particulate load (Pailles and Moody 1992, Harris 1999; Sherman et al. 2001; Rahman and Al Bakri 2010). Additionally, in a review of nutrient biogeochemistry in Australian rivers, Harris (2001) suggested that the proportion of DIP remains relatively constant across land uses (10-30%), which is at odds with our findings. The solubility of soil P is controlled by the concentration of P in solution, the quantity of P in the soil that equilibrates with the solution, and the buffering capacity of the soil (McDowell et al. 2004). So it is not surprising that there are differences in the proportion of dissolved P between studies.

The high proportion of P input from the unregulated river highlights the need to reduce erosion processes and ensure adequate vegetation cover in this agricultural catchment in order to minimise P losses. Modification of catchments for agriculture has greatly increased terrestrial nutrient losses (Brodie and Mitchell 2005). Given the global shortage of P reserves for agriculture (Vaccari 2009), conserving P within the catchment is of increasing importance for agricultural yields.

The net monthly N budget indicates that N inputs were typically slightly lower than discharges during low flow conditions, with net N retention when N loads increased dramatically during periods of higher inflow from UBR. Over the entire study period, inflows of TN from the two major tributaries were balanced by TN discharged from

Wivenhoe. This suggests that over the duration of the study, little denitrification occurred. This contrasts with other studies that showed that denitrification and other losses within reservoirs can result in a high proportion of N being removed (Gruca-Rokosz et al. 2009, Harrison et al. 2009). There may be inputs via N fixation, but the ^{15}N ratios in the water column in our study were not indicative of N fixation (Fry 2006). This is consistent with findings in an adjacent reservoir, which found little evidence of N fixation despite the presence of N-fixing cyanobacteria (Burford et al. 2006).

N fixation appeared to be the key source of N to the river, and subsequently to Wivenhoe reservoir, as evidenced by the low $\delta^{15}\text{N}$ values in the sediment, and water column TDN and POM fractions in the river (Fry 2006). N fixers were also observed in the river, including symbiotic cyanobacteria within the aquatic plant, *Azolla*, and filamentous cyanobacteria, much of which are attached to the abundant macrophyte biomass (Kerr 2009). Other studies have shown that N fixation by cyanobacteria can be an important source of N in rivers, e.g. Amazon floodplain (Fiore et al. 2005).

As with DIP, there were high NH_4^+ concentrations in bottom waters of Wivenhoe reservoir in periods of summer thermal stratification (Burford and O'Donohue 2006) when dissolved oxygen concentrations were low. This suggests that sediment remineralization was also an important process generating NH_4^+ for algal growth, although availability may be limited until autumn water overturn.

In summary, this long term study showed that the unregulated UBR was the major contributor of P to Wivenhoe reservoir, accounting for 60 % of the total TP input over

a period of 6 years. Comparable loads of N were delivered from both the UBR and Somerset reservoir, and the inputs of N to Wivenhoe were balanced by discharges over the study period. The reservoir was a sink for P, but not N, and this principally due to P delivered by large inflow events in the unregulated upstream river. The mass of P retained over the study period was approximately equally to the mass of P delivered by the unregulated UBR.

Reducing P accumulation in reservoir sediments is important both in maintaining P availability for agricultural production, and preventing eutrophication of water supplies. Hence this study highlights the importance of appropriate catchment land-use and management practices to minimise sediment loss during rain.

Acknowledgments

We wish to thank Rob Dehayr (Queensland Department of Environment and Natural Resources) and Joanne Burton for flow data; Dan Wruck and his team (Queensland Health & Scientific Services) and Noreen Dejores for nutrient data; Rene Diocares for stable isotope data; Katherine O'Brien, Stephen Faggotter and seqwater staff for assistance with sampling; Gary Forsdike for sequential extraction data; seqwater for nutrient and flow data. Stephen K. Hamilton, Catherine Leigh, David Roberts, Peter Rothlisberg and anonymous reviewers provided helpful comments on the manuscript. The Australian Research Council, seqwater and Southeast Queensland Healthy Waterways Partnership provided financial support for this project.

