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Transport and retention of nitrogen and phosphorus in the sub-tropical Richmond River estuary, Australia – A budget approach

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Abstract. Nitrogen and phosphorus loads in the sub-tropical Richmond River estuary were quantified and material budgets were developed over two years of contrasting freshwater discharge. During both years >74% of the nitrogen and >84% of the phosphorus load entered the estuary during one month when flooding occurred in the catchment. Due to larger flood magnitude, loads during the 1995/96 year were 3.3 and 2.5 times greater than during the 1994/95 year for nitrogen and phosphorus respectively. During floods the estuarine basin was completely flushed of brackish water and the majority of the nutrient loads passed directly through the estuary. The nutrient load retained in the estuary during floods was inversely proportional to flood magnitude. Annual budgets show that >97% of the nutrient load entering the estuary was from diffuse catchment sources; precipitation, urban runoff, and sewage were negligible. Less than 2.5% of the nitrogen and <5.4% of the phosphorus loads entering the estuary were retained in sediments. During dry seasons the estuary became a net sink for nitrogen input from the ocean and the estuarine sediments remained a net source of phosphorus to the water column and ocean. The process of flood scouring is likely to be the cleansing mechanism responsible for maintaining water quality both on an annual basis and over the last 50 years and may also be responsible for potential nitrogen limitation. The sub-tropical Richmond River estuary contrasts with the majority of temperate systems of North America and Europe which typically have lower inter- and intra-annual nutrient load variability, longer and less variable flushing times, and greater nutrient retention.

Introduction

Freshwater replacement time is an important factor influencing the processing of nutrients within estuaries (Balls 1994; Nixon et al. 1996). For example, Nixon et al. (1996) found that the percentage of the yearly terrestrial and atmospheric nutrient loads that are exported through an estuary to the adjacent ocean are inversely proportional to freshwater replacement time of the system. An important control on nitrogen export is the loss through denitrification which increases with increased freshwater replacement time (Nixon et al. 1996). Balls (1994) demonstrated that estuarine flushing time was an important control on the extent of biological and abiological nutrient processing in estuaries on the Scottish east coast. In the sub-tropical Richmond River estuary, the extent in which nutrients are biologically processed is also related to the flushing time of the system (Eyre & Twigg 1997).

In order to quantify nutrient retention in an estuary, either (or both) nutrient storage in sediments and nutrient exchange with the ocean must be quantified. Nutrient storage in sediments is difficult to measure due to large spatial and temporal gradients (e.g. Boynton et al. 1995). Nutrient exchange with the ocean is complicated by tidal currents and large temporal and spatial gradients (Kjerfve & Proehl 1979; Kjerfve et al. 1981; Balls et al. 1994). As such, ocean exchange is most often quantified by difference and incorporates the additive errors of all the other terms (Nixon et al. 1996). In some systems, this may be unsuitable when nutrient fluxes with the adjacent ocean are associated with complex water circulation patterns (Mackas & Harrison 1997) or if the ocean exchange is a major component of the budget. Despite these difficulties, many nutrient budgets have been constructed for temperate systems (Correll 1981; Billen et al. 1985; Lucotte 1989; Doering et al. 1990; Correll et al. 1992; Valiela et al. 1992; Pejrup et al. 1993; Boynton et al. 1995; Nielsen et al. 1995; Nixon et al. 1996; Engqvist 1996; Galloway et al. 1996; Beddig et al. 1997; Kelly 1997; Klump et al. 1997; Mackas & Harrison 1997; Rendell et al. 1997) as a tool for assessing the transport, modification, and retention of nutrients (Nixon et al. 1996). In contrast, nutrient budgets that quantify the retention of nutrients in tropical and sub-tropical Australian systems are rare (e.g. Eyre 1995).

Tropical and sub-tropical Australian estuaries are typified by more variable flushing times compared to other parts of the world (Eyre & Twigg 1997; Eyre et al. 1998) due to more variable catchment discharges (Finlayson & McMahon 1988). It has been suggested that tropical and sub-tropical Australian estuaries have a low nutrient retention efficiency due to regular flushing of material to the continental shelf during floods (Eyre & Twigg 1997; Eyre 1998), however, there has been no quantitative assessment of the effects of flushing time on nutrient retention in these types of systems. Clearly this information is needed for predicting the impacts of external nutrient loads and improving management of these systems.

The aims of this study were (1) to present a method for quantifying ocean exchange in systems with singular simple cross-sections at the ocean boundary, (2) to evaluate the relative importance of the various sources and sinks of nitrogen and phosphorus during seasonal extremes, (3) to quantify nutrient retention on a seasonal and annual basis and relate this to flushing times of the system, and (4) to compare the sub-tropical Richmond River estuary to other Australian systems and systems in North America and western Europe. In this study a closed phosphorus budget has been achieved. Gaseous nitrogen exchange with the atmosphere was calculated using two methods; by difference and by stoichiometric mass balance.

Study area

The Richmond River estuary is a sub-tropical shallow bar built system that meanders south-west along the Pacific coast between its mouth at Ballina and Coraki (Figure 1). During the driest part of the year (September) the estuary is well mixed and ocean salt penetrates 40–50 km upstream, sometimes as far as the junction with Bungawalbin Creek. During the wet season the Richmond estuary can be flushed fresh to the mouth for several days or weeks each time heavy rain occurs in the upper or coastal catchments (Eyre & Twigg 1997; Hossain 1998). The estuary has a surface area of 15 km^2, a catchment: estuary surface area ratio of 449, an average volume of about 54 million m^3, and a semi-diurnal tidal cycle. The tidal range varies from a minimum of 0.65 m on neap tides to a maximum of 1.9 m on spring tides. Average coastal rainfall varies from 1,302 mm at Woodburn to 1,775 mm at Ballina and rainfall has a seasonal late summer dominated pattern. The estuary receives the majority of its freshwater discharge (annual average = 11.7 $Ls^{-1}km^{-2}$) from the Richmond catchment above Woodburn which comprises 87% of the total catchment area (6,861 km^2). The organic content of bottom sediment ranges from 1% near Ballina to 14% in the upper reaches (Woodburn). The main land uses in the coastal plain include sugar cane, beef farming, urban, and scattered rural residential (Table 1). Approximately 68 constructed drains enter the estuary between Ballina and Coraki which help to reduce flooding and improve agricultural productivity in the coastal plain. The estuary receives urban stormwater from small towns (Ballina, Wardell, Broadwater, Woodburn, and Coraki). There are no major industrial discharges although treated sewage is discharged into the lower Richmond River estuary at Ballina.

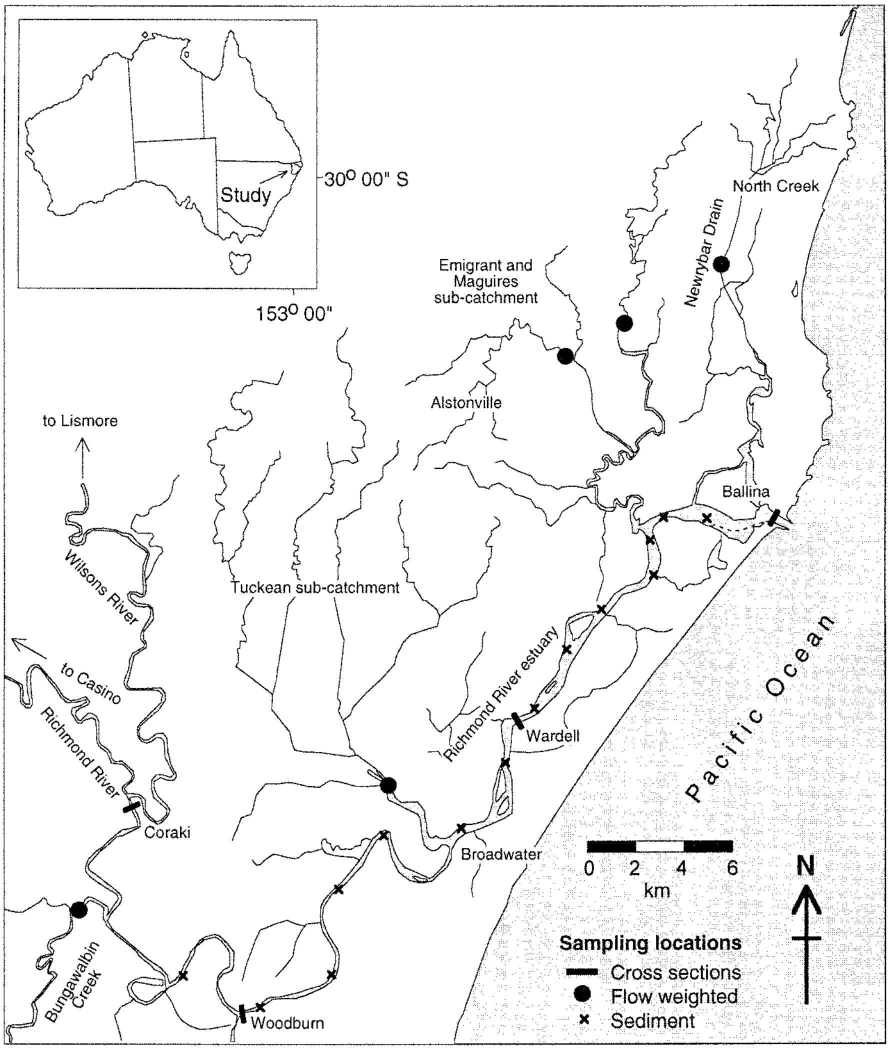

Figure 1. Sampling locations on the Richmond River estuary.

Methods

Definition of boundaries and conceptual model

The Richmond River estuary was defined as the upper limit of salt penetration (downstream from Coraki) (Figure 1). The conservation of mass equation was applied as

$$\text{Input} - \text{Output} = \text{Storage} \pm \text{Error}.$$

Table 1. Land use adjacent to the Richmond River estuary.

	Richmond (above Woodburn)	Tuckean	Emigrant Creek	Coastal	North Creek	Total	
Land use	(ha)	(ha)	(ha)	(ha)	(ha)	(ha)	(%)
Cropping	7,236	1,328	2,349	12,200	1,497	24,610	3.6
Horticulture	7,333	2,097	1,982	?	70	11,482	1.7
Dairy	26,568	2,592	648	0	0	29,808	4.3
Beef	288,217	15,001	10,862	11,885	5,892	331,857	48.4
Forest/national park	263,989	3,537	1,146	10,470	3,443	282,585	41.2
Urban + roads	3,857	220	438	1,247	?	5,762	0.8
Total	*597,200*	*24,775*	*17,425*	*35,802*	*10,902*	*686,104*	*100.0*
Population and stock	(head)	(head)	(head)	(head)	(head)	(head)	
Urban	42,620	0	4,941	13,160	0	60,721	
Rural + rural residential	27,506	3,035	2,802	5,192	886	39,421	
Humans (total)	70,126	3,035	7,743	18,352	886	100,142	
Beef cattle	173,522	13,051	9,450	10,340	5,126	211,489	
Dairy cattle	30,175	1,821	389	0	032,385		
Pigs	57,518	?	?	?	?	62,371	

? No information available.

