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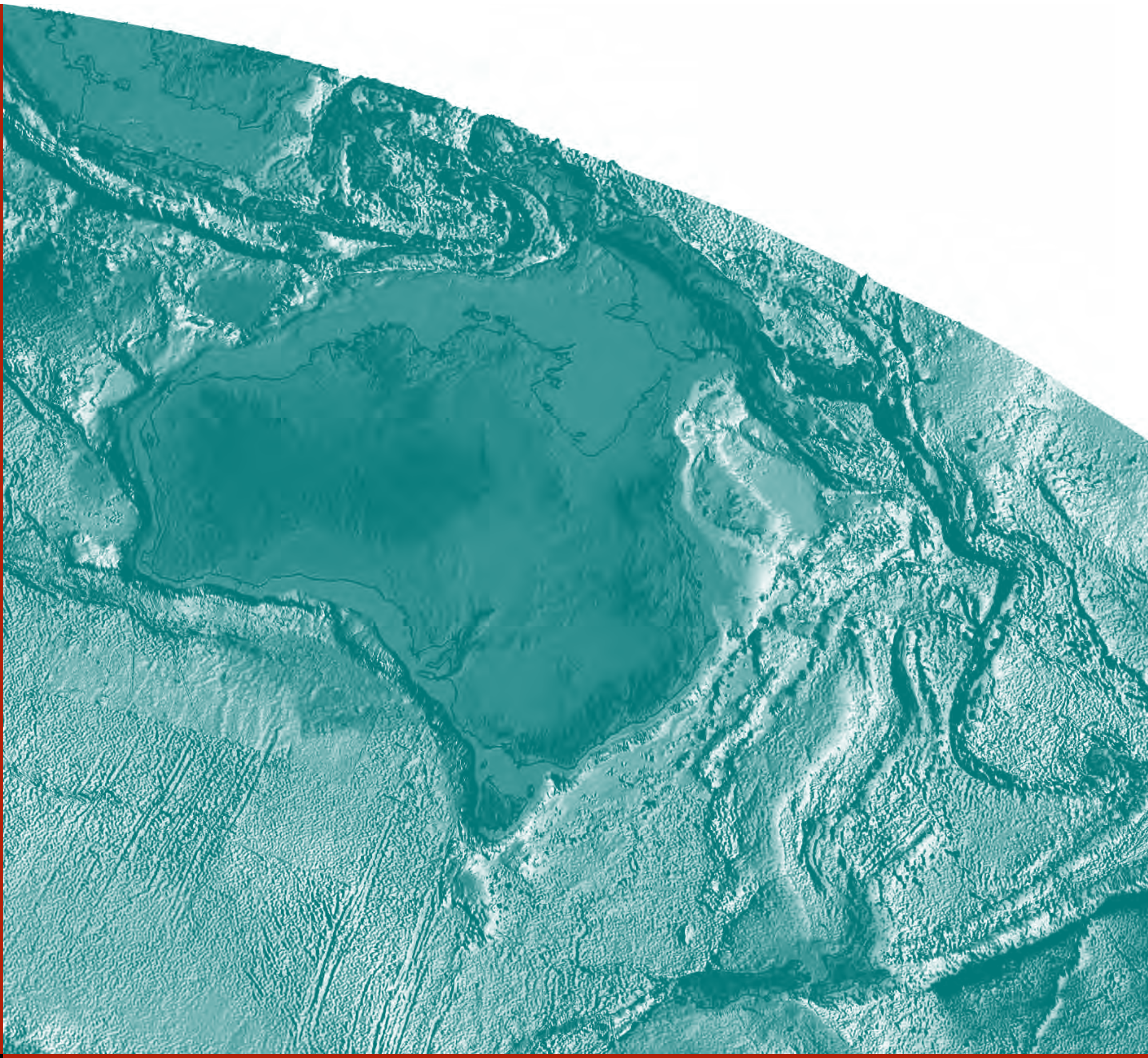

APPLYING GEOSCIENCE TO AUSTRALIA'S MOST IMPORTANT CHALLENGES

Oxygen demand and nutrient release from sediments in the upper Swan River estuary

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by

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Executive Summary

The upper Swan River estuary, located in the eastern suburban area of Perth in Western Australia, experiences periods of poor water quality in the form of high nutrient levels, anoxic bottom water conditions and occasional nuisance algae bloom. It has long been suspected that oxygen uptake and nutrient release from estuarine sediments are major drivers for these poor water quality conditions. Geoscience Australia, in conjunction with the Department of Water in Western Australia, investigated these issues in the upper Swan River estuary through water and sediment quality studies in October 2006, September 2007 and May 2008. The objectives of these studies were: (1) to characterise the distribution of different sediment types, in particular to identify areas of high nutrient release; (2) to better understand conditions that lead to high oxygen consumption and nutrient release; and (3) to determine the influence of the bottom water oxygen status on nutrient release from sediments.

Nutrient release and oxygen uptake were measured using benthic chambers at two sites in October 2006, following the annual period of high flow, and at two sites in May 2008 after some small river flows which led to extensive salinity stratification. Porewater nutrient inventories, sediment porosity and total organic carbon content were measured at 31 sites in September 2007.

Fine sediments, enriched in organic matter and with the highest rate of nutrient release, were found at deeper sites (>2.5 m) and at the confluence of creeks entering the estuary. Fine sediments accumulate at these locations because of decreased water velocity which enables fine particles to settle out of suspension. During high-flow events these areas are likely to be eroded and fine sediments transported to the lower estuary or the ocean. However, larger flushing events appear to have decreased in frequency in recent decades and flows from the major tributary of the Swan River estuary, the Avon River, are likely to decrease significantly in a future drying climate (Kelsey *et al*. 2009). This decrease in flow means that flushing will be reduced and the estuary may be more prone to long-term deposition of fine sediments and increased release of nutrients from sediments.

The largest benthic nutrient fluxes were observed following the annual winter to early spring high river discharge period, which is likely related to the deposition of catchment-derived reactive organic matter. As the river flow deceases, a salt wedge migrates upstream leading to stratification within the estuary. As the deposition of catchment-derived organic matter ceases, the rate of organic matter decomposition decreases. Consequently, low benthic nutrient fluxes were found in May after the long, no-flow period from late spring to autumn.

The anoxic bottom water imposed by stratification will impact the water quality in three ways. Firstly, the anoxia is likely to inhibit the permanent establishment of benthic invertebrates, leading to lower benthic nutrient fluxes. Secondly, anoxia reduces iron oxyhydroxides in the surface sediments which release adsorbed and co-precipitated phosphorus, thereby limiting the phosphorus retention capacity of the sediments. And lastly, denitrification efficiencies will be reduced as oxygen is vital for coupled nitrification-denitrification to occur.

Acknowledgements

The authors would firstly like to thank Emma Murray, Matt Carey and John Jaycock for their assistance during the field surveys. All surveys ran smoothly due to the support from the Swan River Trust who provided laboratory space, suitable boats and competent boat drivers.

We would also like to acknowledge the National Measurement Institute in Perth, Geoscience Australia's laboratories in Canberra and Environmental Isotopes Pty Ltd in Sydney for the prompt and high quality sample analysis. Assistance from Jodie Smith in the preparation of GIS maps is greatly appreciated.

This work would not be possible without the continued support from the Department of Water in Western Australia, and in particular Malcolm Robb and Zoe Goss from the Water Science Branch. Zoe was also instrumental in site selection, assisted in the field, and provided feedback on scientific findings.

Finally, we would like to thank Jodie Smith and Rachel Przeslawski for their comprehensive reviews of the report, their suggestions greatly increased the quality of this report.

