

# The effect of residence time and hypoxia on nitrogen loading in the Yarra River Estuary, Australia.

Keryn Roberts<sup>1</sup>, Michael Grace<sup>2</sup>, Perran Cook<sup>2</sup>

<sup>1</sup> Water Studies Centre, Monash University, Wellington, Clayton, Victoria, 3800, Australia, roberts.keryn@gmail.com

<sup>2</sup> Water Studies Centre, Monash University, Wellington, Clayton, Victoria, 3800, Australia

## Abstract

Estuaries provide the final stage of nitrogen processing before its release into coastal waters. However, residence time, oxygen conditions and hydraulic mixing determine the nitrogen removal capacity of an estuary. Long residence times can lead to low oxygen conditions significantly affecting nutrient transformation pathways including, but not limited to, inhibition of nitrification and the competition for nitrate between denitrification and dissimilatory nitrate reduction to ammonium (DNRA). The study site for this research, the Yarra River estuary, is a shallow (3 – 5m) salt wedge estuary prone to hypoxia resulting from the extended residence time of the bottom waters during low flow events. The estuary is one of the main freshwater nitrogen inputs into Port Phillip Bay (PPB), a nitrogen limited system. This research examined nitrogen processing over the period 2009 – 2011, extending over two summers of contrasting rainfall. Nitrogen loads were driven by rainfall in the catchment and ensuing freshwater inflow.  $\text{NO}_3^-$  was the main form of dissolved inorganic nitrogen (DIN) entering the system, being  $87 \pm 2\%$  of total DIN. Low oxygen conditions promoted nitrogen recycling within the system leading to an accumulation of  $\text{NH}_4^+$  in the stratified bottom waters of the estuary. Estimates of nitrogen removal were low for the Yarra River estuary at  $< 5\%$  of total DIN compared to 20 – 50 % for other estuarine systems. This study highlights the importance of understanding estuarine specific conditions (residence time and oxygen) on nitrogen dynamics in the management of nitrogen loads into receiving waters.

## Key Words

Denitrification, hypoxia, nitrogen loads, estuary

## Introduction

Nitrogen loads entering coastal waters have increased considerably in recent decades, largely in response to increased use of synthetic fertilizers and land use change (Howarth and Marino, 2006). Estuaries provide the final stage of nitrogen processing from freshwater inputs before it is transported further into coastal waters (Bianchi, 2007). Several studies have shown the importance of nitrogen processing in estuaries, reporting 20 – 50 % removal of the inorganic nitrogen load, citing denitrification (removal of  $\text{NO}_3^-$  as  $\text{N}_2$  gas) as the main mechanism for nitrogen removal (Seitzinger, 1988; Soetaert and Herman, 1995). However, these estimates are not always applicable and estuarine specific conditions should be considered in approaching the management of nitrogen loads into receiving waters. The success of an estuary to act as a nitrogen sink is dependent on a number of variables including oxygen conditions, residence time of the water and hydraulic mixing (Bianchi, 2007). Oxygen heavily regulate nitrogen transformation pathways; for example, nitrification, denitrification and DNRA (Bianchi, 2007). Extended residence times can lead to low oxygen conditions, hypoxic ( $\text{O}_2 < 100 \mu\text{mol-O}_2 \text{ L}^{-1}$ ) or anoxic ( $0 \mu\text{mol-O}_2 \text{ L}^{-1}$ ), which can shift nitrogen processing from nitrogen removal to recycling (or vice versa).

The Yarra River estuary, Melbourne, Australia was the study site for this research and is a salt wedge estuary prone to frequent hypoxia in the bottom waters owing to high residence times during periods of low freshwater inflow, particularly during summer (Roberts et al. 2012). The estuary is a conduit for the transport of nitrogen from a large ( $> 4000\text{km}^2$ ) and highly developed ( $> 50\%$  urban and agricultural land use) catchment, into the nitrogen-limited Port Phillip Bay (CSIRO, 1996). With the increased frequency of drought forecast for South-eastern Australia (Mc Alpine et al, 2009), the estuary is at risk of extended residence times and ensuing hypoxia in the bottom waters. At present there is very limited information on how residence time and oxygen conditions within a salt wedge estuary will influence nitrogen loads, hence this study examined nitrogen loading from 2009 – 2011 over a range of oxygen conditions.

## Method

### Site description

A nitrogen budget was calculated for the Yarra River Estuary, Australia, between September 2009 and March 2011. The estuarine region extends up to 22km from the estuary mouth to an artificial barrier, Dights Falls (Hart and Davies 1981). The estuary exhibits a typical salt wedge structure and is prone to periods of hypoxia in the bottom waters during low freshwater inflow.