The framework that was used for the numerical budget calculations is shown in Figure 2(A). A coupled (TDN: TDP) stoichiometric approach (Figure 2(B)) was used to calculate nitrogen exchange with the atmosphere (net N-fixation – denitrification). The stoichiometric approach (Gorden et al. 1996; Kemp et al. 1997; Smith & Hollibaugh 1997) used here relies upon the two important assumptions. Firstly, the breakdown of organic matter releases dissolved N and P in a constant and known ratio, and secondly, that all allochthonous phosphorus regenerated within the system occurs through the breakdown of organic material and not through other processes such as desorption or diffusion (Froelich 1988). When these two assumptions are made, the difference between the residual of the TDN budget and 16 times the residual of the TDP budget (7.2× by mass) must be accounted for by exchange of N_2 with the atmosphere (i.e. N-fixation or denitrification) where negative denotes net denitrification:

$$(\mathrm{TDN}_{\mathrm{inputs}} - \mathrm{TDN}_{\mathrm{outputs}}) - 16(\mathrm{TDP}_{\mathrm{inputs}} - \mathrm{TDP}_{\mathrm{outputs}})$$
$$= (\text{N-fixation} - \text{Denitrification}) \pm \text{Error}.$$

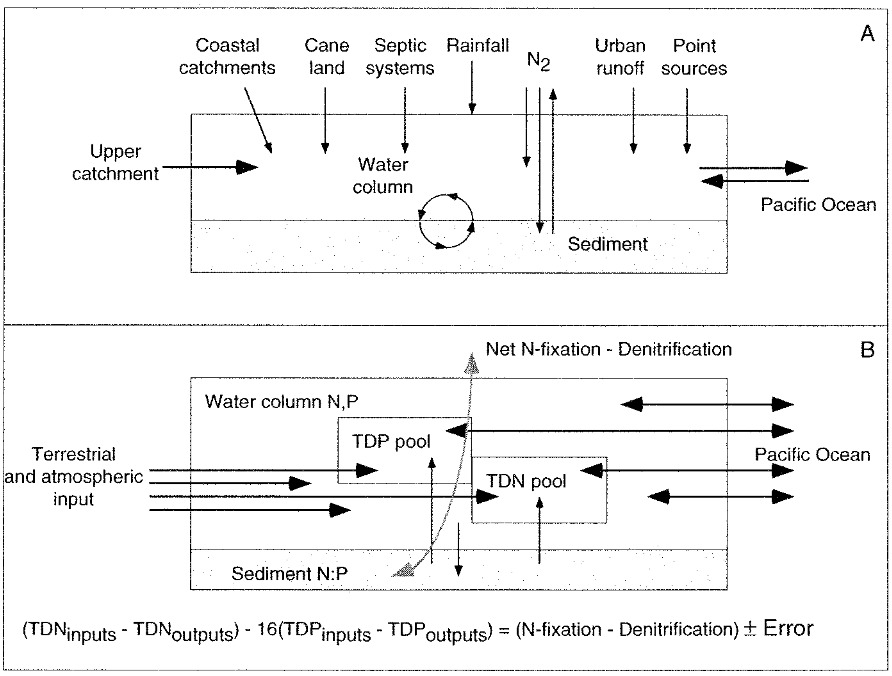

Figure 2. Conceptual framework for budgetary numerical calculations. (A) The input-output conservation of mass approach; (B) N:P stoichiometric approach.

Data collection, and numerical calculations

Catchment areas

Water sampling was carried out on a discharge-weighted basis at Lismore (on the Wilsons River and Leycester Creek), Casino (on the Richmond River), Bungawalbin Creek, Tuckean, Emigrant Creek, and Maguires Creek (Figure 1). Samples were taken at monthly intervals during low discharge and up to six times per day during floods. Loads were calculated by multiplying nutrient concentrations with calculated discharges (Hossain 1998) at Bungawalbin, Tuckean, Emigrant Creek, and Maguires Creek on a monthly basis during low discharge and on a hourly basis during floods, interpolating between samples (Walling & Webb 1985; Kronvang & Bruhn 1996). The loads entering the upper estuary at Coraki included areas that were not monitored downstream from Lismore and Casino. There are several methods (ratio, land use, and regression) available for evaluating nutrient loads generated from nonmonitored areas (Richards 1989). Richards concluded that whereas no method offered high precision, the ratio method was less biased than the other methods. Loads entering the upper estuary at Coraki from the

Richmond and Wilsons sub-catchments were calculated by summing monthly loads calculated for Lismore and Casino and multiplying by an area ratio of 1.34 to take into account the area not sampled. Monthly loads were added to give total yearly loads.

Loads generated from sugar cane land

Discharge from the coastal plain adjacent to the estuary mainly occurs from 68 modified or constructed drainage lines which enter the estuary between Ballina and Coraki. Discharge from drained land was estimated on an area basis by calculating monthly rainfall input using rainfall at Woodburn and Ballina and the area of cane land adjacent to the upper estuary above Wardell (6,075 ha) and lower estuary (7,425 ha), and multiplying rainfall volume by monthly runoff coefficients derived from the Tuckean sub-catchment (Hossain 1998). Water samples were collected from Newrybar drain on a monthly basis with spot sampling during heavy rainfall. Newrybar drain receives the majority of its runoff from cane land in the North Creek sub-catchment (Figure 1). Loads from cane land were calculated by multiplying concentration data (collected in North Creek and averaged on a monthly basis) by discharge (interpolating for months when no sampling occurred). Loads obtained were equivalent to 7.8 and 12.5 kg TN $ha^{-1}yr^{-1}$ and 0.4 and 0.6 kg TP $ha^{-1}yr^{-1}$ for 1994/95 and 1995/96 respectively. These nitrogen exports compare closely to those of (Bramley et al. 1994) for cane land in the tropical Australian Herbert River catchment (8.3 kg $ha^{-1}yr^{-1}$). However, the Richmond P exports were less than half those of the Herbert. Cane farmers in the Richmond River catchment are encouraged to apply P for soil maintenance only. P management may have reduced export via surface runoff.

Loads from rainfall

Rainfall samples were collected at several coastal locations (Alstonville and Coraki) using identical sampling containers (a 500 mL polyethylene bottle with a 15 cm diameter polyethylene funnel glued to the top). At the start of a rain event or on the morning of a day when rain was forecasted, the sampling device was fixed to the top of a fence post 1m from the ground; samples were collected at the end of the rain event. Atmospheric load was calculated by multiplying the average monthly TN or TP concentration found in rainfall by estuarine surface area (upper estuary = 8 km^2 (above Wardell); lower estuary = 7 km^2) and monthly rainfall from Woodburn (upper estuary) and Ballina (lower estuary).

Load due to leaching from septic systems

Nutrient loads via leaching from septic systems adjacent to the estuary were estimated using loads of TN (4 kg person^{-1}yr^{-1}) and TP (1 kg person^{-1}yr^{-1}) (Hoare 1984) and applying these to the non-sewer population adjacent to the estuary (Wardell and Broadwater). Sewage from Woodburn is treated and discharged at Evans Head on the coast and therefore not included in the budget. Soils adjacent to the Richmond River Estuary are clay rich suggesting the loads calculated for the Richmond estuary were probably an overestimate because it was assumed that all TN and TP from septic systems reaches the estuary over time.

Loads from urban sewage and urban runoff

The load of urban sewage from Ballina was estimated by integrating metered discharges (kL) and monthly average concentrations of nitrate, ammonium, and total phosphorus obtained from local authorities. Nitrogen loads associated with urban runoff were calculated by multiplying the average TN concentration (1.4 mg L^{-1}) found in Lismore urban drains (C_{Urb}) (Kerr & Eyre 1995) by monthly rainfall at Lismore (R) and impervious area (A_{Imperv}), using a runoff coefficient of 50%, summing from July to June for each year of the study.

$$\mathrm{Load}(\mathrm{kgyr}^{-1}) = \sum_{\mathrm{Jun}}^{\mathrm{Jul}} C_{\mathrm{Urb}} 0.5 R A_{\mathrm{Imperv}}$$

Runoff coefficients in urban areas can range from 95% in paved areas to 20% in low density urban areas (Hopkinson & Vallino 1995). During the wet season, 50% runoff from urban areas in the Richmond River catchment was likely to be an underestimate whereas during the driest months of the year, 50% runoff may be a slight overestimate.

Phosphorus loads were calculated similarly using a TP concentration of 0.7 mg L^{-1} (Kerr & Eyre 1995). Loads from the coastal towns of Ballina, Wardell, Broadwater, Woodburn, and Coraki were estimated by the ratio of each towns population to the population of Lismore since no nutrient concentration data has been collected in the small towns adjacent to the estuary.

Estuarine 24 hour sampling (for cross section nutrient flux)

Water samples were collected at approximately 1.5 hour intervals over 23–26 hours during consecutive spring and neap tides at Ballina, Wardell, Woodburn, and Coraki (Figure 1). Sampling was carried out over a range of catchment discharges on five occasions between July 1994 and June 1996.

At Ballina, three buoys were anchored with even spacing between the training walls 500 m inside the estuary mouth. Samples were collected using a boat, tying up to the first buoy and winching a 10 mm ID plastic hose and a Braystoke Directional Current Velocity Meter into the water column. Water samples (one litre) were pumped to the surface with a hand pump from three depths (0.5 m 2 m, and 3 m). Water velocity was recorded at three depths. This process was repeated for each buoy successively adding each pumped sample to an enclosed ten litre plastic bucket (sealable lid) to make a 9 L composite sample. The collection process took less than five minutes for each buoy with the whole collection process taking approximately 20 minutes.

At Wardell, Woodburn, and Coraki data were collected by winching a Braystoke Directional Current Velocity Meter into the water column from road bridges. Velocity was measured at three depths and at three locations across the estuary. Water samples were taken at mid depth using a sample rinsed submergible sampling bottle at the same positions as the velocity measurements and homogenised in a ten litre plastic bucket. This process was continued at 1.5 hour intervals for 23–26 hours.

The Ballina transect was echo-sounded to obtain a cross-sectional area profile. This area was adjusted for tidal fluctuations over each sampling period to give a cross-sectional area at a given time during each survey. Discharge was calculated by multiplying the average velocity in a vertical section (three sub-sections) by the sectional area (adjusted for tide height). Total discharge (m^3) was calculated by summing the sub-sections and multiplying by the time between samples (usually 1.5 hours). Nutrient loads for each tide at Ballina were calculated by multiplying the sample concentration (mg L^{-1}) by discharge (m^3) for each 1.5 hour period and summing over the full tidal cycle (25 hours).

Flood event sampling

Sampling was undertaken on three occasions during flood events when the estuary was flushed fresh to the mouth at Ballina. During February 1995, the estuary ran fresh for approximately three days. Data were collected from Coraki, Wardell, and Ballina during flood discharge. During January 1996 a flood of similar magnitude occurred that was sampled during flood discharge at Ballina. During both of these small flood events, water samples and velocity measurements were carried out in the manner as described for tidal sampling. During May 1996, a larger flood occurred which flushed the estuary fresh at the mouth for approximately ten days. Water samples were taken up to four times a day from Coraki, Woodburn, Wardell, and Ballina. Logistical difficulties did not allow the direct measurement of velocity during the May 1996 flood or during dry times when no sampling was undertaken.

During these times, velocity and discharge were modelled using the one dimensional nonsteady flow model (DUFLOW) (Hossain 1998). Model parameters included cross-sectional data at 18 locations, daily discharge from four sub-catchments, and three hourly water level at Ballina (DLWC unpublished data). The model was calibrated using 3 hourly water level at Woodburn (DLWC unpublished data). Nutrient loads during the flood events were calculated using the same methods described for tidal sampling. Mass loads for the rest of each month when a flood event occurred were calculated by multiplying modelled discharge (Hossain 1998) by the nutrient concentration of the last sample taken during flood event sampling.

Sediment nutrients

Sediment samples were collected on three occasions for analysis of sediment nitrogen (SN) and sediment phosphorus (SP). The top 2–4 cm of sediment was collected by hand from depositional areas below low tide level near the edge of the estuary at 13 locations (2.5, 4, 5.5, 7.5, 9.5, 12, 14, 16.5, 17.5, 21, 25.5, 28, 32, 36, and 41.5 km from the estuary mouth) between Ballina and Woodburn (Figure 1). Historical sediment data were collected on two occasions on 31/8/46 and 2/2/48 at seven locations (1, 3, 6, 10, 17.5, 24.5, and 41 km from the mouth of the estuary) (Rochford 1951).