Contents

1. Introduction

1A. BACKGROUND

The upper Swan River estuary experiences periods of poor water quality at certain times of the year including widespread hypoxia and elevated nutrient concentrations (DoW 2000). It has long been suspected that nutrient release and oxygen uptake from the sediments are major drivers of poor water quality conditions. Additionally, predicted reductions in rainfall and runoff in the catchment may severely impact water quality in the future (Kelsey *et al*., 2009). In response to the identified need to better understand the role of sediments on estuarine water quality, a research partnership between the Department of Water in Western Australia and Geoscience Australia was established. The inventory of dissolved nutrients and the organic matter content in the sediments, the rate of nutrient release and the rate of oxygen consumption by sediments have all been studied. A report entitled *Sediment Water Interaction in the Swan River Estuary* (Smith *et al.* 2007) documents the findings of the Geoscience Australia surveys between 2000 and 2006 and focuses on the lower/central region of the estuary from Armstrong Spit to the confluence of Bennett Brook. This report documents the findings of three surveys from 2006 – 2008 focussing on sites upstream of Ron Courtney Island in the upper reaches of the estuary.

The Swan River estuary is permanently open to the Indian Ocean and generally receives the highest river flows during winter and early spring. The estuary is brackish and well mixed during high flow periods, but once river flow ceases, marine waters propagate upstream (the salt wedge). Once the salt wedge is established it is likely to remain throughout the summer months, moving upstream and downstream anywhere from tens of meters to several kilometres each day with tidal and atmospheric pressure influences (Thomson *et al.* 2001).

Smaller rainfall events in autumn are unable to shift the salt wedge and instead fresher catchment flows pass over the top of the more saline waters. Depending upon the volume of runoff and the extent of wind-driven mixing, the system may remain stratified for some time. When this occurs there is limited interaction between the more saline water at depth and the surface waters exposed to the atmosphere. As oxygen is consumed in the bottom water by the degradation of organic matter within the sediment (Smith *et al.* 2007), dissolved oxygen concentrations diminish rapidly restricting benthic life and eventually leading to anoxic conditions in the bottom water (Thompson & Hosja, 1996; Hamilton *et al.* 2001; Kurup & Hamilton 2002).

1B. AIMS AND OBJECTIVES

The overarching aim of the sediment investigations was to develop an understanding of the impact of sediments on water quality in the upper Swan River estuary. More specifically, surveys in October 2006 and May 2008 aimed to gather baseline sediment data relevant for the design of a potential second oxygenation plant in the upper Swan River estuary. The September 2007 survey aimed to characterise the distribution and identify the physiographic conditions for the accumulation of sediments with a particularly high oxygen demand and nutrient release rate.

This report addresses the following objectives:

1. To determine nutrient pool sizes and organic matter content in surface sediments in order to characterise the distribution of fine sediments and their potential influence on water quality.
2. To determine and compare oxygen and nutrient exchange between sediment and bottom water at different sites and at different times of the year to better understand conditions of high oxygen consumption and nutrient release.

3. To determine the influence of the bottom water oxygen status on nutrient release from sediments.

2. Methods

2A. SITE LOCATIONS AND DESCRIPTION

The Swan River estuary is located adjacent to the city of Perth in south-Western Australia (Figure 1). The estuary covers an area of approximately 40 km^2 and extends from Fremantle on the coast to 60 km upstream. The upper Swan River estuary consists of a narrow channel that drains a large (18 000 km^2) catchment and is dominated by freshwater runoff events. The sample site locations (Figure 1) cover a distance of approximately 15.5 km upstream from Ron Courtney Island and are described in Table 1.