Sediment biogeochemical processing was examined in three sections of the estuary the upper, middle and lower reaches. Three fixed sediment sampling sites were selected from each section: Bridge Rd (Upper), Scotch College (Middle) and Morell Bridge (Lower). Nitrogen loads were determined after the measurement of *in situ* nutrient concentrations, sediment nutrient fluxes and nitrate reduction pathways from intact sediment cores collected from the three fixed sampling sites (fluxes and rates  $\pm$  SE in Roberts et al. 2012).

### Flow

Yarra River flow was gauged just upstream of Dights Falls at Chandler Highway (Melbourne Water Corporation). Merri Creek (Upper) and Gardiners Creek (Middle) flow into the estuary and are also potential sources of nitrogen. Flow and nitrogen concentrations for these waterways were obtained from the monitoring program conducted by the Melbourne Water Corporation and included in the calculation of nitrogen loads. Rainfall and smaller drainage pathways were not included in the estimation of flow.

### Calculations

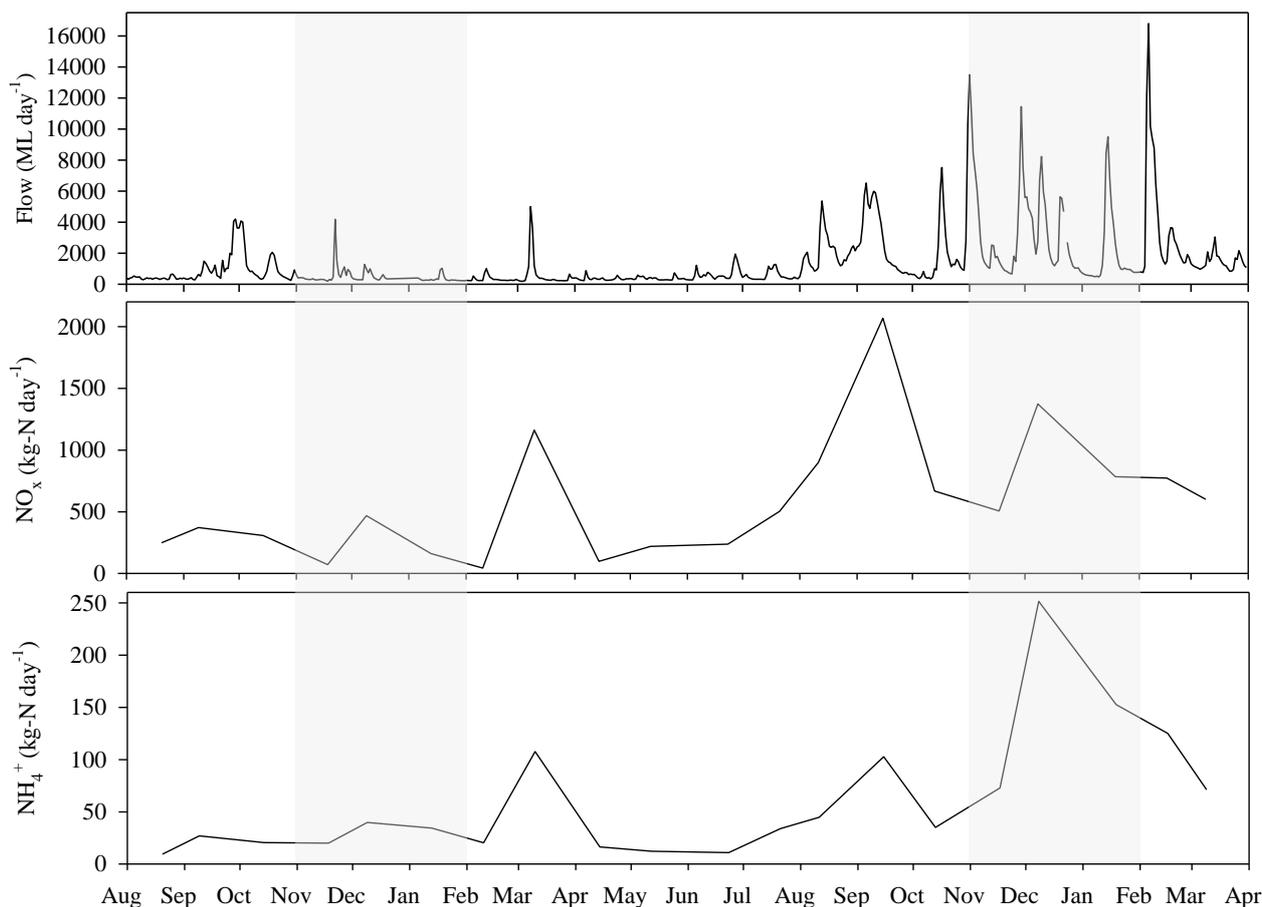
The freshwater nitrogen load was calculated as the flow (L/day) multiplied by the *in situ* nitrogen concentration (g/L). To determine the amount of nitrogen removed or recycled via denitrification and DNRA, respectively, the surface area of the sediment was estimated via measurements taken from Google Earth (bathymetry was not taken into consideration). Measured sediment fluxes of NO<sub>x</sub> and NH<sub>4</sub><sup>+</sup> were used to calculate overall nutrient loads, whilst rates of denitrification and DNRA were used to calculate the contribution of NO<sub>3</sub><sup>-</sup> reduction to NO<sub>3</sub><sup>-</sup> removal. The estuary was separated into three regions upper, middle and lower estuary.