Loads of nutrients stored in the estuarine sediments were estimated by multiplying net sedimentation rates (Hossain 1998) for the 1994/95 year (5,423 t upper estuary, 12,497 t lower estuary) and for the 1995/96 year (4,664 t upper estuary, 9,256 t lower estuary) by average sediment nutrient composition (upper estuary: 2.0 kg N t^{-1}, 0.9 kg P t^{-1}, lower estuary: 0.9 kg N t^{-1}, 0.5 kg P t^{-1}).

Sample storage and laboratory analysis

Rainfall, estuarine, catchment, and flood samples were all treated in the same manner. Immediately ($<$30 minutes after collection) an unfiltered and filtered (0.45 μm cellulose acetate membrane filter) sample was collected in acid rinsed and sample rinsed 10 mL polyethylene tubes and placed on ice until frozen. Water samples were analysed using a Lachat Instruments Quikchem Automated Ion Analyser less than 2 weeks after collection (Table 2). The coefficient of variation (CV) was determined using replicate samples were taken on 32 occasions covering a range of sampling locations, nutrient concentrations, and river discharges. Physiochemical parameters (temperature, conductivity, pH, salinity, dissolved oxygen, and turbidity) were measured *in situ* using a Horiba U10 multiprobe calibrated in the laboratory. Water samples were taken for analysis of chlorophyll-a concentration when an algal bloom (*Anabaena* sp.) occurred in the upper estuary between Woodburn and Coraki and analysed using standard methods (Table 2). Sediments were ana-

Table 2. Analytical methods, detection limits and errors.

Nutrient form		Method	Reference	Detection limit (μg L^{-1})	CV[1] %
Total phosphorus	TP	Persulphate digestion	Valderrama, 1981	10	3.5
Total dissolved phosphorus	TDP	Persulphate digestion	Valderrama, 1981	5	3.2
Dissolved inorganic phosphorus	DIP	Ascorbic acid + molybdate blue	Parsons et al., 1984	21.8	
Total particulate phosphorus	TPP	TP – TDP	—	—	6.7
Dissolved organic phosphorus	DOP	TDP – DIP	—	—	5.0
Total nitrogen	TN	Persulphate digestion	Valderrama, 1981	10	4.4
Total dissolved nitrogen	TDN	Persulphate digestion	Valderrama, 1981	5	2.4
Nitrate + nitrite	NO_x	Cadmium reduction + sulphanilamide + NED	Parsons et al., 1984	21.9	
Ammonium	NH_4^+	Hypochlorite + phenol + nitroprusside	Parsons et al., 1984	5	5.4
Total particulate nitrogen	TPN	TN – TDN	—	—	6.8
Dissolved organic nitrogen	DON	TDN – NO_x – NH_4^+	—	—	9.7
Chlorophyll-a	Chl-a	0.45 μm filter, 90% acetone	APHA, 1995	1	3.1
				g kg^{-1}	
Sediment nitrogen	SN	Kjeldahl digestion	APHA, 1995	0.2	6.0
Sediment phosphorus	SP	Ash (550 °C), HCl extraction, ascorbic acid, molybdate blue	Eyre, 1993	0.1	4.7
Organic carbon	OC	Weighing dried and crushed sample, ash at 550 °C and reweighing	APHA, 1995	1.0	—

[1]Coefficient of variation (CV).

lysed for carbon, nitrogen and phosphorus using standard methods (Anon 1995) (Table 2).

Analysis of the historical total sediment nitrogen concentration was determined by a method similar to the recent TKN method (Anon 1995). Each sample was digested at 400 °C for one hour using selenium oxychloride, sulphuric acid, and saturated potassium sulphate. The ammonium formed was steam distilled into 2% boric acid. Historical total sediment phosphorus was determined by digesting a sample aliquot in sulphuric acid with a small amount of perchloric acid added at 150 °C on a sand tray until white fumes appeared. After the addition of 100 mL of distilled water, stirring, and standing for 24 hours, phosphate concentration was determined by the addition of stannous chloride and the use of a colour comparator. Further details of the methods can be found in (Rochford 1951) and references therein. No attempt has been made here to compare current and historical methods.

Analysis of variance

Data were grouped as either dry season (November 1994 and September 1995) or "post flood" (March 1995 and June 1996) for each sampling location on the estuary. An ANOVA was performed for each sampling location to test if there were significant differences (95% confidence) in water quality (concentration, percentage of each form, and N:P ratio) associated with the season. None of the water quality variables had normal distributions (Kolmogorov-Smirnov test), therefore data were log transformed prior to analysis.

Results

Inputs from diffuse catchment surfaces

Nutrient loads from diffuse sources entered the estuary mainly in response to flood discharge during the wet season (Figure 3). Of the TN (856,053 kg) and TP load (198,699) that entered the estuary from diffuse sources during 1994/95 (an extreme dry year), 74% TN and 84% of the TP load entered during the months of February and March. In 1995/96 (a year with approximately average discharge), 82% of the diffuse TN load (2,793,083 kg) and 84% of the diffuse TP load (498,704 kg P) entered the estuary during the months of January and May. When averaged over both years, the diffuse nitrogen load entered the estuary as 21% DIN, 49% DON, and 30% TPN. In contrast, the diffuse phosphorus load entered the estuary as 33% DIP, 17% DOP, and 50% TPP. Averaged across the catchment area (674,121 ha), nutrient loads were equivalent to catchment exports of 1.2 kg TN $ha^{-1}yr^{-1}$ and 0.29 kg TP

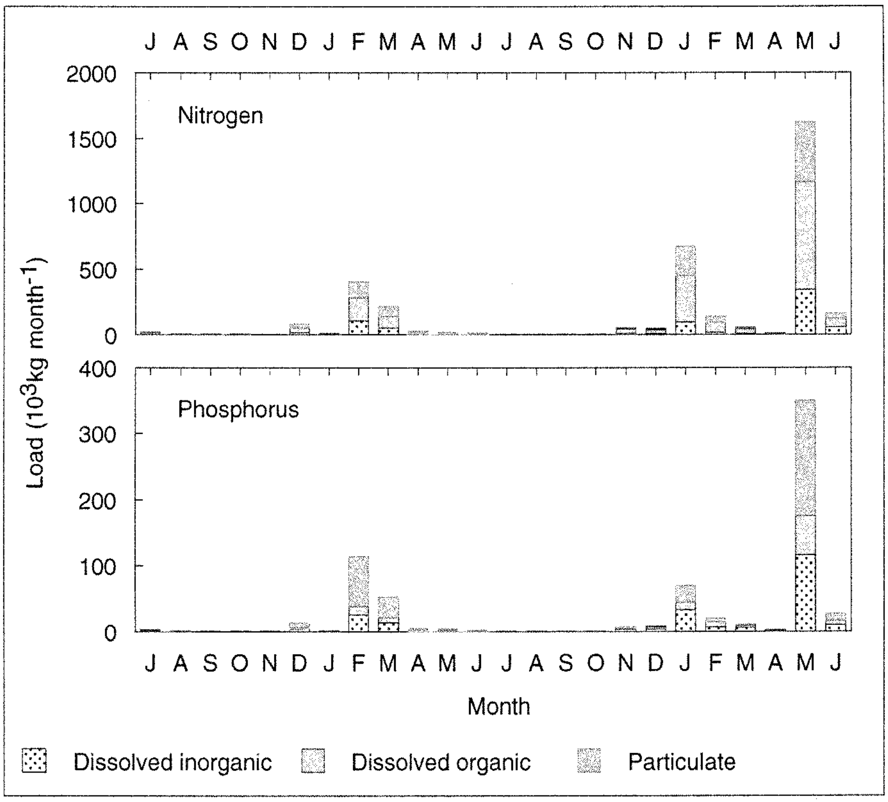

Figure 3. Loads of diffuse source nutrients entering the Richmond River estuary during July 1994 to June 1996.

ha^{-1}yr^{-1} during 1994/95 and of 4.1 kg TN ha^{-1}yr^{-1} and 0.73 kg TP ha^{-1}yr^{-1} during 1995/96.

Estuarine nutrient dynamics during dry season and post-flood

Nutrient concentrations at Ballina followed sinusoidal relationships out of phase with the tide (Figure 4). TN and TP concentrations usually peaked late in the ebb or early in the flood tide and dropped off rapidly as comparatively nutrient poor sea water entered the estuary after the turn of the tide. The difference between the concentration of nutrients in the estuarine water compared to ocean water was largest during the wet season. During the two surveys conducted during the dry season, the estuary was apparently depleted in nitrogen; similar or higher average concentrations of nitrogen flowed into the estuary from the ocean on the flood tide. This was an indication that the lower Richmond estuary undergoes a seasonal change from being nitrogen

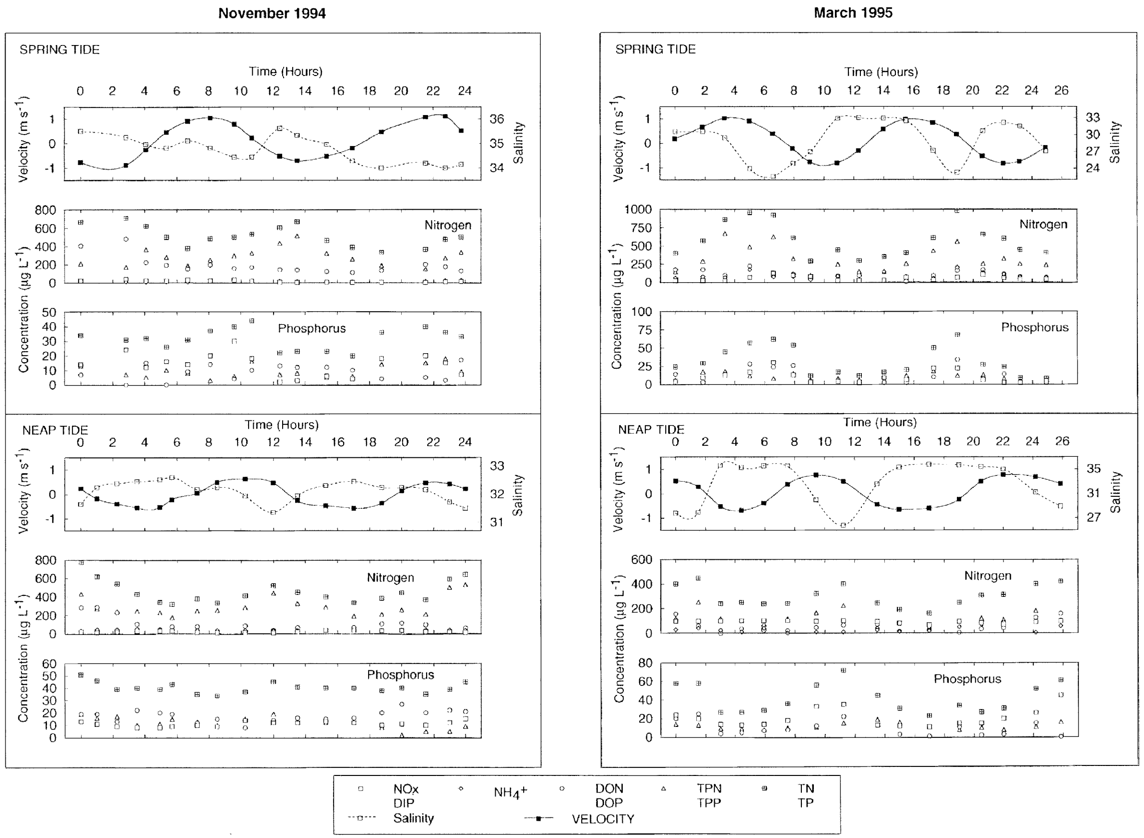

Figure 4. An example of tidal velocity, salinity, and nutrient concentration over spring and neap tidal cycles at Ballina during a dry season (November 1994) and during post-flood (March 1995).

rich to nitrogen poor. Phosphorus concentrations remained elevated in the estuary relative to the ocean during both the wet and dry seasons.