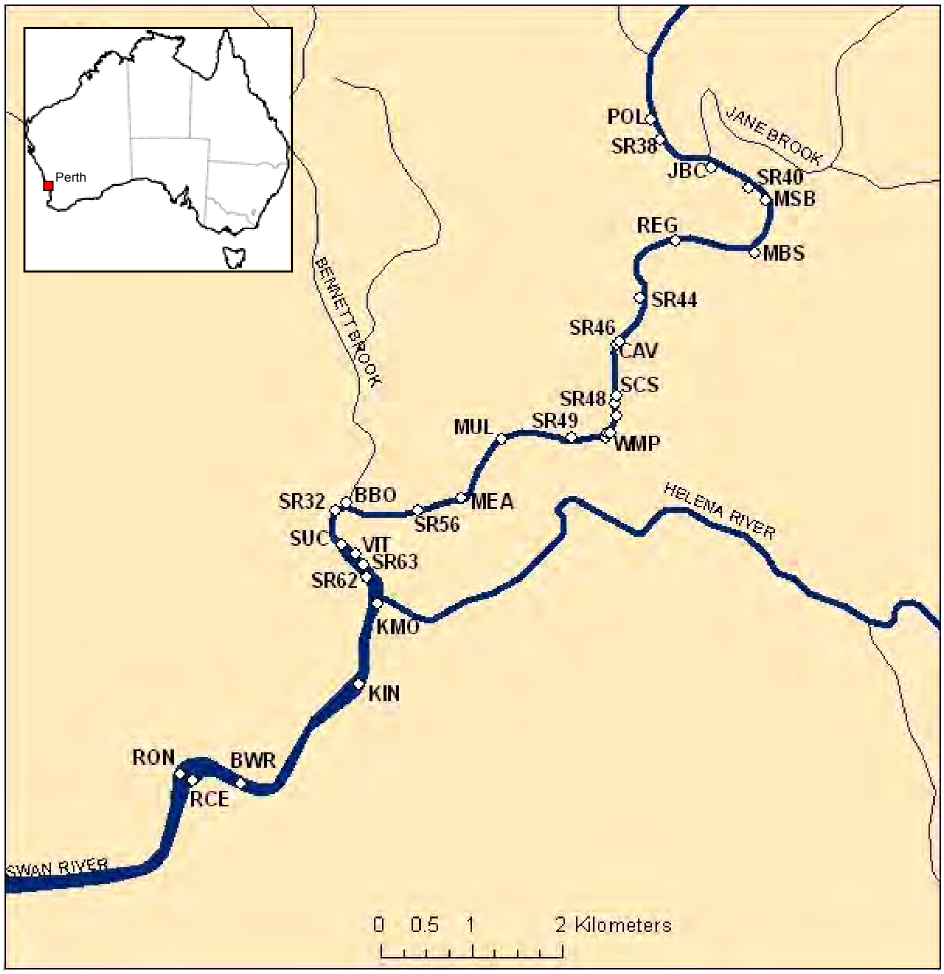

Figure 1 Site locations in the upper Swan River estuary

Table 1 Sample site locations and descriptions

Date	Site Code	Latitude	Longitude	Location	Depth (m)	GA Site Name
Oct-06	RON	-31.92122	115.93996	Ron Courtney Island – west side	4.0	SR1
	SR32	-31.89513	115.95846	110 m downstream of Bennett Brook	3.5	SR32
Sept-07	RON	-31.92122	115.93996	Ron Courtney Island – west side	1.8	SR1
	RCE	-31.92196	115.94135	Ron Courtney Island – east side	1.2	SR59
	BWR10	-31.92221	115.94707	Sandy Beach Reserve - 700 m upstream of RON	1.2	SR60
	KIN	-31.91253	115.96101	Kingsley Drive	4.5	SR61
	KMO	-31.90443	115.96331	King Meadow Oval - Helena River confluence	2.3	SR36
	SR62	-31.90178	115.96203	310 m upstream of KMO - Brook Street drain outlet	0.6	SR62
	VIT	-31.90060	115.96173	Vitox Plant	2.4	SR35
	SR63	-31.89948	115.96072	150 m upstream of VIT, between railway bridges	2.8	SR63
	SUC	-31.89845	115.95918	Success Hill	2.5	SR58
	SR32	-31.89513	115.95846	110 m downstream of Bennett Brook	5.0	SR32
	BBO	-31.89427	115.95963	Bennett Brook confluence	0.2	SR57
	SR56	-31.89511	115.96812	840 m upstream of Bennett Brook	1.7	SR56
	MEA	-31.89395	115.97318	150 m upstream of West Swan Rd (Meadow St) bridge	1.2	SR55
	MUL	-31.88816	115.97798	Mulberry Farm	1.2	SR54
	SR53	-31.88804	115.98611	Tea house - 400 m downstream of WMP	1.3	SR53
	WMP-RB	-31.88815	115.99017	West Midland Pool – east bank	2.8	SR52
	WMP-LB	-31.88761	115.99025	West Midland Pool – west bank	1.3	SR51
	SR50	-31.88756	115.99066	West Midland Pool – concrete outlet	3.5	SR50
	SR49	-31.88595	115.99144	Drain outlet - 200 m upstream of WMP	1.2	SR49
	SR48	-31.88473	115.99119	90 m downstream of Black Adder Creek confluence, west bank	1.2	SR48
	SCS01	-31.88390	115.99146	Black Adder Creek confluence	1.0	SR47
	SR46	-31.87885	115.99149	Caversham Ave – east bank	1.2	SR46
	CAV	-31.87846	115.99182	Caversham Ave – mid river	2.5	SR45
	SR44	-31.87414	115.99433	550 m upstream of CAV	1.2	SR44
	REG	-31.86853	115.99846	Reg Bond Park	1.2	SR43
	MBS	-31.86973	116.00768	Midland Brick - 1040 m upstream of REG	1.2	SR42
	MSB	-31.86447	116.00900	Middle Swan Road Bridge	1.0	SR41
	SR40	-31.86327	116.00711	200 m upstream of MSB	1.0	SR40
	JBC	-31.86130	116.00270	Jane Brook Confluence	2.7	SR39
	SR38	-31.85833	115.99686	750 m upstream of JBC	0.2	SR38
	POL	-31.85637	115.99564	Under powerlines - 260 m upstream of SR38	1.6	SR37
May-08	VIT	-31.90060	115.96173	Vitox Plant	2.4	SR35
	RBP	-31.86853	115.99846	Reg Bond Park	3.0	SR43
	KMO	-31.90474	115.96317	Helena River Confluence - King Meadow Oval	2.3	SR36
	WMP	-31.88785	115.99000	West Midland Pool	6.0	SR50

2B. SAMPLING AND ANALYSIS

2B1. October 2006

During the October 2006 survey two sites were sampled in the upper Swan River estuary, RON at Ron Courtney Island and SR32 downstream of Bennett Brook. Benthic chambers were deployed at both RON and SR32 while sediment cores were only collected at SR32. RON had been extensively sampled during 2000 and 2001 (see Fredericks *et. al*. 2002; Smith *et. al*. 2007). All fluxes were measured under dark conditions at both sites. Four automatic chambers were deployed at RON and five manual chambers deployed at SR32. Five to six samples were drawn from each chamber over a period of 6 – 8 hours. Samples were analysed for nutrients (NH_4^+, NO_X, N_2, PO_4^{3-} and SiO_4^{4-}), DIC and O_2 (see Appendix 1 Analytical Methods) and benthic fluxes calculated as the change in concentration over time. For detailed methods of benthic chamber and sediment coring operations, see Murray *et al.* (2007).

Depth profiles of temperature, salinity and dissolved oxygen were measured in the water column at each site using a YSI 600XLM sonde. Surface and bottom water nutrients (NH_4^+, NO_X, N_2, PO_4^{3-} and SiO_4^{4-}) and surface water total nitrogen and phosphorus (TN and TP) were also measured at each site.

Two sediment cores were collected at SR32 using a manually operated push-corer to determine porewater and solid phase properties. The porewater core was sectioned in 0.5 – 5.0 cm intervals down to 30 cm, with the finer sampling resolution closest to the core top. Porewaters were extracted from sediments by centrifuging at 11 000 rpm for 5 minutes then filtered through a 0.45 μm filter. The porewaters were analysed for NH_4^+, NO_X, PO_4^{3-} and SiO_4^{4-} at the National Measurement Institute (NMI) laboratories in Perth. The solid phase core was sectioned into 0.5 cm increments down to 6 cm. Sediments were analysed for chlorophyll a and porosity. Total Organic Carbon (TOC) was determined on only the surface sample (see Appendix 1 Analytical Methods).

2B2. September 2007

31 sites were sampled in the upper Swan River estuary during the September 2007 survey. Surface sediments (top 2 cm) were collected at each site using a push-corer, then two sub-samples of 20 ml were taken from the core by inserting cut-off syringes vertically into the sediment. The two sediment samples were then transferred into centrifugation vials. One of the vials was centrifuged within hours (‘t0’) and the other sample was incubated without oxygen, under dark conditions and at 20 ºC for 12 to 24 hours (‘t1’) before it was centrifuged. Supernatant water of sample t0 was sub-sampled for nutrient (NH_4^+, NO_X, PO_4^{3-} and SiO_4^{4-}) and dissolved inorganic carbon (DIC) analysis. Supernatant water of sample t1 was only analysed for DIC. At each site an additional sub-sample was taken from the sediment core and analysed for porosity and Total Organic Carbon (TOC). The nutrient concentration of sample t0 reflects the porewater inventory integrated over the uppermost 2 cm. The increase in DIC concentration between t0 and t1 is used to calculate the rate of organic matter decomposition.

Additionally, water column profiles (temperature, salinity and dissolved oxygen) were measured at most sites using a YSI 600XLM sonde.

2B3. May 2008

During May 2008, benthic chambers were deployed at two sites in the upper Swan River estuary; KMO and WMP. Five manual chambers were deployed at KMO and three automatic chambers were deployed at WMP. Five to six samples were drawn from each chamber over a period of four to six hours. Samples were analysed for nutrients (NH_4^+, NO_X, N_2, PO_4^{3-} and SiO_4^{4-}), DIC and O_2 and benthic fluxes calculated as the change in concentration over time.

Water column profiles (temperature, salinity and dissolved oxygen) were measured at KMO and WMP using a YSI 600XLM sonde. Surface and bottom water samples also collected at these sites and analysed for dissolved (NH_4^+, NO_X, N_2, PO_4^{3-} and SiO_4^{4-}) and total (TN and TP) nutrients.

Surface sediments were collected at four sites (KMO, WMP, VIT and RBP) in order to assess the spatial variability of reactive sediments within sites. At each of the sites sediments were collected in a transect across the river. Samples were collected, treated and analysed as per the September 2007 survey.

Sediment cores were collected at each of the 4 sites (KMO, WMP, VIT and RBP) to determine the down core porewater nutrient profiles. Cores were collected using a manually operated push-corer. Cores were extruded from the core barrel and sliced into 1-3 cm intervals down to 25 cm. Each slice was centrifuged at 11 000 rpm for 5 minutes to extract the porewaters. Porewaters were filtered through a 0.45 μm filter and analysed for NH_4^+, NO_X, PO_4^{3-} and SiO_4^{4-} at the National Measurement Institute (NMI) laboratories in Perth. Additional solid phase samples were collected at each interval and used for porosity determination.

3. Results

3A. WATER COLUMN CONDITIONS

The water column conditions varied markedly between the 3 surveys due to the time of year the surveys were conducted (Figure 2). The first survey (October 2006) took place when the typical winter rains had ceased and marine waters were intruding back up the Swan River. The second survey (September 2007) took place a little earlier in the season when freshwater catchment runoff was still occurring and as a consequence much of the upper reaches of the Swan River were fresh or brackish. The third survey (May 2008) was undertaken in late autumn when the seasonal rainfall had just commenced, with fresher catchment water flowing over the top of marine waters resulting in stratified conditions throughout the length of the upper Swan River estuary.