## Results and Discussion

Figure 1 shows the input of DIN into the estuary; NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> peak during high flow events, however the removal of DIN during high flow remained < 5% (Table 1). In summer 2011, during unseasonably high rainfall and resulting freshwater inflow, nitrogen loads entering the Yarra River estuary were highest (January 2011, Table 1). During this time NO<sub>3</sub><sup>-</sup> removal was < 2% of the total NO<sub>3</sub><sup>-</sup> load and only 25% of this removal was due to denitrification (Figure 1; Table 1). In contrast during periods of low freshwater inflow the Yarra River estuary becomes stratified and as a result of the extended residence time the bottom waters become depleted in oxygen (January 2010; Figure 1, Table 1). For example, in January 2010 (a period of low flow) NO<sub>3</sub><sup>-</sup> removal was limited and the estuary a source of DIN owing to an efflux of NH<sub>4</sub><sup>+</sup> into the bottom waters (Roberts et al 2012; Table 1).

**Table 1: Summary of whole estuary nutrient loads for the sampled months, actual flux rates in Roberts et al (2012). A negative percent value represents removal whilst positive values represent addition.**

Sampling Dates	Avg. Bottom Water O <sub>2</sub> (μmol L <sup>-1</sup> )	NO <sub>x</sub> Load (kg-Day)	% NO <sub>x</sub> removal	NH <sub>4</sub> <sup>+</sup> Load (kg-day)	% NH <sub>4</sub> <sup>+</sup> removal	Total % DIN Removal
September 2009	110	190	-3	24	54	3
December 2009	85	540	-4	69	0	-4
January 2010	58	110	1	13	340	38
February 2010	54	130	0	16	-46	-5
April 2010	120	140	-12	18	260	18
May 2010	92	180	-3	22	130	12
June 2010	130	180	9	22	-9	7
December 2010	230	720	-2	92	-2	-2
January 2011	230	1,600	-1	220	0	-1
March 2011	190	780	-3	100	-7	-3

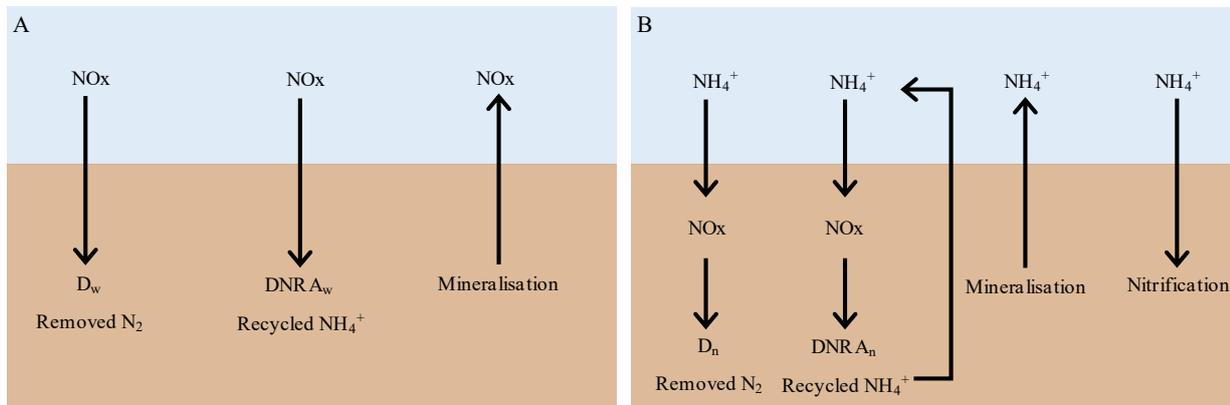


**Figure 1. The influence of freshwater inflow on nutrient loads entering the estuary plotted from August 2009 to April 2011; NO<sub>x</sub> (NO<sub>3</sub><sup>-</sup> + NO<sub>2</sub><sup>-</sup>) and NH<sub>4</sub><sup>+</sup> (kg-N day<sup>-1</sup>). Shading represents summer months. Data from Melbourne Water Corp.**