At Wardell and during the dry season, TN concentrations were highest on the ebb tide further supporting the observation that the lower estuary was depleted in nitrogen during the dry season. TP concentrations at Wardell were greater than at Ballina during all tidal surveys and ebb tides at Wardell contain higher concentrations of TP relative to flood tides suggesting that the upper estuary remained a source of phosphorus to the lower estuary during all seasons.

Nutrient forms during the transition from post-flood to dry season

In general, nutrient concentrations decreased from the upper Richmond River estuary towards the mouth (Table 3). TN and TP concentrations reached a minimum during the dry season at all locations as the estuary recovered following floods. During wet season post-flood, the estuary was rich in inorganic nitrogen (33–39% of TN) and rich in inorganic phosphorus (44–49% of TP). During the transition from post-flood to the dry season, the forms of nitrogen and phosphorus in the estuary were gradually modified so that during the dry season, the estuary as a whole was relatively depleted in inorganic nutrients (2–15% of TN and 17–40% of TP). Although in general the whole estuary declined in relative proportions of inorganic nitrogen to organic nitrogen during the seasonal transition, the upper estuary showed the largest decline associated with dry season algal blooms (up to 52 μg L^{-1} chlorophyll-a). The proportion of inorganic phosphorus also declined to a greater extent in the upper estuary relative to the lower estuary, however, not to the same extent as nitrogen. Mass ratios (DIN:DIP) were similar to or less than the Redfield ratio (Redfield 1934) during both post-flood and dry seasons and the middle and upper reaches had lower ratios relative to the mouth at Ballina.

Nutrient loads during dry season and post-flood

The magnitudes of net nutrient exchange with the Pacific Ocean were variable (Table 4). In November 1994 and September 1995 there was a net input of TN to the estuary from the ocean. In both cases this input was dominated by organic nitrogen (TPN and DON) although there were also inputs of NO_x and NH_4^+. Although there were inputs of various forms of phosphorus during the dry season, phosphorus contrasts with nitrogen in that there was always net loss of phosphorus from the estuary when averaged over spring-neap cycles. During the post-flood period (March 1995 and June 1996) the lower estuary was a net exporter of both nitrogen and phosphorus.

Table 3. Average concentrations and nutrient forms (%TN or %TP) during the transition from post-flood to dry season at Ballina, Wardell, Woodburn, and Coraki.

	Total nitrogen					Total phosphorus				Mass ratio
	μg L^{-1}	NO_x%	NH_4^+%	DON%	TPN%	μg L^{-1}	DIP%	DOP%	TPP%	DIN:DIP[4]
Ballina										
Dry[1]	343	9	6	31	54	35	40	27	32	4.0
Post flood[2]	417	21	12	38	30	43	46	30	24	7.5
Significance	—	*0.000*	*0.000*	—	*0.000*	*0.007*	*0.018*	—	*0.014*	*0.000*
Wardell										
Dry[1]	269	5	6	47	42	56	41	29	31	1.2
Post flood[2]	695	31	6	38	26	70	48	26	36	9.9
Significance	*0.000*	*0.000*	—	*0.015*	*0.000*	*0.000*	*0.015*	—	—	*0.000*
Woodburn										
Dry[1]	798	1	3	62	34	87	17	41	42	2.7
Post flood[2]	855	32	3	27	38	152	44	31	25	4.7
Significance	—	*0.000*	—	*0.000*	—	*0.000*	*0.000*	*0.002*	*0.000*	*0.000*
Coraki										
Dry[1]	693	1	1	46	51	95	21	33	46	0.7
Post flood[2]	767	26	13	30	30	127	49	36	16	4.8
Significance	—	*0.000*	*0.000*	*0.000*	*0.000*	*0.000*	*0.000*	—	*0.000*	*0.000*

[1] "Dry" includes data from November 1994 and September 1995.
[2] "Post flood" includes data from March 1995 and June 1996.
[3] Significant differences tested with ANOVA after log transformation (only $p < 0.05$ is reported).
[4] A mass ratio of 7.2N:1P is equivalent to the Redfield molar ratio of 16N:1P.

Table 4. Nutrient loads during post-flood and dry season conditions at Ballina. Loads are quoted in kg tide^{-1} where a tide is 24–25 hours.

			Nitrogen					Phosphorus			
Season	Tide	Date	NO_x	NH_4^+	DON	TPN	TN	DIP	DOP	TPP	TP
Dry	S	5/11/94	159	160	–3,805	–735	–4,221	443	83	254	780
	N	12/11/94	–582	–420	–1,545	128	–2,419	–45	–177	–126	–347
Post flood	S	18/3/95	429	2,225	2,410	14,287	19,350	648	426	481	1,554
	N	25/3/95	576	650	1,770	3,545	6,541	645	224	25	894
Dry	S	9/9/95	–743	–173	797	988	869	–15	614	347	946
	N	2/9/95	210	149	–546	–1,769	–1,956	60	–38	–87	–65
Mixed[1]	S	25/11/95	1,782	701	4,709	–359	6,833	239	236	554	1,029
	N	2/12/95	77	179	3	128	387	72	59	–21	110
Post flood	S	15/6/96	5,397	1,545	7,121	2,148	16,211	465	29	485	979
	N	8/6/96	1,309	882	1,318	–507	3,002	262	91	51	404

[1]Samples taken prior to and just after a small catchment rain event.
(–) Negative sign indicates net flow of nutrients from the ocean into the lower estuary.
(S) Spring tide sampling.
(N) Neap tide sampling.

Nutrient dynamics during storm discharge

Complete flushing of the Richmond estuary was observed on three occasions lasting for periods of three to ten days between July 1994 and June 1996. Since rainfall in the catchment during the first year was lower than average and for the second year slightly above average, it is suggested that the estuary is flushed fresh to the mouth on a less than 1 year return period. During May 1996, the estuary remained fresh for approximately ten days during which two discharge peaks occurred 4 days apart in response to two separate rain events. Nitrogen concentrations at Coraki were variable probably reflecting various catchment nutrient sources reaching the estuary at different times (Figure 5). As nutrient loads passed through the estuary, this variability decreased as peaks were attenuated and nutrients associated with estuarine sediments were mixed into the water column. Peak nutrient concentrations occurred later than peak discharges. During the first event, peak TN concentration was lower at Wardell than at Coraki suggesting deposition in the upper estuary and increased again at Ballina suggesting erosion in the lower estuary (Table 5). During the second event, TN concentrations decreased form Coraki to Woodburn probably as a result of the input of comparatively low nutrient water from the Bungawalbin sub-catchment. There was an increase from Woodburn to Ballina suggesting net erosion. Total phosphorus concentrations indicate deposition during the first event and erosion in the upper estuary followed by deposition in the lower estuary during the second event. When averaged across both events, there was a net increase in TN concentration and a net decrease in TP concentration from Coraki to Ballina, suggesting the estuary was a source of nitrogen and a sink for phosphorus during the May flood.

Nutrient load verses discharge relationships for the estuary at Ballina

Loads calculated for months with storm discharge and loads derived from 24 hour sampling were used to develop rating relationships between catchment discharge and load (Figure 6). Variation in catchment discharge accounted for greater than 98% of the variation in nutrient loads. This enabled prediction of loads during periods when no sampling was undertaken. The data suggest that there was a net landward transport of nitrogen at Ballina during September, October, and November 1994 and July, August, September, and October 1995 (Figure 7). In contrast, the phosphorus rating curves developed for Ballina show a net monthly export of phosphorus to the Pacific Ocean over the whole range of discharge. Flood tide concentrations as Ballina during dry season sampling (November 1994 and September 1995) were greater than ebb tide

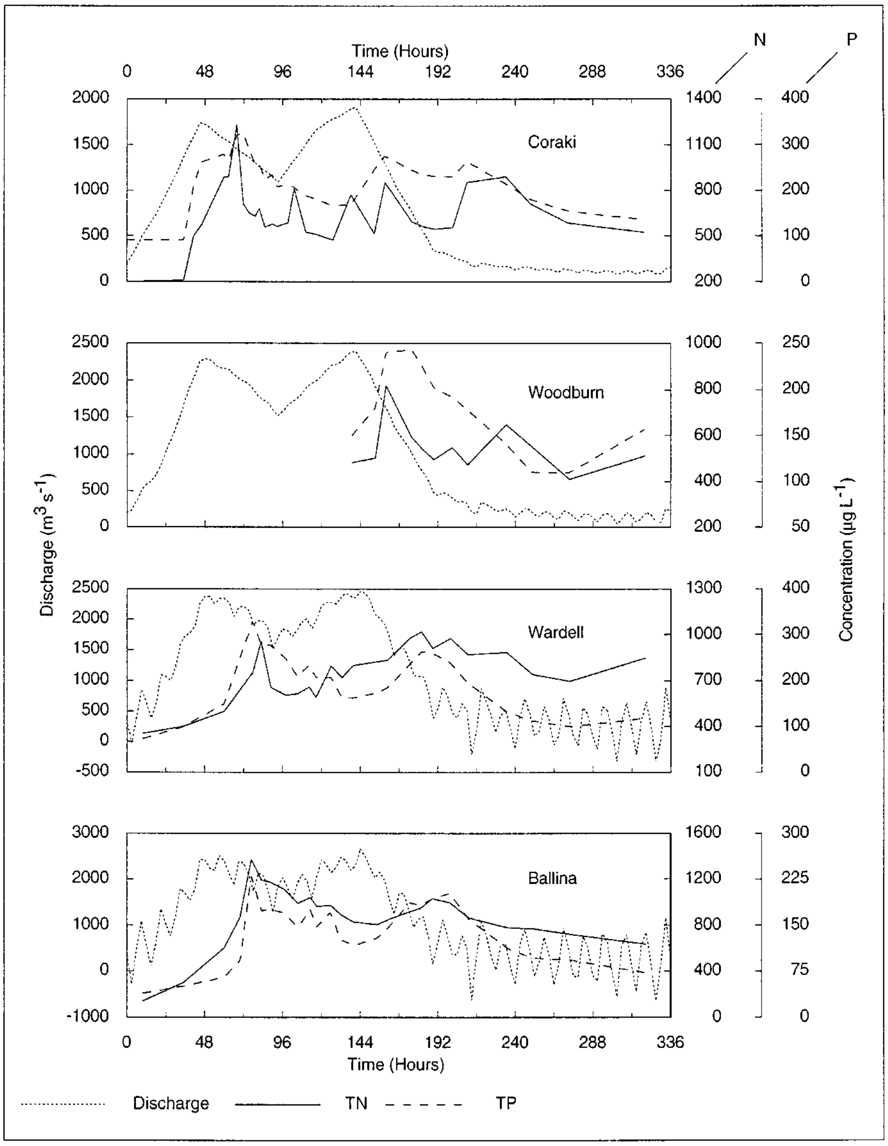

Figure 5. Discharge and nutrient concentration over the rising and falling stages of two flood peaks at Coraki, Woodburn, Wardell, and Ballina during the May 1996 flood. Time zero was 0:00 am 1/5/96.

Table 5. Flood event peak nutrient concentration and forms (%TN or %TP) and the averages for the 10 day flood period when the estuary was flushed fresh at the mouth during May 1996.

		Total nitrogen					Total phosphorus				Travel
		μg L^{-1}	NO_x%	NH_4^+%	DON%	TPN%	μg L^{-1}	DIP%	DOP%	TPP%	time (hrs)[1]
Event 1											
	Coraki	1,228	13	9	42	37	326	5	7	88	0
	Woodburn	—	—	—	—	—	—	—	—	—	—
	Wardell	954	17	13	29	41	278	6	9	84	10
	Ballina	1,175	12	9	40	39	176	10	11	80	20
Event 2											
	Coraki	855	11	7	42	40	276	21	12	68	0
	Woodburn	817	3	6	47	34	243	18	13	69	11
	Wardell	1,018	11	7	51	31	263	15	6	79	26
	Ballina	1,029	10	6	48	37	202	12	14	74	38
May 1^{st}–10^{th}											
	Coraki[2]	615	22	8	52	17	214	27	15	58	—
	Woodburn[2]	—	—	—	—	—	—	—	—	—	—
	Wardell[2]	761	16	11	52	22	224	11	12	77	—
	Ballina[2]	936	21	5	45	29	174	23	35	42	—

[1]Travel time for peak nutrient concentrations adjusted using Coraki as the time zero.
[2]Flow weighted average.