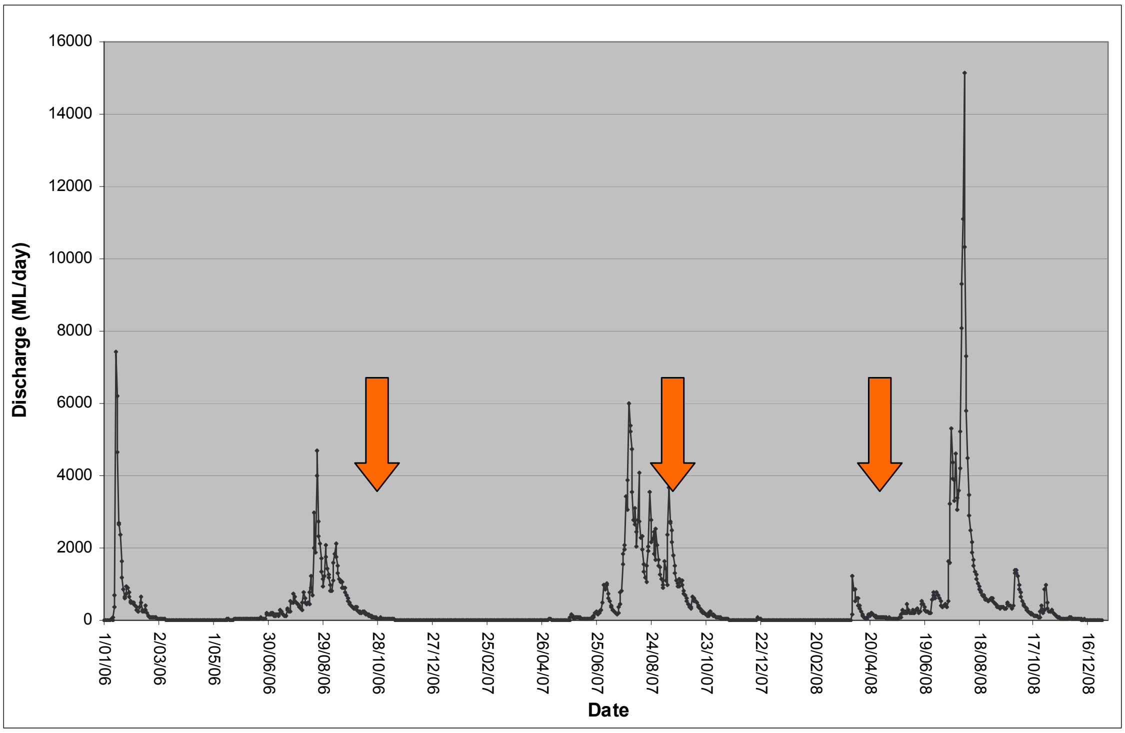

Figure 2 Estimated flow in the upper Swan River estuary, 2006 – 2008. Flow is estimated from the sum of discharge from the main tributaries (Avon River, Ellen Brook, Susannah Brook and Jane Brook). Orange arrows indicate survey times.

3A1. October 2006

The salinity profile (Figure 3a) shows that marine conditions existed in the lower Swan River (salinity of ~34 ppt) and relatively fresh conditions in the upper Swan River (salinity of ~2 ppt) in October 2006. The salt-wedge between Nile Street (NIL) and Kingsley Drive (KIN) resulted in stratified conditions and reduced bottom water oxygen (Figure 3b) in this part of the Swan River. The salt-wedge was moving upstream at the time of the survey.

At the two sites sampled during this survey, RON (Ron Courtney Island) was within the stratified zone, and SR32 was in the fresher part of the upper Swan River estuary. The salinity at RON ranged from 7.5 in the surface waters to 12.4 in the bottom waters. Dissolved oxygen at this site was 9.31 mg/L in the surface waters and 3.91 mg/L in the bottom waters. At SR32 the water column was relatively well mixed with salinity ranging from 4.3 in the surface waters to 4.4 in the bottom waters. Dissolved oxygen was slightly depleted in the bottom waters with a concentration of 7.24 mg/L compared to 7.73 mg/L in the surface water.

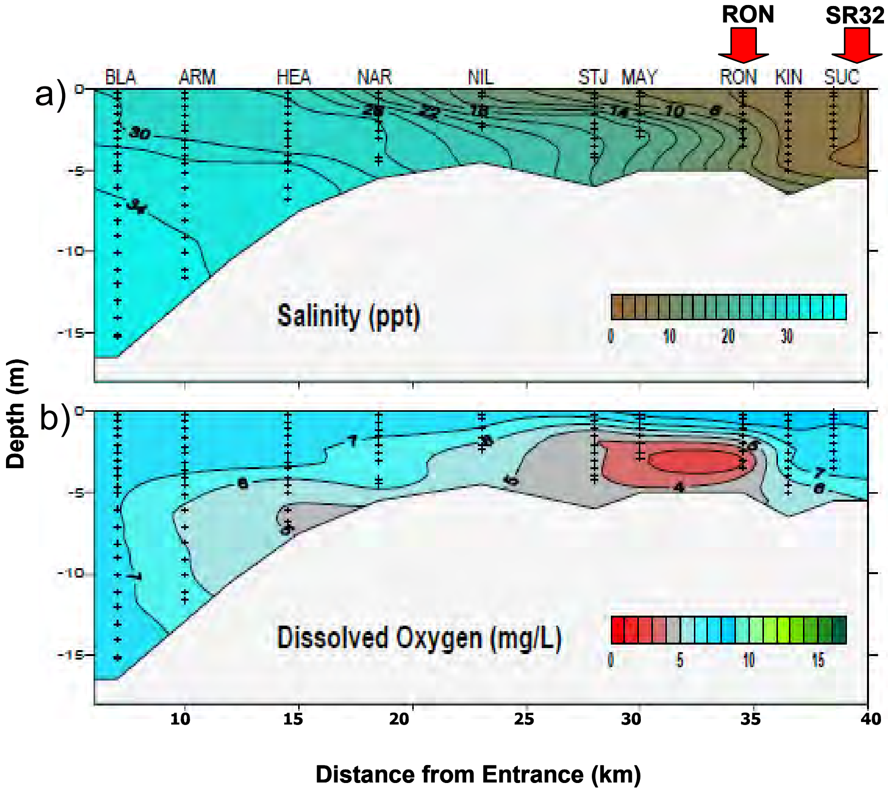

Figure 3 a) Salinity and b) dissolved oxygen profiles of the Swan River on the 23rd October 2006. The red arrows show the sample locations during this survey.

Nutrient concentrations were higher in the bottom waters compared to the surface waters at both sites in the upper Swan River estuary. NH_4^+ concentrations at RON (Figure 4a) were an order of magnitude higher in the bottom waters than in the surface waters (0.145 mg/L and 0.014 mg/L respectively) whereas bottom water concentrations were slightly higher than the surface waters at SR32 (0.07 mg/L and 0.042 mg/L respectively). Bottom water concentrations of NH_4^+ at both sites exceed the ANZECC Trigger Value for southern Western Australian estuaries (ANZECC, 2000). This value (0.04 mg/L) represents the conservative assessment level at which possible risk to the environment may occur and an investigation or management response is advised (ANZECC, 2000).

PO_4^{3-} concentrations (Figure 4b) were below detection limits in the surface waters of both sites while bottom water concentrations ranged from 0.011 mg/L at SR32 to 0.042 mg/L at RON. The concentrations measured in the bottom waters of both sites exceed the

ANZECC Trigger Value for PO_4^{3-} in southern Western Australian estuaries (0.005 mg/L; ANZECC, 2000).

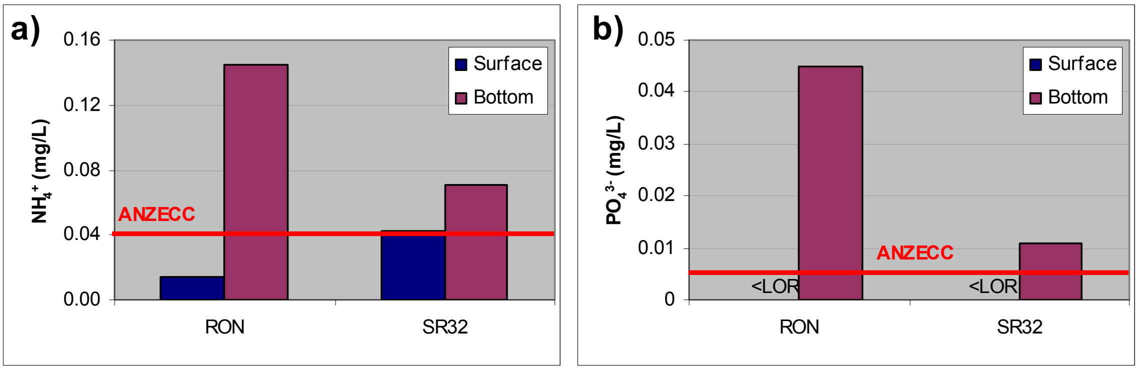

Figure 4 Surface and bottom water NH_4^+ (a) and PO_4^{3-} (b) at sampled sites within the upper Swan River estuary on the 23rd October 2006. The red lines represent the ANZECC Trigger Values for South-west Australian estuaries (ANZECC, 2000). <LOR = less than the limit of reporting.