References

- American Public Health Association (APHA) (1995) Standard Methods for the Examination of Water and Wastewater. 20th Edn, Greenburg AE, Clesceri LS, Eaton AD. (eds) American Public Health Association, Washington, D.C.
- Bosch NS, Allan JD. (2008) The influence of impoundments on nutrient budgets in two catchments of Southeastern Michigan. *Biogeochem* 87:325-338.
- Bramley RGV, Roth CH. (2002) Land use effects on water quality in an intensively managed catchment in the Australian humid tropics. *Mar Freshwat Res* 53:931-940.
- Brodie JE, Mitchell AW (2005) Nutrients in Australian tropical rivers: changes with agricultural development and implications for receiving environments. *Mar Freshwat Res* 56:279-302.
- Burford MA, McNeale KL, McKenzie-Smith FJ. (2006) The role of nitrogen in promoting *Cylindrospermopsis raciborskii* in a subtropical water reservoir. *Freshwater Biol* 51:2143-2153.
- Burford MA, O'Donohue MJ. (2006) A comparison of phytoplankton community assemblages in artificial and naturally mixed subtropical water reservoirs. *Freshwater Biol* 51:973-982.
- Douglas G, Palmer M, Caitcheon G, Orr P. (2007) Identification of sediment sources to Lake Wivenhoe, south-east Queensland, Australia. *Mar Freshwat Res* 58:793-810.
- Fiore MF, Neilan BA, Copp JN, Rodrigues JLM, Tsai SM, Lee H, Trevors JT. (2005) Characterization of nitrogen-fixing cyanobacteria in the Brazilian Amazon floodplain, *Water Res* 39:5017-5026.
- Friedl G, Wüest A. (2002) Disrupting biogeochemical cycles – Consequences of damming. *Aquatic Sci* 64:55-65.
- Fry B. (2006) Stable Isotope Ecology. Springer, New York.

- Gruca-Rokosz R, Tomaszek JA, Koszelnik P. (2009) Denitrification in the sediment of a eutrophic reservoir measured with the isotope pairing technique. *Oceanol Hydrobiol Studies* 38:75-81.
- Harris GP. (1999) Comparison of the biogeochemistry of lakes and estuaries: ecosystem processes, functional groups, hysteresis effects and interactions between macro- and microbiology. *Mar Freshwat Res* 50:791-811.
- Harris GP (2001) Biogeochemistry of nitrogen and phosphorus in Australian catchments, rivers and estuaries: effects of land use and flow regulation and comparisons with global patterns. *Mar Freshwat Res* 52: 139-149.
- Harrison JA, Maranger RJ, Alexander RB, Giblin AE, Jacinthe PA, Mayorga E, Seitzinger SP, Sobata DJ, Wollheim WM (2009) The regional and global significance of N removal in lakes and reservoirs. *Biogeochem* 93:143-157.
- Jeffrey SW, Welshmeyer NA. (1997) Spectrophotometric and fluorometric equations in common use in oceanography. In: Jeffrey SW, Mantoura RFC, Wright SW (eds), *Phytoplankton Pigments in Oceanography. Monographs on Oceanographic Methodology* No.10. UNESCO Publishing, Paris. pp. 597-615.
- Jones GJ, Poplawski W. (1998) Understanding and management of cyanobacterial blooms in sub-tropical reservoirs of Queensland, Australia. *Water Sci Technol* 37:161-168.
- Jossette G, Leporcq B, Sanchez N, Philippon (1999) Biogeochemical mass balances (C, N, P, Si) in three large reservoirs of the Seine Basin (France). *Biogeochem* 47:119-146.
- Kennard MJ, Pusey BJ, Olden JD, Mackay SJ, Stein JL, Marsh N. (2010) Classification of natural flow regimes in Australia to support environmental flow management. *Freshwater Biol* 55:171–193.