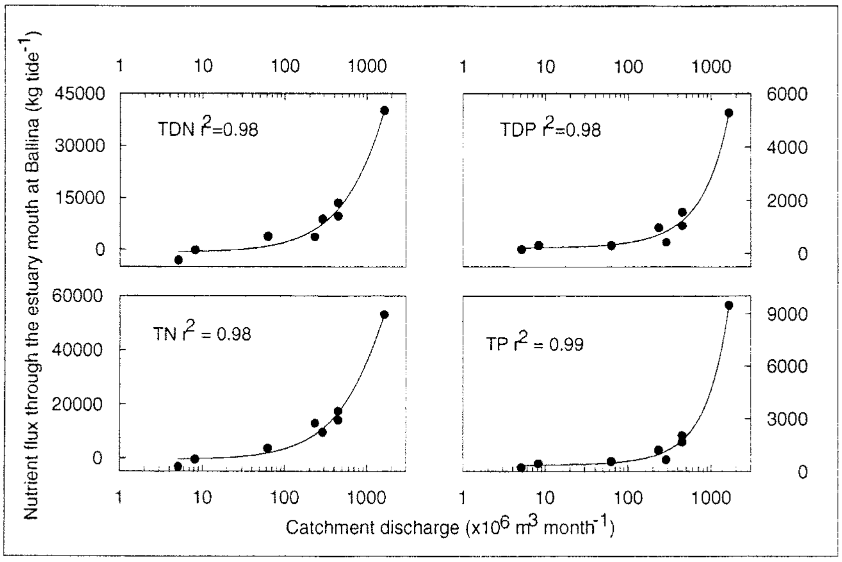

Figure 6. Discharge verses load relationships for Ballina developed using 24 hour sampling and flood event data. Monthly loads calculated for floods were divided by the number of tides in the month to make the data comparable to 24 hour sampling.

concentrations therefore these findings were not a result of tidal discharge asymmetry during sampling.

Estuarine sediment nutrients

Nitrogen was present in estuarine sediments at concentrations ranging from 0.2 to 3.3 g kg^{-1} (Figure 8). Concentrations generally increased from Ballina to the head of the estuary. Phosphorus concentrations varied between 0.1 and 1.2 g kg^{-1} and also showed a general increase toward the fluvial dominated reaches of the estuary. Sediments analysed for inorganic N (NO_x and NH_4^+) had concentrations at the detection limit and the strong relationship between sediment nitrogen (SN), sediment phosphorus (SP) and organic carbon (LOI) (Figure 11) suggests that most TN and TP within sediments was organic. Comparison with historical data (Rochford 1951) suggested no significant (ANOVA $p < 0.05$) changes in sediment nutrient concentrations in the past 50 years.

Nitrogen and phosphorus budgets

Nutrients from diffuse sources contributed greater than 96.9% of the TN and TP load to the estuary even during the 1994/95 period (an extreme dry year)

Table 6. Annual nitrogen and phosphorus budgets for 1994/95 and 1995/96.

	Total nitrogen						Total phosphorus					
	1994/95			1995/96			1994/95			1995/96		
	Mass(kg)	%	%	Mass(kg)	%	%	Mass(kg)	%	%	Mass(kg)	%	%
Inputs												
Upper catchment[1]	533,890	60.6		1,910,605	67.7		139,268	67.9		383,556	76.0	
Bungawalbin	1,234	0.1		379,001	13.4		110	0.1			26,308	5.2
Tuckean	157,544	17.9	97.2	256,212	9.1	99.0	37,096	18.1	96.9	54,276	10.8	98.9
Emigrant Creek	58,180	6.6		78,619	2.8		17,008	8.3		25,811	5.1	
Coastal plain (Cane lands)	105,204	11.9		168,646	6.0		5,218	2.5		8,753	1.7	
Precipitation	13,719	1.6		19,058	0.7		885	0.4		1,229	0.2	
Urban runoff	1,140	0.1		1,598	0.1		571	0.3		800	0.2	
Ballina sewage	5,714	0.6		4,271	0.2		3,884	1.9		2,676	0.5	
Septic leachate	4,028	0.5		4,028	0.1		1,007	0.5		1,007	0.2	
Total	*880,653*	*100.0*		*2,822,038*	*100.0*		*205,047*	*100.0*		*504,416*	*100.0*	
Outputs												
Exchange with Pacific Ocean	750,695			2,823,249			195,697			492,067		
Retention												
Sediment nutrients[2]	22,075	2.5		17,659	0.6		11,129	5.4		8,826	1.7	
Residual[3]	107,883			–18,870			1,779			–3,523		

Table 6. Continued.

	Total nitrogen						Total phosphorus					
	1994/95			1995/96			1994/95			1995/96		
	Mass(kg)	%	%	Mass(kg)	%	%	Mass(kg)	%	%	Mass(kg)	%	%
N-fixation – Denitrification[4]	643,751			46,306								
N-fixation – Denitrification[5]	369,395			–78,747								

[1]Includes the catchment area above Coraki (Richmond River and Wilsons River sub-catchments).
[2]%sedimentation (nutrients retained in sediments) = sediment nutrients(kg) / Σinputs(kg) $\times$ 100.
[3]The residual in the nitrogen budget represents the sum of N-fixation – denitrification (N-fix – denit) and also includes any errors associated with the construction of the budget. The residual of the phosphorus budget represents errors in the budget calculation only. Confidence in the both the N and P budgets is inferred by the small residual in the phosphorus budget compared to the larger budget terms (catchment inputs and ocean exchange).
[4]Calculated using Redfield stoichiometry N:P = 16:1 (molar) = 7.2:1 (mass).
[5] Calculated using Richmond River estuarine sediment stoichiometry N:P = 1.9:1 (mass).

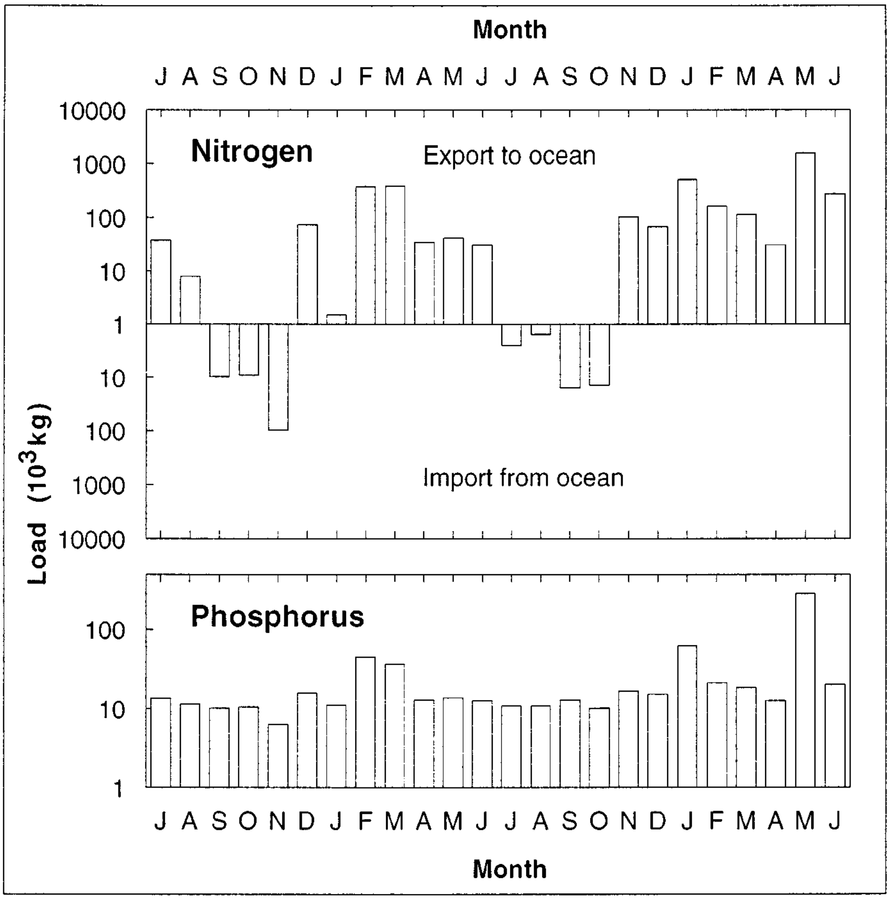

Figure 7. Nitrogen and phosphorus loads at Ballina for July 1994 to June 1996. There was a net input of nitrogen from the ocean to the estuary during the dry season of each year. In contrast, the was net export of phosphorus to the ocean independent of season.

(Table 6). Whereas nutrients from urban sources made up on average 4% of the nitrogen and phosphorus loads entering the estuary from the “diffuse” catchment areas, nutrient loads from urban runoff and sewage that directly impacted the estuary contributed only 0.7% TN and 2.2% TP to the nutrient budget even during the 1994/95 period. There were large spatial and inter-annual variations in the contributions from each sub-catchment area caused by discharge and land use heterogeneity. For example, during the 1994/95 period (when the catchment rainfall distribution was more coastal), the coastal areas (Tuckean, Emigrant Creek, and Cane lands) contributed 36.4% TN and 28.9% of the TP load to the estuary despite being only 11.4%

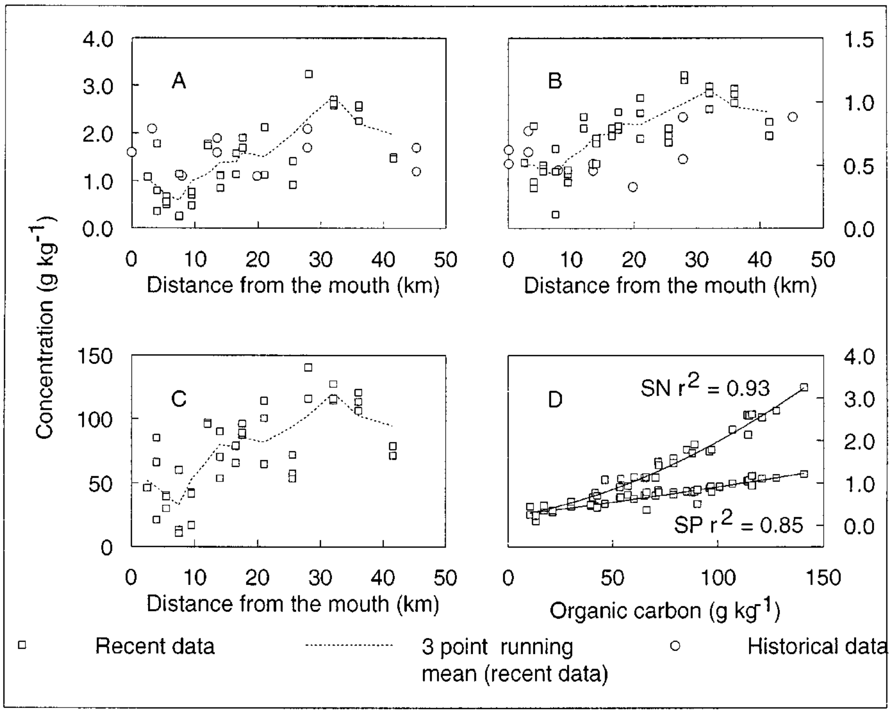

Figure 8. Concentrations of nitrogen, phosphorus and organic carbon in the sediments of the Richmond River estuary. (A) sediment nitrogen; (B) sediment phosphorus; (C) organic carbon (LOI); (D) correlations.

of the total catchment area. The Bungawalbin sub-catchment (25% of the total catchment area) showed the greatest inter-annual variation; during the 1994/95 period it contributed only 0.1% TN and 0.1% TP whereas in the 1995/96 period it contributed 13.4% TN and 5.2% of the TP load to the estuary. During both years precipitation contributed less than 1.6% N and 0.4% of the P loads to the estuary.