3A2. September 2007

The salinity and dissolved oxygen profiles for the Swan River estuary during the September 2007 survey (Figure 5a & b) were similar to the October 2006 survey, however, the salt-wedge was located further downstream. This was due to the survey being slightly earlier in the season, and runoff being larger and continuing further into spring in 2007 compared to 2006 (see Figure 2). The freshwater flows were still migrating seaward at the time of this survey and the estuary was stratified from Blackwall Reach (BLA) to Nile Street (NIL).

Surface water salinities were fresh (< 5) in the upper reaches of the Swan River down to the Narrows Bridge (NAR) during this period. Much of Perth and Melville Waters were stratified and had severely depleted dissolved oxygen in the bottom waters. The focus area of this survey (upstream of Ron Courtney Island) was generally well mixed with only very slight dissolved oxygen depletion in the bottom waters.

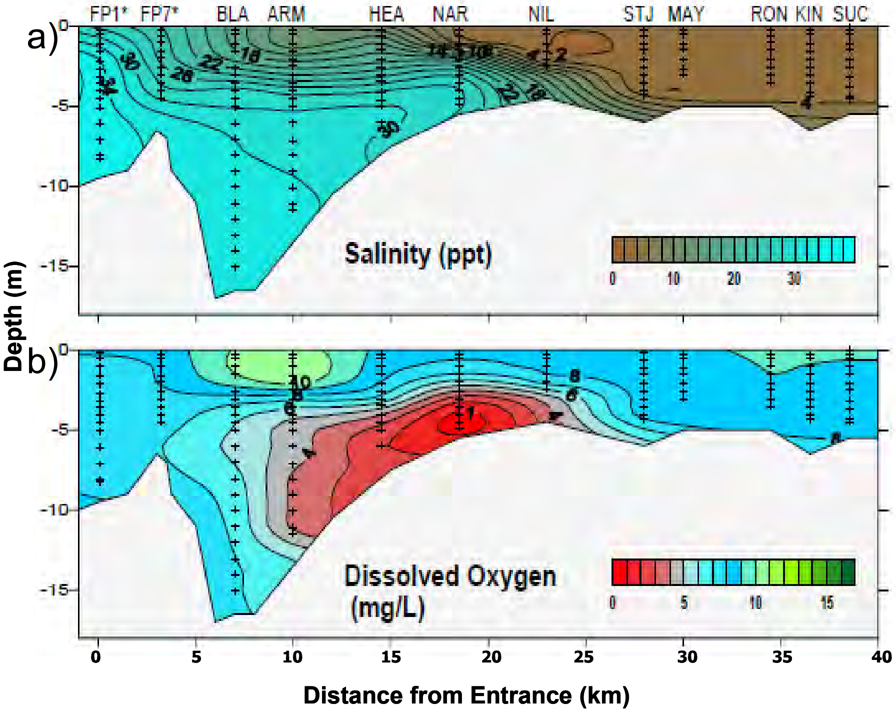

Figure 5 a) Salinity and b) dissolved oxygen profiles of the Swan River on the 17th September 2007.

3A3. May 2008

The May 2008 survey took place at the very beginning of the annual rainfall period (see Figure 2). The resultant freshwater flows created stratified conditions in the upper Swan River estuary stretching down to Melville Waters (downstream of NAR; Figure 6). Anoxic conditions existed in the bottom waters of much of the upper Swan River.

Profiles of dissolved oxygen and salinity at West Midland Pool (WMP) and King Meadow Oval (KMO) taken during this survey show the degree of stratification in the upper Swan River. Dissolved oxygen concentrations (Figure 7a) in the surface waters of WMP and KMO were 6.8 mg/L and 7.8 mg/L respectively, and decreased to anoxic levels (0.15 mg/L and 0.28 mg/L) in the bottom waters of these sites. The surface water salinity (Figure 7b) was 12 - 14 compared with 24 – 27 in the bottom waters.

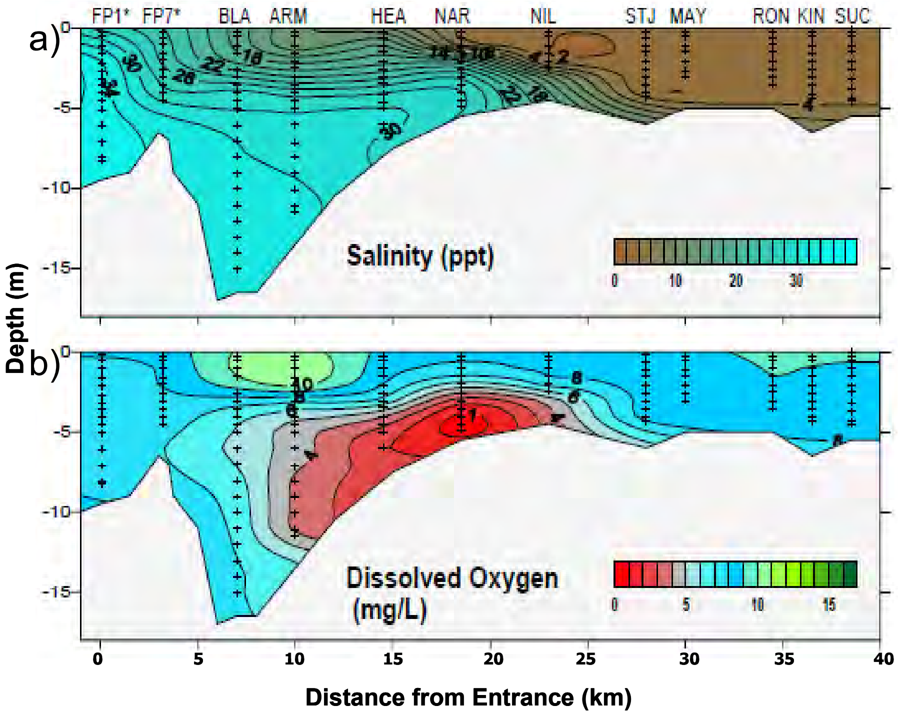

Figure 6 Salinity and dissolved oxygen profiles of the Swan River on the 5th May 2008.

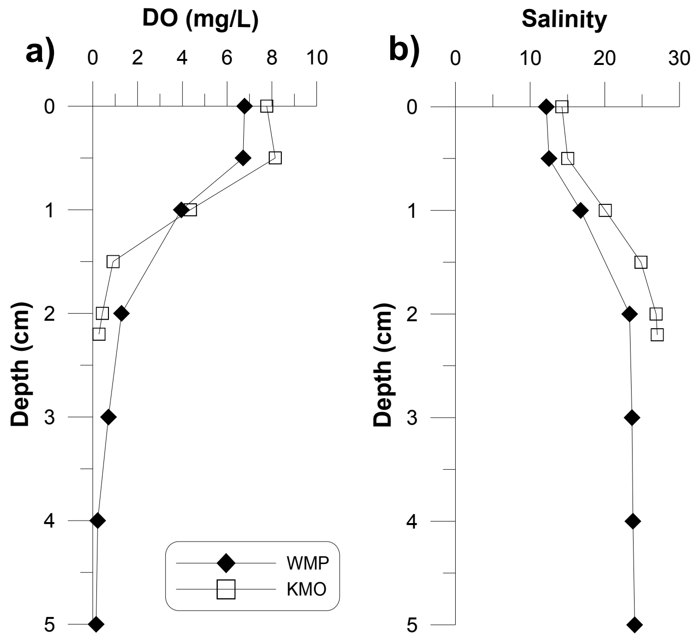

Figure 7 Water column profiles of a) dissolved oxygen and b) salinity from West Midland Pool (WMP) and King Meadow Oval (KMO) on the 5th May 2008.