- Kerr JG. (2009) The Transformation of Catchment Phosphorus in Dry Subtropical River Systems. PhD Dissertation, Griffith University.
- Kerr JG, Burford MA, Olley J, Udy J. (2010a) Phosphorus sorption in soils and sediments: implications for phosphate supply to a subtropical river in southeast Queensland, Australia. *Biogeochem* 102:73-85.
- Kerr JG, Burford MA, Olley J, Udy J. (2010b) The effects of drying on phosphorus sorption and speciation in subtropical river sediments. *Mar Freshwater Res* 61:928-935.
- Kopáček J, Borovec J, Hejzlar J, Ulrich K, Norton SA, Amirbahman A. (2005) Aluminium control of phosphorus sorption by lake sediments. *Environ Sci Technol* 39: 8784-8789.
- McDowell RW, Biggs BJF, Sharpley AN, Nguyen L. (2004) Connecting phosphorus loss from agricultural landscapes to surface water quality. *Chem Ecol* 20:1-40.
- Pailles C, Moody PW. (1992) Phosphorus sorption-desorption by some sediments of the Johnstone Rivers Catchment, North Queensland. *Aust J Mar Freshwat Res* 43:1535-1545.
- Psenner R, Bostrom B, Dinka M, Pettersson K, Puckso R, Sager M (1988) Fractionation of phosphorus in suspended matter and sediment. *Arch Hydrobiol, Beih, Ergeb Limnol* 30:98-103
- Rahman AKMM, Al Bakri D. (2010) Contribution of diffuse sources to the sediment and phosphorus budgets in Ben Chifley Catchment, Australia. *Environ Earth Sci* 60:463-472.
- Redfield AC. (1958) The biological control of chemical factors in the environment. *Am Sci* 46:205-222.

- Schindler DW (1977) Evolution of phosphorus limitation in lakes: Natural mechanisms compensate for deficiencies of nitrogen and carbon in eutrophied lakes. *Science* 195:260-262.
- Sherman BS, Ford PF, Hatton P, Whittington J, Green D, Baldwin D, Oliver RL, Shiel R, van Berkel J, Beckett R, Grey L, Maher W. (2001) The Chaffey Dam Story – Final report to the CRC for Freshwater Ecology. Canberra, Australia.
- Sterner RW, Anderson T, Elser JJ, Hessen DO, Hood JM, McCauley E, Urabe J. (2008) Scale-dependent carbon:nitrogen:phosphorus seston stoichiometry in marine and freshwaters. *Limnol Oceanogr* 53:1169-1180.
- Vaccari DA (2009) Phosphorus famine: The threat to our food supply. *Scientific American*, June 2009, p. 36.
- Yeoast JG, Morel FMM (1978) Empirical insights into lake response to nutrient loadings, with applications to models of phosphorus in lakes. *Environ Sci Technol* 12:195-201.

Figure Legend

Figure 1: Map of study site in southeast Queensland, Australia. Sampling sites in the Upper Brisbane River (R) and Wivenhoe reservoir are shown. The following sites in the river and reservoir were sampled during the high flow event: Crossing 12, Arababy, Gregors, UBR confluence, Stanley River (R), and sites 2a, 4 and 5 in Wivenhoe reservoir.

Figure 2: (a) Daily Wivenhoe reservoir volume (ML), (b) monthly water flow (ML mo^{-1}) at the gauging station at Gregors at Upper Brisbane River (UBR) and (c) monthly water releases (ML mo^{-1}) from Somerset reservoir into the Stanley River, and from Wivenhoe reservoir from 2002 to 2008.

Figure 3: (a) Total phosphorus (TP) and (b) Total nitrogen (TN) inputs (t mo^{-1}) to Wivenhoe reservoir from Upper Brisbane River (UBR) and Somerset reservoir from 2002 to 2008.

Figure 4: Proportion of the overall nutrient loads delivered by the Upper Brisbane River (UBR) over the study period (2002 – 2008), as a function of daily flow-rate for (a) total phosphorus (TP) and (b) total nitrogen (TN)

Figure 5: (a) Net total phosphorus (TP) and (b) total nitrogen (TN) retained (t mo^{-1} , $\pm$ calculated uncertainty) in Wivenhoe reservoir from 2002 to 2008, based on TN and TP leaving through outlet, and delivered from Upper Brisbane River and Somerset reservoir. Dashed line reflects zero net retention.

Figure 6: Molar nitrogen (N) and phosphorus (P) ratios in upper Brisbane River (UBR), Somerset and Wivenhoe reservoirs from 2002 to 2008. Dashed line is Redfield (1958) ratio 16:1.

Figure 7: (a) Ammonium (NH_4^+), (b) nitrate plus nitrite ($\text{NO}_3 + \text{NO}_2$), (c) dissolved inorganic phosphorus (DIP) and dissolved oxygen concentrations (mg L^{-1}) at the surface (S) and bottom (B) of the water column at site 1 at Wivenhoe reservoir from 2002 to 2008.

Figure 8: Mean ($\pm$ SD) $\delta^{15}\text{N}$ -nitrogen values in (a) total dissolved nitrogen (TDN); (b) particulate organic matter (POM) in the water column and (c) sediment in the upper Brisbane River (UBR) and Wivenhoe reservoir (WIV) sites from November 2005 and March 2006.