The majority of both nitrogen and phosphorus loads that were delivered to the estuary during each year were transported directly off shore during flood discharge when the estuary was flushed fresh at the mouth. As such, there was little opportunity for the deposition of flood-borne nutrient loads. During the 1994/95 period 2.5% TN and 5.4% of the TP loads that were input to the estuary were retained in the estuary. During the 1995/96 period, retention was reduced to 0.6% TN and 1.7% TP as a result of the larger flood in May.

Discussion

Estuarine hydrology and forcing

The factors that can influence the movement of nutrients in estuarine systems include tidal range and asymmetry, ocean currents, upwelling, wind, density stratification / gradients (salinity or temperature), catchment hydrology, rate and magnitude of biotic cycling and flushing time (Pennock et al. 1994; Naiman & Sibert 1978; Uncles et al. 1991; Vorosmarty & Loder 1994; Justic et al. 1995; Yin et al. 1995a–c; Doval et al. 1997; Mackas & Harrison 1997).

The main forcing mechanisms operating in the Richmond River estuary change seasonally. During the wet season, the estuary in driven by fluvial discharge when the estuary may be flushed fresh at the mouth. Following floods, the estuary recovers via a salt wedge penetrating landward and for several weeks the estuary can be stratified. With the onset of dry weather, the salt water / freshwater stratification breaks down, gravitationally induced tidal currents begin to dominate, and the resulting vertically homogeneous brackish water continues to advance to about 50 km upstream from the mouth (Rochford 1951; Eyre & Twigg 1997; Hossain 1998).

The large intra-annual variation (1,300 times) in daily runoff from the Richmond catchment between July 1994 and June 1996 (0.29 to 376.09 $Ls^{-1}km^{-2}$ averaged on a daily basis) resulted in a wide range of estuarine flushing times (<1 to 176 days) depending on the season (Hossain 1998). A similar variable flushing time was also found for the sub-tropical Brisbane River estuary (250 km north of the Richmond River estuary) where flushing times during 1996 ranged from <1 to 415 days (Eyre et al. 1998). Eyre and Twigg (1997) concluded that hydrological factors and consequently flushing times were the dominant control on the degree to which nutrients are processed in the Richmond River estuary. This variable flushing is likely to be the major difference between Australian systems and typical systems from North America and western Europe (Eyre 1998).

Nutrient retention efficiency

During periods of flood, flushing times were reduced to less than one day resulting in a large proportion of the nutrients delivered to the estuary being discharged directly off shore to the continental shelf. When the nutrients exported to the continental shelf were compared to those entering the estuary and graphed against flushing time, a model of estuarine behaviour during flood discharge was developed (Figure 9). Nutrient retention in the estuary during floods was proportional to flushing time. During small floods, such as occurred in February 1995 and January 1996 (1:1 return period), 57–62%

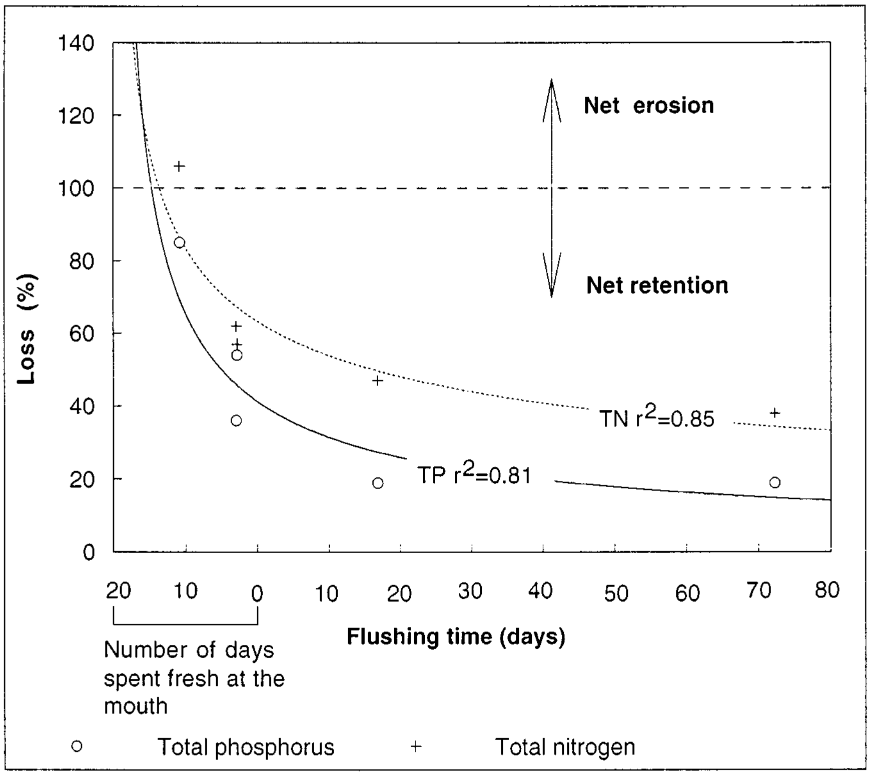

Figure 9. A model of the impacts of flood discharge on the retention of nutrients in the Richmond River estuary. As flood magnitude increases, the proportion of terrestrially derived material retained in the estuary decreases. Losses greater than 100% represent erosion from the estuarine basin. Calculations were made using the nutrient loads during the rising and falling stages of the flood hydrograph only. Data included flood loads from February 1995, January 1996, May 1996, and two minor events in March 1995 and November 1995. Loss (%) = export to ocean / input from catchment $\times$ 100.

TN and 36–54% of the TP load was exported directly off shore. During the May 1996 flood (1:5 return period), 106% TN (6% erosion from the estuarine basin) and 85% of the TP load was deposited off shore. In the Richmond River estuary (and probably other tropical and sub-tropical systems) it was the minimum flushing time which determined the nutrient retention rather than an "average flushing time" which may be appropriate only for less episodic temperate systems of either short or long flushing times.

Low nutrient retention in the Richmond River estuary contrasts with temperate systems such as Chesapeake Bay where about 70% of the nitrogen is retained within the system. The majority of temperate systems in the study of Nixon et al. (1996) showed a retention >75%. However, some temperate systems do have low retention efficiency in response to a low freshwater residence time (Norsminde Fjord) or a large tidal prism relative to the volume of the system (Gradyb tidal area) (Pejrup et al. 1993; Nielsen et al. 1995).

For instance, the Guadalupe estuary, Texas, shows an inter-annual variation in retention that is related to catchment discharge (dry year 30% TN, 107% TP; wet year 76% TN, 86% TP) (Nixon et al. 1996). In the Richmond system, greater retention of phosphorus relative to nitrogen within the estuary was related to a greater proportion of TP relative to TN being transported during floods in a particulate form (Table 5). Suspended sediments carried in the waning stages of flood discharge were deposited in the estuary (Hossain 1998) along with associated particulate phosphorus whereas the majority of the nitrogen was transported directly off shore in a dissolved form during flood discharge.

Retention of phosphorus may also be enhanced by inorganic adsorption to sediment (Froelich 1988) or flocculation of colloids (Sholkovitz 1976) and subsequent deposition during post-flood and the dry season in the low salinity reaches of the recovering estuary (Eyre & Twigg 1997). Low freshwater residence time (1–14 days) was responsible for generally low nutrient (N, P, Si) retention in the Great Ouse estuary, England (Rendell et al. 1997). In the Great Ouse estuary, inorganic removal of phosphorus via adsorption and flocculation leads to a greater retention of phosphate (21%) than nitrate and silica (1%). It was likely that a combination of these processes may have lead to greater P relative to N retention in the Richmond River estuary.

Some temperate systems, although having short flushing times, differ from the Richmond River estuary in that flushing times are less variable (Eyre 1998). The sub-tropical Richmond River estuary can have years when there are no floods large enough to flush the system. It is suggested that during a non-flood year, nutrients (especially P) entering the system during small catchment rains with be almost entirely retained in the system. If this is the case, the Richmond (and probably other sub-tropical systems) can vary between very low retention to high retention. This contrasts with temperate systems which are usually more constant (e.g. low or high retention).

Nutrient dynamics during the dry season

The Pacific Ocean was a source of nitrogen to the Richmond River estuary during the dry season. The importance of the ocean as a source has been highlighted in some temperate systems for phosphorus (Lucotte 1989; Boynton et al. 1995; Nixon et al. 1996), nitrogen (Nielsen et al. 1995; Mackas & Harrison 1997) and both N and P (Nixon et al. 1995; Engqvist 1996). In some systems the input from the ocean on an annual basis is larger than from

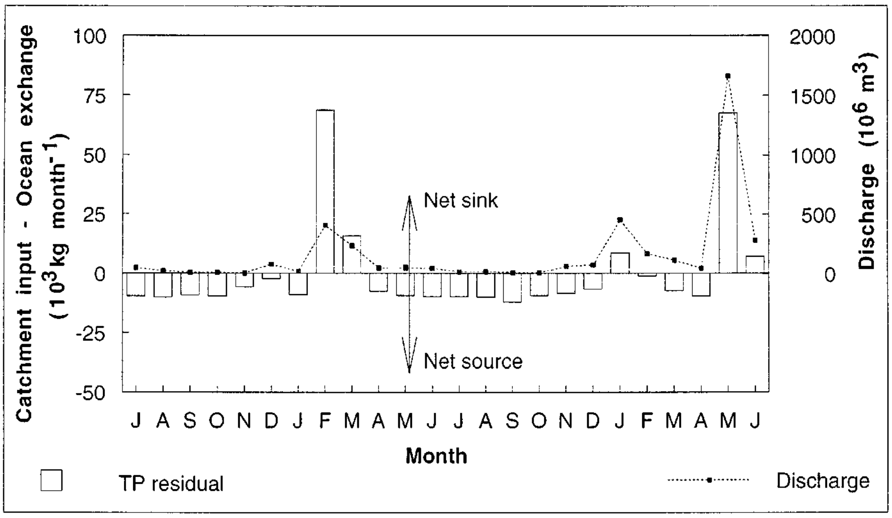

Figure 10. The dynamics of phosphorus in the Richmond River estuary. During months when high catchment discharge occurred, the estuary acted as a net sink. In contrast during post-flood and the dry season there was greater net export from the estuary to the ocean than was input from terrestrial sources suggesting that estuarine sediments were a net source of phosphorus to the water column.

terrestrial sources (Lucotte 1989; Engqvist 1996; Mackas & Harrison 1997; Eyre & France 1997).

In the Richmond system, the majority of the nitrogen input from the ocean was organic (DON or TPN). However, the input of inorganic nutrients (NO_x, NH_4^+, DIP) varied for each survey and was apparently not related to the spring-neap tidal cycle (Table 4). For example, during the spring tide in November 1994, inorganic nutrients were exported to the ocean and organic N was imported to the lower estuary whereas during the neap tide (sampled one week later), inorganic nutrients were imported from the ocean along with a smaller proportion of organic N, and DOP and TPP. The reverse pattern occurred during the survey in the following dry season. The cyclic transformation from inorganic to organic nutrient forms has been observed in many temperate estuaries (e.g. Fisher et al. 1992). They reported turnover times in Cheasapeake bay ranging from 1 hour to several weeks for NH_4^+ and PO_4. Turnover times tended to be fast when DIN supply was limited. It seems likely that N turnover times in the Richmond River estuary may be occurring on a temporal scale of less than a week during the dry season when nitrogen concentrations were low.