Surface and bottom water nutrient concentrations at KMO and WMP during the May 2008 survey are shown in Figure 8. NH_4^+ concentrations are higher in the bottom waters than the surface waters, particularly at WMP where concentrations increased from 0.014 mg/L in the surface waters to 0.53 mg/L in the bottom waters. NH_4^+ concentrations exceeded the ANZECC trigger value of 0.045 mg/L for South-west Australian estuaries in the bottom waters of both sites and the surface waters of KMO.

NO_X concentrations were generally low or below detection limits at the time of the survey. The highest NO_X concentrations were measured in the surface waters (0.026 mg/L and 0.024 mg/L at KMO and WMP respectively) which is due to the freshwater input.

PO_4^{3-} concentrations were also considerably higher in the bottom waters compared to the surface waters of KMO and WMP. Concentrations were above the ANZECC trigger value of 0.005 mg/L for South-west Australian estuaries. PO_4^{3-} concentrations were as high as 0.03 mg/L and 0.05 mg/L in the bottom waters of KMO and WMP respectively.

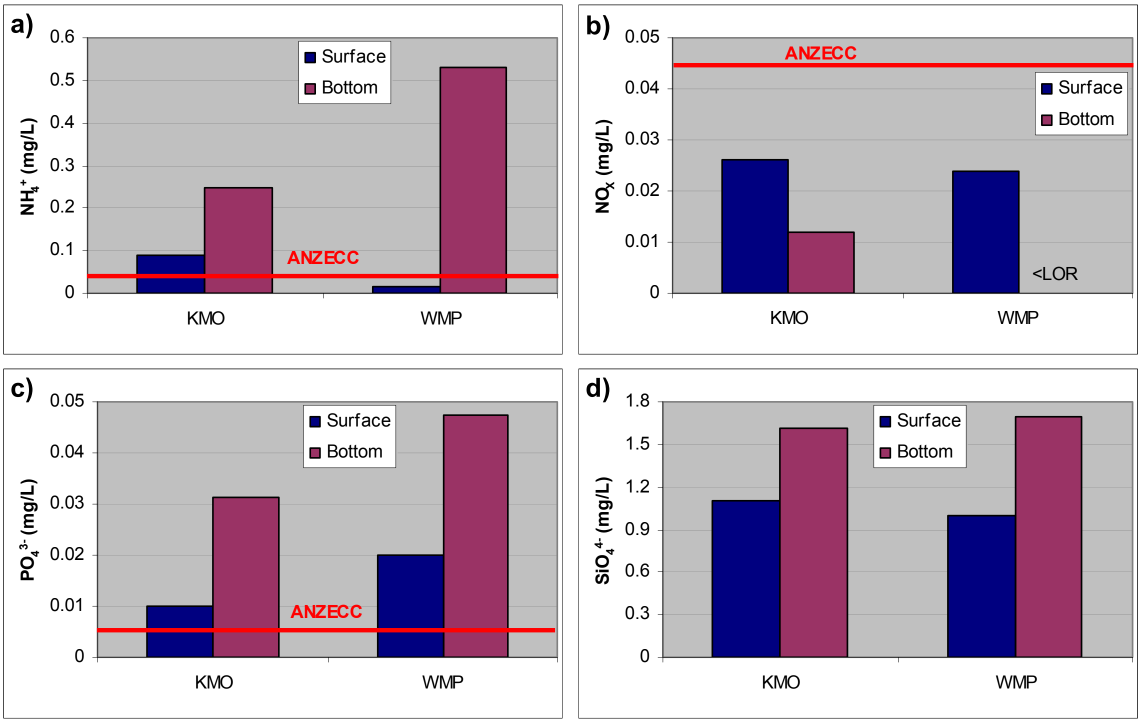

Figure 8 Surface and bottom water nutrient (a) NH_4^+, b) NO_X, c) PO_4^{3-}, d) SiO_4^{4-}) concentrations at King Meadow Oval (KMO) and West Midland Pool (WMP), May 2008. The red lines represent the ANZECC Trigger Values for South-west Australian estuaries (ANZECC, 2000), LOR = less than the limit of reporting.

3B. POREWATER NUTRIENTS

Down core porewater profiles from sites sampled in October 2006 and May 2008 are shown in Figure 9. Porewater DIC and nutrient concentrations at sites SR32 and WMP were consistently higher than other sites and were also larger than those measured in other south-western Australian estuaries (Lake Powell, Murray *et al.*, 2005; Wellstead Estuary, Beaufort Inlet, Gordon Inlet, Murray *et al.*, 2007; Stakes Inlet, Murray *et al.*, 2008; Hardy Inlet, Haese et al., 2010; Parry Inlet, Irwin Inlet, Walpole/Nornalup, Leschenault Estuary, unpublished data). Most other profiles are similar except the PO_4^{3-} profile at REG. This profile suggested elevated PO_4^{-3} in the porewaters just below the surface and possible release into the overlying water column.

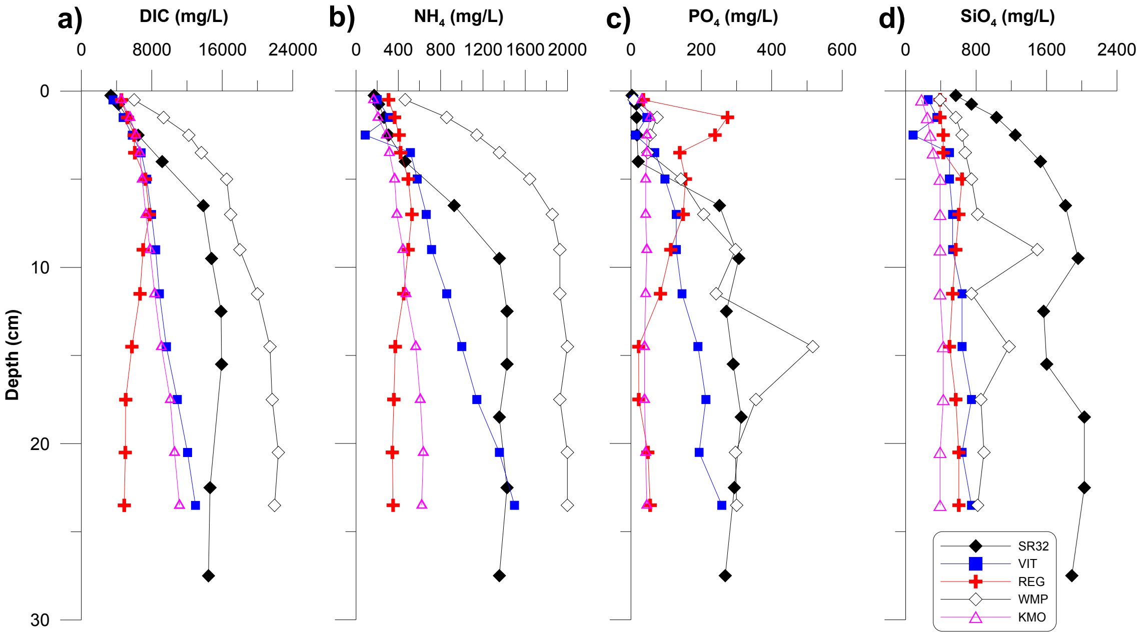

Figure 9 Down core porewater profiles of a) DIC, b) NH_4^+, c) PO_4^{3-} and d) SiO_4^{4-} from sites in the upper Swan River estuary. All sites were sampled in May 2008 except for site SR32, which was sampled in October 2006.