A conceptual diagram (Figure 2) outlining the key processes involved in NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> removal and recycling within the estuary will be referred to in the preceding discussion (the oxygen dependence of these processes is outlined in the figure caption). Throughout the study period, the Yarra River estuary had a very low nitrogen removal capacity with the maximum DIN removal efficiency of <5 %, and in some months the estuary was a source of DIN in the form of NH<sub>4</sub><sup>+</sup> (Table 1). The low DIN removal capacity can be explained by: (1) the residence time under high flow conditions is not sufficient for significant nitrogen processing to occur, (2) the high residence time of the water under low freshwater inflow results in stratification and hypoxia in the saline bottom waters inhibiting nitrification coupled denitrification leading to a disconnect between NH<sub>4</sub><sup>+</sup> produced via mineralisation and NH<sub>4</sub><sup>+</sup> removal by nitrification coupled denitrification (Figure 2B), (3) under oxic conditions denitrification competes directly with DNRA a recycling process (Figure 2A) which contributed up to 40 % of total NO<sub>3</sub><sup>-</sup> reduction under oxic conditions (Roberts et al 2012) and (4) the most significant inputs of nutrients to the estuary were from freshwater inflow (Figure 1) under stratified conditions hypoxic saline bottom waters separate benthic denitrification from the high NO<sub>3</sub><sup>-</sup> in the upper freshwater layer.

Nixon et al (1996) showed a negative relationship between the amount of nitrogen exported from an estuary and residence time, with prolonged residence time promoting nitrogen removal. In the Yarra River estuary during a high flow event (> 5000 ML day<sup>-1</sup>, summer 2011) the residence time is less than 1 day whilst under medium flow conditions (2000 - 3000ML day<sup>-1</sup>, summer 2010) the residence time can be up to 2 weeks and bottom water oxygen becomes depleted (Beckett et al 1982; Figure 1; Table 1). In contrast to Nixon et al (1996) prolonged residence time in this study led to limited DIN removal and in some cases DIN production (Table 1). Under either low or high freshwater inflow conditions the estuary did not remove a significant portion of DIN (< 5 %) in comparison to other estuarine systems with estimates of up to 20 – 50% (Dong et al., 2000; Ogilvie et al., 1997; Seitzinger, 1988; Soetaert and Herman, 1995). The main mechanism of

removal in these studies was denitrification, however, in the Yarra River estuary denitrification removed < 2 % of  $\text{NO}_3^-$  in the water column. We hypothesise residence time, stratification and oxygen conditions owing to the salt wedge structure of the estuary led to low denitrification rates and the limited nitrogen removal capacity of the estuary.



**Figure 2. (A)  $\text{NO}_x$  consumption and production processes,  $D_w$  – water column driven denitrification (anaerobic),  $\text{DNRA}_w$  – water column driven DNRA (anaerobic) and mineralisation. (B)  $\text{NH}_4^+$  production and consumption processes,  $D_n$  – nitrification-denitrification coupling,  $\text{DNRA}_n$  – nitrification coupled DNRA, mineralisation and nitrification (aerobic). Blue represents the water column and brown the sediment.**

## Conclusion

The Yarra River estuary has a low DIN removal capacity, explained by the residence time of the water under different flow regimes and low denitrification rates. During high inflow events residence times are inadequate for significant DIN removal and during low inflow events the prolonged residence time of the bottom waters leads to hypoxia and a net production of DIN within the system. The low nitrogen removal capacity of the Yarra River estuary indicates the management of nitrogen loads to PPB is reliant on the reduction of catchment derived nutrients rather than internal nutrient cycling within the estuary. In contrast to the low nitrogen removal capacity of the Yarra River estuary, several studies have reported DIN removal capacities of up to 50% (Dong et al., 2000; Ogilvie et al., 1997; Seitzinger, 1988; Soetaert and Herman, 1995). This study highlights the importance of examining estuarine type (salt wedge, mixed, partially mixed) alongside site specific nutrient dynamics when considering the management of nitrogen loads to receiving waters.

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