When the export of phosphorus was compared to the input from catchment surface on a monthly basis and the residual plotted as a function of time, a seasonal pattern emerged (Figure 10). Net deposition occurred in the estuary during the wet season. Soon after flood deposition ceased and during the dry season, the estuary became a net source of phosphorus due to either desorption or mineralisation of estuarine sediments. An increase in NH_4^+ concentration was observed in the lower Richmond estuary during the dry season; a feature observed previously (Eyre & Twigg 1997). The input of sewage to the lower estuary is too small to account for the NH_4^+ concentration; the source is likely from decomposing organic sediments (e.g. Balls 1994). Given the relationship of both nitrogen and phosphorus to organic carbon in the sediments of the Richmond River estuary (Figure 8) and the observation of an ammonium source in the lower estuary, mineralisation seems most likely source of phosphorus. Some of the phosphorus was also exported in particulate form (Table 4) during both post-flood and the dry season probably as a result of tidal reworking and sediment re-suspension (mainly post-flood) and assimilation in the water column.

In a previous study conducted in the Richmond River estuary, Eyre and Twigg (1997) found that the lower estuary was a source of NH_4^+, DIP, and DOP during the dry season (4 September 1994) and that DON, TPN, and TN concentrations were higher at the ocean end-member. Although their results were consistent with the results of this study, (the estuary was depleted in nitrate during the dry season), they neglected to consider the oceanic source; instead concluding that once the mineralisation of sediment organic matter to ammonia was exhausted, riverine nitrate became an important source of nitrogen. The work of Eyre and Twigg (1997) helps to validate the model that enabled the calculation of nutrient loads during months when no sampling was conducted on the estuary (Figure 6) by illustrating the persistence of the estuarine source of P and the estuarine sink for N during the 1994 dry season. An oceanographic study near Ballina found a winter surface nitrate maximum which persisted for several months during the spring and an upwelling later in the spring was the cause of a second but more temporally transient nitrate maximum (Rochford 1984). The existence of coastal upwelling adjacent to the Richmond River estuary is probably responsible for the external supply of nutrients and organic matter from the ocean to the estuary during the spring dry season months (September–November).

Nutrient limitation

Primary production in the Richmond River estuary was potentially nitrogen limited for the majority of the study illustrated by low DIN:DIP ratios especially during the dry season (Table 3). Sediments of the Richmond River estuary also display relatively low TN: TP ratios (average = 1.9:1). Eyre and Twigg (1997) found low water column DIN:DIP ratios of 5:1 (molar) equivalent to 2.4:1 (mass) in the Richmond River estuary between March and September 1994 and concluded that the estuary was potentially nitrogen limited. They suggested that leaching of phosphorus from basaltic lithology combined with denitrification was a likely cause of N limitation in the Richmond River estuary. To an extent, low N:P ratios in the water column and sediments reflect the low ratio of TN:TP loads (4.3:1 and 5.6:1 for the 1994/95 and 1995/96 years respectively) entering the estuary from diffuse and point sources (Table 6). However, low TN:TP input ratios were further modified by low retention efficiency associated with flood discharge. The model for estuarine behaviour during flood discharge (Figure 9) suggests that a lower percentage of TN relative to TP will be retained within the estuary for any given flood. For instance, during February 1995, 215,793 kg TN and 33,028 kg TP (6.5N:1P) were delivered to the estuary during a small flood. Due to complete flushing of the estuarine basin for approximately 3 days, only 38% TN and 64% TP were retained in the estuary; the ratio of TN:TP retained was 3.9:1.

Extremely low N:P ratios in the water column during the dry season and low sediment TN:TP ratios may also result from denitrification when freshwater residence times are long (Nixon et al. 1996; Eyre 1997). If this was the case, the source of phosphorus in the estuary during post-flood and the dry season (Figure 10, and Eyre & Twigg 1997) was mainly a result of the mineralisation of sediment organic matter. Nitrate produced in this manner may be directly denitrified whereas DIP, DOP, and NH_4^+ may be released and become a source of nutrients driving water column productivity. The release of P into the water column from catchment derived sediments would also further reduce the N:P ratio in the water column, a feature that was found in the Rhode River estuary (Jordan et al. 1991). It was likely that a combination of low TN:TP ratios in the catchment, lower TN retention relative to TP during floods, and denitrification during post-flood and the dry season was responsible for low N:P ratios in the Richmond River estuary.

Errors associated with the budgets

There were several possible inputs to the Richmond River Estuary that were not quantified including nutrient removed by commercial and recreational fishing, nutrient inputs associated with groundwater discharge, and dry deposition from the atmosphere. These inputs are likely to have been small relative to the larger terms such as fluvial inputs and ocean exchange. Errors in nutrient analysis were 4.4% (TN) and 3.5% (TP). Errors associated with the measurement of discharge from catchment surfaces has been estimated at 7.5% (Winter 1981). The error associated with the calibration of the hydrodynamic model used to calculate the water exchange through the Richmond

River estuary was 16% and sedimentation rates had errors of 41% (1994/95) and 49% (1995/96) (Hossain 1998). Errors associated with the analysis of sediment nutrients were 6% (SN) and 4.7% (SP).

Given that diffuse input and nutrient exchange through the mouth of the estuary at Ballina were the dominant terms in the nutrient budget, errors associated with the other input terms (coastal plain, precipitation, urban runoff, sewage, septic leachate) were assigned the same errors as diffuse catchment loads. Whereas the errors associated with individual terms were relatively small, the errors associated with the residual of the nutrient budgets were (quoted to 2 significant figures) ±270,000 kg TN and ±66,000 kg TP in 1994/95 and ±920,000 kg TN and ±160,000 kg TP in 1995/96. When determined as the residual in the nitrogen budget, N_2 exchange with the atmosphere also incorporated the errors from all the other terms (Table 6).

The flood regime – a natural buffer to anthropogenic impacts

During May 1996 (a 1 in 5 year flood), erosion occurred in the estuary suggesting that the Richmond River estuary undergoes periodic self cleansing (or resetting). The majority of nutrients that were stored during small floods were released on an annual basis during the dry season. The estuary was depleted in nitrogen during the dry season resulting in net input from the ocean. Even during the dry season, nutrient loads from point sources had little impact on the estuary compared to release of phosphorus from sediments and input of nitrogen from the ocean.

A comparison of water quality changes in the Richmond River estuary over the past 50 years (Eyre 1997) also found that nutrient concentrations during the dry season 50 years ago were also controlled by internal processes. Eyre (1997) suggested that whereas nitrate and phosphate concentrations following a flood in 1994 were 2–3 times greater than similar floods of 50 years ago, nutrient concentrations in the water column during the dry season have not changed despite large changes in land use practices and human population in the catchment over time. There has also been no change in sediment nutrient concentrations over the past 50 years (Figure 8) further supporting the self cleansing hypothesis.

Stoichiometric considerations

The residual in the nitrogen budgets (Table 6) was the difference between total loads and total losses. In the case of TN, this may be accounted for by the net effect of N-fixation – denitrification (Nfix-Denit). There was net Nfix-Denit during 1994/95 of –20 ± 49 mg $m^{-2}d^{-1}$ and during 1995/96 of 3 ± 168 mg $m^{-2}d^{-1}$. Clearly, these estimates cannot be distinguished from zero due to the size of the errors. Another estimate of Denit-N-fix can be made using TDN and TDP budgets and stoichiometric relationships found within the sediments of an estuary. Assuming that the sediment have a Redfield ratio (N:P = 7.2:1 mass) and given the errors associated with the calculation of the TDN and TDP budgets there was a net denitrification of 118 $\pm$ 68 mg $m^{-2}d^{-1}$ (1994/95) and 11 $\pm$ 223 mg $m^{-2}d^{-1}$ (1995/96). When the average TN:TP ratio (1.86:1) of sediments in the Richmond River estuary was used in the calculations there was a net denitrification of 68 $\pm$ 35 mg $m^{-2}d^{-1}$ (1994/95) and a net denitrification of 14 $\pm$ 139 mg $m^{-2}d^{-1}$ (1995/96). Again, these estimates are not distinguishable from zero and thus it appears that the processes of denitrification and nitrogen fixation may be approximately balanced over the annual cycle.

When the dry seasons were considered separately, a different conclusion emerges. During the dry season of 1994/95 there was net denitrification in the estuary of 65 $\pm$ 11 mg $m^{-2}d^{-1}$ (Redfield) or 39 $\pm$ 7 mg $m^{-2}d^{-1}$ (Richmond sediment). During the dry season of 1995/96 there was net denitrification in the estuary of 47 $\pm$ 8 mg $m^{-2}d^{-1}$ (Redfield) or 22 $\pm$ 4 mg $m^{-2}d^{-1}$ (Richmond sediment). These rates were significantly different from zero and therefore suggest that the Richmond River estuary was net denitrifying during the dry season. When stoichiometric calculations where made using the annual budgets for the estuary, the errors associated with determining nutrient exchanges at the boundaries of the model were large compared to the residual of the TDN and TDP budgets. Therefore, it is probably more appropriate to calculate stoichiometricly linked budgets on a seasonal basis in tropical and sub-tropical systems which exhibit highly seasonal discharges.

Synthesis

This study along with previous work (Eyre & Twigg 1997; Eyre 1997; Hossain 1998; Eyre 1998) strongly supports a three stage (flood, recovery, normal) model of intra-annual variation. Here, a model of inter-annual variation was developed (flood year, nonflood year) which builds on previous work. Although inherently simplistic (for instance, it does not include the possibility of a wetter than normal dry season or a wet season with no floods), it serves as an illustration of the highly variable nature of the Richmond River estuary which may be more typical of other tropical and sub-tropical Australian systems.

Scenario 1: flood year

During years in which a flood occurs in the catchment, almost 100% of nutrient loads enter the estuary from diffuse sources during short lived flood events. During the rising and falling stages of flood discharge, the estuary is flushed entirely of brackish water for days to weeks. As a result of flood forcing, the system is "cleansed" or "reset" due to net erosion that occurs in the estuarine basin. During the waning stages of flood discharge, and during post-flood, sediment bound nutrients are deposited in the estuary in response to two layer stratification thus replacing some of the eroded sediments and associated nutrients. In the 3–4 months that follow a large flood, nitrogen and phosphorus are exported from the estuary to the ocean probably as a result of mineralisation from freshly deposited sediment organic matter. As flushing times increase, external nutrient loads from diffuse catchment sources decrease and biological nutrient cycling becomes more important. The release of phosphorus from sediments continues throughout the annual cycle, whereas the ocean becomes an important source of nitrogen during the dry season.

Scenario 2: nonflood year

It has been shown that Australian catchments have higher variability relative to the rest of the world in their intra-annual flood regime (Finlayson & McMahon 1988). Although on average small floods (similar to February 1995 and January 1996) occur on a 1:1 year return period, there are no floods during the "wet" season of some years. In years when no, or only minor, flood discharge occurs from the catchment, it is suggested that close to 100% of nutrients entering the estuary would be retained during the wet season. Flushing times would remain long relative to biogeochemical process and therefore internal nutrient processing would continue to operate in the estuary during both the wet and dry seasons modifying any external nutrient loads entering the estuary. Denitrification may become a more important removal mechanism compared to ocean exchange and, on an annual basis, denitrification is likely to be greater than N-fixation. During the dry season, net input of nitrogen may still occur in response to coastal upwelling and N depletion in the estuary via denitrification. It seems likely that the internal sediment sink would continue to be the dominant source of phosphorus during the dry season and net loss to the ocean would continue all year. On an annual basis it is likely that $\gg$2.5%N and 5.4%P (results from the 1994/95 year) would be retained in the sediments. However, even if this occurred for several consecutive years, the next large flood would "cleanse" the system.