Porewater nutrients measured in the surface sediments (top 2 cm) of the upper Swan River estuary (Table 2) during the September 2007 survey were highly variable. DIC concentrations exceed 100 mg/L at the sites immediately downstream of the Helena River confluence (KMO and KIN) and were as low as 25.7 mg/L at SR56 (840 m upstream of Bennett Brook). NH_4^+ and PO_4^{3-} concentrations were also largest at the Helena River confluence (KMO; 9.9 mg/L and 1.8 mg/L respectively) and lowest at SR56 (0.43 mg/L and 0.02 mg/L respectively). NO_X concentrations were below the limit of reporting (LOR) at many sites. Where NO_X was detectable, it ranged from 0.01 mg/L at SR49 (200 m upstream of WMP) to 0.029 mg/L at SR44 (550 m upstream of CAV). The maximum SiO_4^{4-} concentration was found at WMP (15 mg/L) and the lowest at SR56 (5 mg/L).

Table 2 Porewater DIC and nutrient (NH_4^+, NO_X, PO_4^{3-} and SiO_4^{4-}) concentrations and porosity from surface sediments collected during the September 2007 survey.

Site Code	GA Site Name	DIC (mg/L)	NH_4^+ (mg/L)	NO_X (mg/L)	PO_4^{3-} (mg/L)	SiO_4^{4-} (mg/L)	Porosity (%)
RON	SR1	58.5	4.3	0.014	1.6	11	82.1
RCE	SR59	32.8	1.5	<LOR	0.13	11	81.6
BWR10	SR60	35.3	0.63	<LOR	0.13	8	67.0
KIN	SR61	126.7	n/a	n/a	n/a	n/a	80.3
KMO	SR36	115.1	9.9	0.023	1.8	8.9	81.2
SR62	SR62	27.3	0.6	<LOR	0.13	5	33.1
VIT	SR35	52.6	3.3	0.018	0.98	12	75.6
SR63	SR63	27.1	0.76	<LOR	0.17	7	71.4
SUC	SR58	33.8	n/a	n/a	n/a	n/a	66.3
SR32	SR32	56.6	4.4	0.011	1.6	14	76.0
BBO	SR57	32.4	n/a	n/a	n/a	n/a	82.3
SR56	SR56	25.7	0.43	<LOR	<LOR	5	46.6
MEA	SR55	32.0	1.1	<LOR	0.02	7	55.5
MUL	SR54	31.9	n/a	n/a	n/a	n/a	67.4
SR53	SR53	40.8	1.9	0.016	0.24	10	79.1
WMP-RB	SR52	54.3	0.8	<LOR	0.27	12	77.4
WMP-LB	SR51	54.5	4.8	0.023	0.31	12	82.8
WMP	SR50	34.9	0.92	<LOR	0.66	15	83.0
SR49	SR49	46.0	2.5	0.01	0.33	9	75.7
SR48	SR48	29.1	0.7	<LOR	0.11	8.4	74.2
SCS01	SR47	36.9	2.1	0.013	0.52	10	77.5
CAV	SR46	40.4	0.75	0.015	0.11	8	57.5
SR44	SR44	34.7	1.3	0.029	0.074	8.9	87.3
REG	SR43	34.7	1.2	0.011	0.045	8.3	62.6
MBS	SR42	33.4	0.81	<LOR	0.14	6.5	56.6
MSB	SR41	42.6	1.4	<LOR	0.088	12	70.9
SR40	SR40	40.7	2.1	0.011	0.78	13	59.7
JBC	SR39	44.7	1.3	<LOR	0.19	11	51.5
SR38	SR38	38.6	1.7	0.027	0.2	6.9	65.0
POL	SR37	45.2	0.84	0.012	0.25	12	75.8

During the May 2008 survey surface sediments were collected in a transect across the river at KMO and WMP (Figure 10); the porosity, DIC and nutrient (NH_4^+, NO_X, PO_4^{3-} and SiO_4^{4-}) concentrations are shown in Table 3. Generally, both sites were highly variable in porosity, DIC and nutrients within a relatively small area. At KMO the porosity values ranged from 79.6% at point C, to 97.2% at point E. Points A and B had the highest DIC (226.24 mg/L and 158.41 mg/L respectively) and nutrient concentrations, while points E and F had the lowest DIC (53.94 mg/L and 56.20 mg/l respectively) and nutrient concentrations.

At WMP the highest porosity (86.7%), DIC (257.35 mg/L) and nutrients (NH_4^+ - 26 mg/L; PO_4^{3-} - 3.5 mg/L; SiO_4^{4-} - 23 mg/L) were found at point B. The lowest porosity (64.4%), DIC (44.83 mg/L) and nutrients (NH_4^+ - 2.2 mg/L; PO_4^{3-} - 0.41 mg/L; SiO_4^{4-} - 6.9 mg/L) were all found at point C.

Figure 10 Location of surface sediment sampling at KMO (left image) and WMP (right image). Image from Google Earth.

Table 3 Porosity, DIC and nutrient concentrations from surface sediments collected at KMO and WMP. <LOR = less than the limit of reporting.

Site	Location	Porosity (%)	DIC (mg/L)	NH_4^+ (mg/L)	NO_X (mg/L)	PO_4^{3-} (mg/L)	SiO_4^{4-} (mg/L)
KMO	A	91.8	226.24	14	0.02	4.2	19
	B	92.3	158.41	15	0.06	2.2	13
	C	79.6	92.96	4.9	<LOR	3.4	8.6
	D	87.5	86.04	5.8	<LOR	3.7	15
	E	97.2	53.94	3.1	<LOR	0.84	11
	F	84.8	56.20	2.1	<LOR	0.18	7.0
WMP	A	82.1	68.08	5.7	<LOR	1.6	13
	B	86.7	257.35	26	<LOR	3.5	23
	C	64.4	44.83	2.2	<LOR	0.41	6.9
	D	82.3	143.05	8.5	<LOR	1.3	13

3C. SEDIMENTS

Sediment characteristics (porosity and TOC%) were determined on surface sediments samples from SR32 during the 2006 survey, from all 31 sites in the upper Swan River estuary during the 2007 survey and from sites KMO, VIT, WMP and REG during the 2008 survey. The porosity and TOC from sites sampled during more than one survey are shown in Table 4. The porosity and TOC from all sites sampled during the 2007 survey are shown in Figure 11. The lowest measurements of porosity and TOC concentrations were found during the 2007 survey (porosity < 83% KMO, VIT, SR32, WMP and REG; TOC 0.47% at VIT, 1.34% at REG and 1.77 at SR32). At SR32, the porosity decreased from 89.9% to

76.0%, and TOC decreased from 4.35% to 1.77% between 2006 and 2007. At sites KMO, VIT, WMP and REG the porosity increased between the 2007 and 2008 surveys. The TOC increased at VIT and decreased at KMO and WMP between the 2007 and 2008 surveys.

Table 4 Porosity and TOC concentrations

	Porosity (%)			TOC (%)		
	2006	2007	2008	2006	2007	2008
KMO		81.2	88.4		13.13	3.71
VIT		75.6	90.1		0.47	3.81
SR32	89.9	76.0		4.35	1.77	
WMP		83.0	89.0		4.03	3.62
REG		62.6	89.3		1.34	

The porosity and TOC values measured during the 2007 survey highlight the spatial variability within the upper Swan River estuary. The porosity values ranged from 33.1% at site SR62 to 87.3% at site SR44. Large porosity values were found at the deep sites including RON and WMP (82.1% and 83.0% respectively) and at the confluences with the Helena River (KMO) and Bennett Brook (BBO - 81.2% and 82.3% respectively). TOC values ranged from 0.29% at SR62 to 13.13% at the adjacent site KMO. The site at the Bennett Brook confluence (BBO) also had a large TOC value (7.80%).