Table 1: Total nitrogen (N) and phosphorus (P) input, outputs and retention ($\pm$ uncertainty) for Wivenhoe reservoir from 2002 to 2008 (excluding June 2006-August 2007, when flow data were unavailable).

2002-2008	Total P load (t)	Mean monthly P load (t mo ⁻¹)	Total N load (t)	Mean monthly N load (t mo ⁻¹)
UBR input	40 (26)	0.6 (0.4)	289 (101)	4.5 (1.6)
Somerset input	21 (2.6)	0.32 (0.04)	309 (23)	4.8 (0.4)
Wivenhoe input	61 (28)	0.95 (0.45)	598 (124)	9.4(2)
Wivenhoe ouput	25 (6)	0.39 (0.09)	607 (37)	9.5(0.6)
Wivenhoe retention	35 (23)	0.56 (0.35)	-8.2 (87)	-0.1 (1.4)
% retained	58%		-1%	

Table 2: Physical and chemical variables in the Upper Brisbane River (UBR) and Wivenhoe reservoir from the two sampling occasions during the low flow period 2005-2006. UBR is the mean ($\pm$ SD) surface data for the eight sites, Sites 1 to 6 are a transect in Wivenhoe reservoir with Site 1 nearest the dam wall. S/B = surface or bottom samples. Bottom = 1 m from the bottom. Total nitrogen (TN), total phosphorus (TP), dissolved inorganic nitrogen (DIN), dissolved inorganic phosphorus (DIP) and TSS (total suspended solids) concentrations in mg L^{-1} . Chlorophyll *a* concentrations in $\mu\text{g L}^{-1}$. Sp. Cond. = specific conductivity

Parameter	S/B	UBR	Site 6	Site 5	Site 4	Site 3	Site 2	Site 1
Depth (m)		0.7 (0.3)	5	3.5	8.5	12.5	16.0	23.0
Temperature ($^{\circ}\text{C}$)	Surface	25.51 (2.44)	27.63	28.70	27.86	27.88	27.15	26.43
	Bottom		24.00	26.96	25.81	24.42	23.46	21.59
Sp. Cond. (ms cm^{-1})		1.83 (0.71)	0.37	0.41	0.50	0.45	0.41	0.41
Euphotic depth (m)		2.1 (0.8)	1.8	1.9	2.9	2.6	4.5	4.9
TN (mg L^{-1})	Surface	0.44 (0.25)	0.64 (0.16)	0.71 (0.10)	0.61 (0.05)	0.61 (0.10)	0.48 (0.09)	0.50 (0.08)
	Bottom		0.88 (0.40)	0.63 (0.08)	0.87 (0.15)	0.99 (0.37)	0.55 (0.05)	0.80 (0.38)
TP (mg L^{-1})	Surface	0.055 (0.029)	0.054 (0.007)	0.055 (0.004)	0.044 (0.008)	0.037 (0.003)	0.015 (0.003)	0.011 (0.004)
	Bottom		0.064 (0.017)	0.054 (0.004)	0.062 (0.029)	0.104 (0.068)	0.030 (0.013)	0.043 (0.003)
Molar TN:TP	Surface	24 (10)	27	28	32	37	69	107
	Bottom		37	26	34	28	49	40
DIN (mg L^{-1})	Surface	0.032 (0.039)	0.126 (0.064)	0.023 (0.021)	0.021 (0.020)	0.041 (0.045)	0.028 (0.033)	0.036 (0.037)
	Bottom		0.333 (0.439)	0.046 (0.007)	0.309 (0.394)	0.592 (0.726)	0.171 (0.131)	0.339 (0.330)
DIP (mg L^{-1})	Surface	0.014 (0.016)	0.003 (0.001)	0.003 (0.004)	0.003 (0.002)	0.008 (0.011)	0.005 (0.006)	0.010 (0.014)
	Bottom		0.006 (0.005)	0.007 (0.007)	0.004 (0.003)	0.005 (0.005)	0.009 (0.010)	0.012 (0.001)
TSS (mg L^{-1})	Surface	10.71 (8.76)	12.97 (3.22)	12.38 (1.25)	10.02 (1.40)	7.61 (1.12)	4.99 (0.22)	3.34 (0.74)
	Bottom		18.67 (5.59)	14.00 (3.29)	9.25 (0.49)	9.25 (1.49)	4.38 (1.37)	2.01 (0.68)