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References

Anon (1991) QuikChem Automated Ion Analyser Methods Manual. LACHAT INSTRUMENTS, Milwaukee, USA

Anon (1995) Standard methods for examination of water and wastewater. Washington, American Public Health Association (APHA), American Water Works Association (AWWA), and Water Pollution Control Federation (WPCF)

Balls PW (1994) Nutrient inputs to estuaries from nine Scottish east coast rivers; influence of estuarine processes on inputs to the North Sea. Estuarine, Coastal and Shelf Science 39: 329–352

Balls PW, Laslett RE & Price NB (1994) Nutrient and trace metal distributions over a complete semi-diurnal tidal cycle in the forth estuary Scotland. Netherlands J. Sea Res. 33: 1–17

Beddig S, Brockmann U, Dannecker W, Korner D, Pohlmann T, Puls W, Radach G, Rebers A, Rick H, Schatzmann M, Schlunzen H & Schulz M (1997) Nitrogen fluxes in the German Bight. Marine Pollution Bull. 34: 382–394

Billen G, Somville M, De Becker E & Servais P (1985) A nitrogen budget of the Scheldt hydrographical basin. Netherlands J. Sea Res. 19: 223–230

Boynton WR, Garber JH, Summers R & Kemp WM (1995) Inputs, transformations, and transport of nitrogen and phosphorus in Chesapeake Bay and selected tributaries. Estuaries 18: 285–314

Bramley RGV, Johnson AKL & Smettem KRJ (1994) Quantifying the effects of different rural land use on water quality in the catchment of the Herbert River – preliminary results. Australian Society of Sugar Cane Technologists

Correll DL (1981) Nutrient mass balances for the watershed, headwaters, intertidal zone, and basin of the Rhode River Estuary. Limnology and Oceanography 26: 1142–1149

Correll Dl, Jorden TE & Weller DE (1992) Nutrient flux in a Landscape: Effects of coastal land use and terrestrial community mosaic on nutrient transport to coastal waters. Estuaries 15: 431–442

Doering PH, Oviatt CA & Pilson MEQ (1990) Control of nutrient concentrations in the Seekonk-Providence River region of Narragansett Bay, Rhode Island. Estuaries 13: 418–430

Doval MD, Alvarez-Salgado XA & Perez FF (1997) Dissolved organic matter in a temperate embayment affected by coastal upwelling. Marine Ecol. Progress Ser. 157: 21–37

Engqvist A (1996) Long-term nutrient balances in the eutrophication of the Himmerfjarden estuary. Estuarine, Coastal and Shelf Science 42: 483–507

Eyre B (1993) Nutrients in the sediments of a tropical north-eastern Australian estuary, catchment and nearshore zone. Australian J. Marine Freshwater Res. 44: 845–866

Eyre B (1995) A first-order nutrient budget for the tropical Moresby estuary and catchment North Queensland, Australia. J. Coastal Res. 11: 717–732

Eyre B (1997) Water quality changes in a well flushed Australian estuary: A 50 year perspective. Marine Chem. 59: 177–187

Eyre BD & Twigg C (1997) Nutrient behaviour during post-flood recovery of the Richmond River estuary northern NSW, Australia. Estuarine, Coastal and Shelf Science 44: 311–326

Eyre B & France L (1997) Importance of marine inputs to the sediment and nutrient load of coastal-plain estuaries: a case study of Pumicestone Passage, southeastern Queensland, Australia. Marine and Freshwater Res. 48: 277–286

Eyre B, Hossain S & McKee L (1998) A suspended sediment budget for the modified subtropical Brisbane River estuary, Australia. Estuarine, Coastal and Shelf Sci. 47: 513–522

Eyre B (1998) Transport, retention and transformation of material in Australian estuaries. Estuaries 21: 540–551

Finlayson BL & McMahon TA (1988) Australia vs the World, A comparative analysis of streamflow characteristics. In: Warner RF (Ed) Fluvial Geomorphology of Australia (pp 17–40). Academic Press of Australia, Sydney

Fisher TR, Peele ER, Ammerman JW & Harding Jr LW (1992) Nutrient limitation of Phytoplankton in Chesapeake Bay. Marine Ecol. Progress Ser. 82: 51–63

Froelich PN (1988) Kinetic control of dissolved phosphate in natural rivers and estuaries: A primer on the phosphate buffer mechanism. Limnology and Oceanography 33: 649–668

Galloway JN, Howarth RW, Michaels AF, Nixon SW, Prospero JM & Dentener FJ (1996) Nitrogen and phosphorus budgets of the North Atlantic Ocean and its watershed. Biogeochemistry 35: 3–25

Gorden Jr DC, Boudreau PR, Mann KH, Ong J-E, Silvert WL, Smith SV, Wulff F & Yanagi T (1996) LOICZ biogeochemical modelling guidelines. Netherlands Institute for Sea Research

Hoare RA (1984) Nitrogen and Phosphorous in Rotorua urban streams. New Zealand J. Marine Freshwater Res. 18: 451–454

Hopkinson Jr CS & Vallino JJ (1995) The relationships among mans activities in watersheds and estuaries: A model of runoff effects on patterns of estuarine community metabolism. Estuaries 18: 598–621

Hossain S (1998) Hydrology and suspended sediment transport in the Richmond River catchment and estuary NSW Australia. PhD Thesis, Southern Cross University, Australia

Jordan TE, Correll DL, Miklas J & Weller DE (1991) Nutrients and Chlorophyll at the interface of a watershed and an estuary. Limnology and Oceanography 32: 251–267

Justic D, Rabalais NN, Turner RE & Dortch Q (1995) Changes in nutrient structure of river-dominated coastal waters: Stoichiometric nutrient balance and its consequences. Estuarine, Coastal and Shelf Sci. 40: 339–356

Kelly JR (1997) Nitrogen flow and interaction of Boston Harbour with Massachusetts Bay. Estuaries 20: 365–380
Kemp WM, Smith EM, Marvin-DiPasquale M & Boynton WR (1997) Organic carbon balance and net ecosystem metabolism in Chesapeake Bay. Marine Ecol. Progress Ser. 150: 229–248
Kerr G & Eyre B (1995) Stormwater quality in Lismore, NSW, a regional urban centre. The Second International Symposium on Urban Stormwater Management, Melbourne, July 1995. The Australian Institution of Engineers
Kjerfve B & Proehl JA (1979) Velocity variability in a cross-section of a well-mixed estuary. J. Marine Res. 37: 409–418
Kjerfve B, Stevenson LH, Proehl JA, Chrzanowski TH & Kitchens WM (1981) Estimation of material fluxes in an estuarine cross section: A critical analysis of spatial measurement. Limnology and Oceanography 26: 325–335
Klump JV, Edgington DN, Sager PE & Robertson DM (1997) Sedimentary phosphorus cycling and a phosphorus mass balance for Green Bay (Lake Michigan) ecosystem. Canadian J. Fisheries Aquatic Sci. 54: 10–26
Kronvang B & Bruhn AJ (1996) Choice of sampling strategy and estimation method for calculating nitrogen and phosphorus transport in small lowland streams. Hydrological Processes 10: 1483–1501
Lucotte M (1989) Phosphorus reservoirs in the St. Lawrence upper estuary. Canad. J. Fisheries Aquatic Sci. 46: 59–65
Mackas DL & Harrison PJ (1997) Nitrogenous nutrient sources and sinks in the Juan de Fuca Straight / Straight of Georgia / Puget Sound estuarine system: Assessing the potential for eutrophication. Estuarine, Coastal and Shelf Sci. 44: 1–21
Naiman RJ & Sibert JR (1978) Transport of nutrients and carbon from the Nanaimo River to its estuary. Limnology and Oceanography 23: 1183–1193
Nielsen K, Neilsen LP & Rasmussen P (1995) Estuarine nitrogen retention independently estimated by the denitrification rate and mass balance methods: a study of Norsminde Fjord, Denmark. Marine Ecol. Progress Ser. 119: 275–283
Nixon SW, Granger SL & Nowicki BL (1995) An assessment of annual mass balance of carbon, nitrogen, and phosphorus in the Narragansett Bay. Biogeochemistry 31: 15–61
Nixon SW, Ammerman JW, Atkinson LP, Berounsky VM, Billen G, Boicourte WC, Boynton WR, Church TM, Ditoro DM, Elmgren R, Garber JH, Giglin AE, Jahnke RA, Owens NJP, Pilson MEQ & Seitzinger SP (1996) The fate of nitrogen and phosphorus at the land-sea margin of the North Atlantic Ocean. Biogeochemistry 35: 141–180
Parsons TR, Maita Y & Lalli CM (Eds) (1984) A Manual for Chemical and Biological Methods for Seawater Analysis. Pergamon, Potts Point, NSW, Australia
Pejrup M, Barthodly J & Jenson A (1993) Supply and exchange of water nutrients in the Gradyb tidal area, Denmark. Estuarine, Coastal and Shelf Sci. 36: 221–234
Pennock JR, Sharp JH & Schroeder WW (1994) What controls the expression of estuarine eutrophication? Case studies of nutrient enrichment in the Delaware Bay and Mobile Bay estuaries, USA. In: Dyer KR & Orth RJ (Eds) Changes in Fluxes in Eestuaries: Implications from Science to Management (pp 139–146). Olsen and Olsen, Fredensborg
Redfield AC (1934) On the proportions of organic derivatives in sea water and their relation to the composition of plankton. James Johnstone Memorial Volume (pp 176-192). Liverpool, Liverpool University Press.
Rendell AR, Horrobin TM, Jickells TD, Edmunds HM, Brown J & Malcolm SJ (1997) Nutrient cycling in the Great Ouse estuary and its impact on nutrient fluxes to the Wash, England. Estuarine, Coastal and Shelf Sci. 45: 653–668

Richards RP (1989) Evaluation of some approaches to estimating non-point pollutant loads for unmonitored areas. Water Resour. Bull. 25: 891–904

Rochford DJ (1951). Studies in Australian estuarine hydrology. Australian J. Marine Freshwater Res. 2: 1–117

Rochford DJ (1984) Nitrates in eastern Australian coastal waters. Australian J. Marine Freshwater Res. 35: 385–397

Sholkovitz ER (1976) Flocculation of dissolved organic matter during the mixing of river water and sea water. Geochimica et Cosmochimica Acta. 40: 831–845

Smith SV & Hollibaugh JT (1997) Annual cycle and interannual variability of ecosystem metabolism in a temperate climate embayment. Ecological Monographs 67: 509–533

Uncles RJ, Stephens JA & Barton ML (1991) The nature of near bed currents in the upper reaches of an estuary. In: Elliott ME & Ducrotoy J-P (Eds) Estuaries and Coasts: Spatial and Temporal Intercomparisons (pp 43–47). Olsen and Olsen, Caen, France

Valderrama JC (1981) The simultaneous analysis of total nitrogen and total phosphorus in natural waters. Marine Chemistry 10: 109–122

Valiela I, Foreman K, LaMontagne M, Hersh D, Costa J, Peckol P, DeMeo-Andreson B, D'Avanzo C, Babionf M, Sham C, Brawley J & Lajtha K (1992) Couplings of watersheds and coastal waters: Sources and consequences of nutrient enrichment in Waquoit Bay, Massachusetts. Estuaries 15: 443–457

Vorosmarty CJ & Loder T (1994) Spring-neap tidal contrasts and nutrient dynamics in a marsh-dominated estuary. Estuaries 17: 537–551

Walling DE & Webb BW (1985) Estimating the discharge of contaminants to coastal waters by rivers: some cautionary comments. Marine Pollution Bull. 16: 488–492

Winter TC (1981) Uncertainty in estimating water balances in lakes. Water Resour. Bull. 17: 82–115

Yin K, Harrison PJ, Pond S & Beamish RJ (1995a) Entrainment of nitrate in the Fraser River estuary and its biological implications. I. Effects of the salt wedge. Estuarine, Coastal and Shelf Sci. 40: 505–528

Yin K, Harrison PJ, Pond S & Beamish RJ (1995b) Entrainment of nitrate in the Fraser River estuary and its biological implications. II. Effects of spring vs neap tides and river discharges. Estuarine, Coastal and Shelf Sci. 40: 529–544

Yin K, Harrison PJ, Pond S & Beamish RJ (1995c) Entrainment of nitrate in the Fraser River estuary and its biological implications. III. Effects of winds. Estuarine, Coastal and Shelf Sci. 40: 545–558