Chlorophyll <i>a</i> ($\mu\text{g L}^{-1}$)	Surface	14.44 (18.27)	30.4 (7.6)	43.4 (18.1)	30.3 (2.4)	23.2 (3.9)	8.8 (0.7)	10.4 (1.5)
---	---------	---------------	------------	-------------	------------	------------	-----------	------------

Table 3: Soil and sediment elemental composition and nitrogen:phosphorus (N:P) ratios in the upper Brisbane River (UBR, mean of 7 sites) and sites within Wivenhoe reservoir. TN = total nitrogen, TP = total phosphorus, $\text{Al}_{\text{NaOH}}:\text{P}_{(\text{H}_2\text{O}+\text{BD})}$ = sodium hydroxide extractable aluminium: extractable phosphorus ratio, $\text{Al}_{\text{NaOH}}:\text{Fe}_{\text{BD}}$ = sodium hydroxide extractable aluminium: extractable iron ratio.

	Soil	Sediment						
Parameter	UBR catchment	UBR	Site 6	Site 5	Site 4	Site 3	Site 2	Site 1
TP (g kg^{-1})	0.76 (0.36)	0.68 (0.18)	1.16 (0.16)	1.05 (0.14)	0.52 (0.03)	0.95 (0.04)	0.84 (0.06)	1.47 (0.15)
TN (g kg^{-1})	1.69 (0.53)	2.21 (1.17)	2.55 (2.25)	3.34 (0.05)	2.12 (1.26)	3.54 (0.09)	3.88 (0.31)	4.62 (0.09)
Molar TN:TP ratio	6.3 (4.5)	6.5 (4.4)	4.9	7.1	9.0	8.2	10.3	7.0
$\text{Al}_{\text{NaOH}}:\text{P}_{(\text{H}_2\text{O}+\text{BD})}$ ratio	nd	nd	nd	nd	7.9	15.5	12.6/23.6	5.0/5.1
$\text{Al}_{\text{NaOH}}:\text{Fe}_{\text{BD}}$ molar ratio	nd	nd	nd	nd	1.5	1.1	1.3/1.3	0.7/0.3

Table 4: Physical and chemical variables at sampling sites in UBR and Wivenhoe reservoir during high flow event. Nutrient and TSS (total suspended solids) concentrations are in mg L^{-1} . Chlorophyll *a* concentrations are in $\mu\text{g L}^{-1}$. Specific cond. = specific conductivity. *Event monitoring data from five composite samples at Gregors in the peak of the flood.

				Stanley R.	Wivenhoe		
Parameter	Depth	UBR	UBR confluence	Confluence	Site 5	Site 4	Site 2a
Depth (m)		2.0	2.0	2.0	5.3	9.0	18.0
Temperature (°C)	Surface	24.45			25.58	26.64	25.74
Sp cond.(ms cm^{-1})		0.49					
TN	Surface	0.83 (0.20) (2.38*)	0.90	0.19	0.63	0.83	0.77
	Bottom				0.63	0.81	1.20
TP	Surface	0.137 (0.560*)	0.190	0.076	0.097	0.110	0.053
	Bottom				0.097	0.110	0.120
Molar TN:TP ratio		18 (9*)	15	28	23	27	132
DIN	Surface	1.004 (0.514)	0.387	0.198	0.250	0.340	0.234
	Bottom				0.240	0.340	0.540
DIP	Surface	0.065 (0.004)	0.110	0.026	0.042	0.047	0.004
	Bottom				0.042	0.050	0.027
TSS	Surface	25.37 (0.68) (697*)	35.53 (2.83)	11.98 (0.73)	15.22 (1.55)	15.02 (0.88)	14.02 (0.21)
	Bottom				15.40 (0.71)	16.69 (0.65)	64.50 (2.40)
Chlorophyll <i>a</i>	Surface	3.8 (0.2)	13.5 (0.7)	1.0 (0)	13.5 (0.7)	11.5 (0.7)	18.5 (0.7)
$\delta^{15}\text{N}$ POM	Surface	1.5 (0.6)	2.8 (0.4)	2.1 (0.4)	2.4 (0.3)	5.6 (0.8)	12.5 (0.4)

Fig. 1

Fig. 2

Fig 3

Fig. 4

Fig. 5

Fig. 6

Fig.7