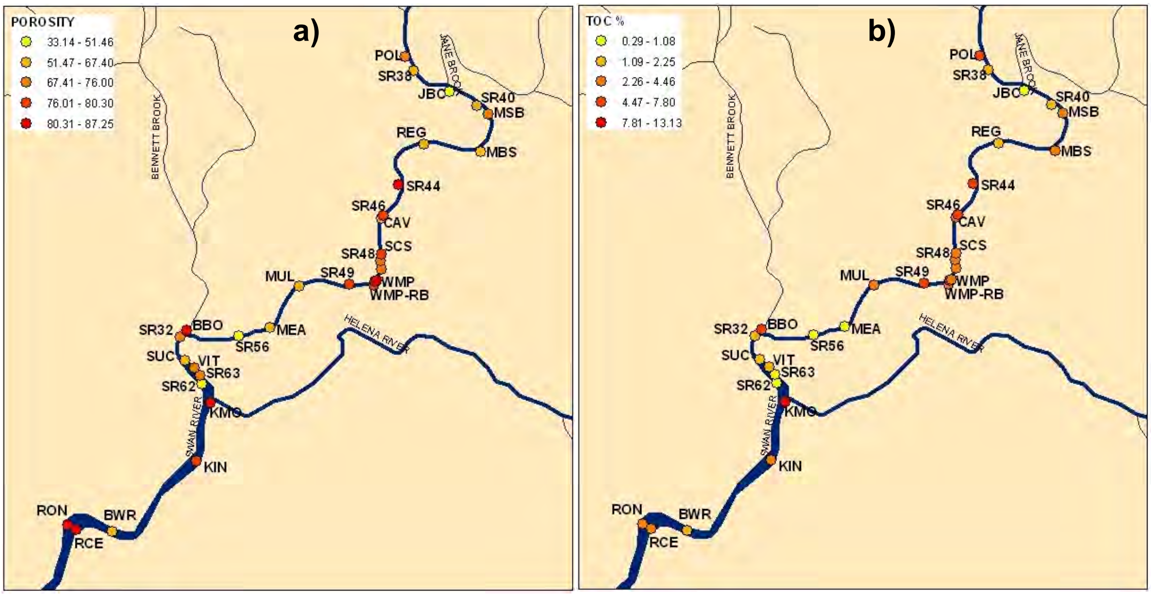

Figure 11 Porosity (a) and TOC (b) concentrations in the upper Swan River estuary measured during the September 2007 survey.

3D. BENTHIC FLUXES

Benthic fluxes were calculated from chambers deployed at sites during the 2006 and 2008 surveys (Table 5). All chambers deployed in the upper Swan River estuary are treated as dark as either the chamber was blanked out to eliminate light reaching the sediment surface, or the turbidity of the water column was such that light was unable to penetrate to the sediment. Photosynthetically Active Radiation (PAR – data not shown) measured in the water column at each sites was less than 5% of ambient light conditions within 50 cm of the water surface and decreased to ~ 0 μmol m^{-2} sec^{-1} at the sediment surface.

Table 5 Benthic fluxes from sites within the upper Swan River estuary. All fluxes have the units: mmol m^{-2} day^{-1}. N/A = not available. <LOR = less than the limit of reporting.

Chamber	Code	Date	O_2	DIC	NH_4^+	NO_X	N_2	PO_4^{3-}	SiO_4^{4-}
SR1F_1	RON	27/10/2006	-41.23	306.78	18.33	<LOR	6.12	1.14	32.59
SR1F_2	RON	27/10/2006	-25.86	460.99	63.67	<LOR	5.53	3.83	30.97
SR1F_3	RON	27/10/2006	-37.47	195.15	18.79	<LOR	-0.44	2.50	33.04
SR1G_1	RON	28/10/2006	-31.12	496.96	9.36	<LOR	-0.05	8.85	48.54
SR32A_5	SR32	22/10/2006	-68.54	224.26	23.16	-0.15	6.50	1.46	63.96
SR32A_6	SR32	22/10/2006	-87.03	89.29	15.49	<LOR	6.70	0.54	35.56
SR32A_7	SR32	22/10/2006	-55.05	348.88	19.57	<LOR	5.64	3.82	45.16
SR32A_9	SR32	22/10/2006	n/a	134.36	7.76	<LOR	1.33	0.001	15.53
SR50A_1	WMP	4/5/2008	n/a	30.16	4.07	<LOR	-1.18	0.15	10.47
SR50A_2	WMP	4/5/2008	n/a	34.45	-2.71	<LOR	6.08	-0.17	1.93
SR50A_3	WMP	4/5/2008	n/a	103.75	15.00	<LOR	7.38	0.68	28.33
SR36A_4	KMO	6/5/2008	n/a	47.80	2.43	0.48	-2.15	<LOR	6.88
SR36A_5	KMO	6/5/2008	n/a	341.82	31.89	<LOR	-4.64	5.12	9.41
SR36A_6	KMO	6/5/2008	n/a	95.55	11.06	<LOR	-2.09	0.96	-18.30
SR36A_7	KMO	6/5/2008	n/a	61.97	7.29	-0.02	-5.19	1.64	18.83
SR36A_8	KMO	6/5/2008	n/a	53.18	1.92	-0.15	-6.13	-0.19	7.74

Due to anoxic bottom water conditions during the May 2008 survey, no O_2 fluxes were recorded at WMP and KMO. O_2 fluxes during the October 2006 survey ranged from -25.86 mmol m^{-2} day^{-1} at RON to -87.03 mmol m^{-2} day^{-1} at SR32. Average O_2 fluxes (Figure 12a) were twice as large at SR32 compared to RON (-70.2 mmol m^{-2} day^{-1} and -33.9 mmol m^{-2} day^{-1} respectively). The DIC fluxes ranged from 30.16 mmol m^{-2} day^{-1} at WMP to 496.96 mmol m^{-2} day^{-1} at RON. Average fluxes were higher during the October 2006 survey than during the May 2008 survey (365.0 and 199.2 mmol m^{-2} day^{-1} at RON and SR32 respectively compared to 56.1 and 120.1 mmol m^{-2} day^{-1} at WMP and KMO respectively; Figure 12b). The O_2 fluxes are much less than the DIC fluxes at all sites indicating significant anaerobic degradation of organic matter.

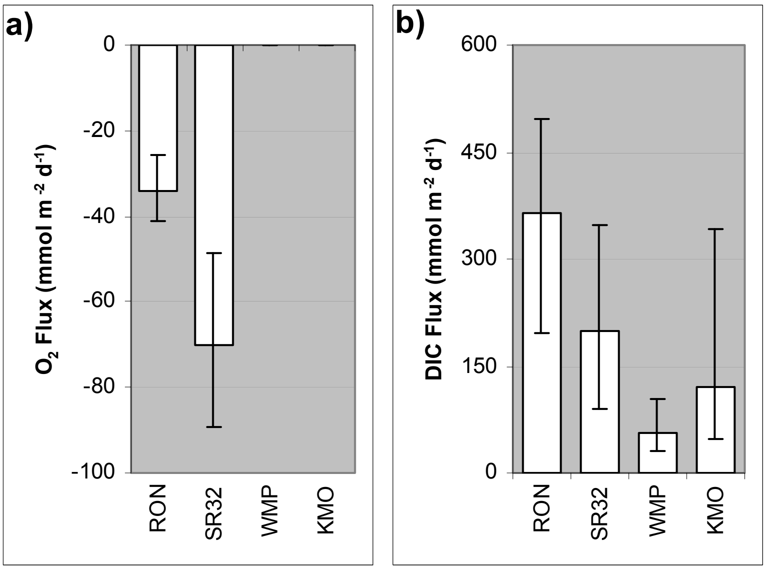

Figure 12 Average and ranges of O_2 (a) and DIC (b) fluxes from sites within the upper Swan River estuary.

NH_4^+ fluxes mirrored the DIC fluxes in that higher rates were measured at sites sampled during the October 2006 survey and lowest during the 2008 survey (Table 5). Average NH_4^+ fluxes were 27.5 and 16.5 mmol m^{-2} d^{-1} at RON and SR32 respectively and 5.5 and 10.9 mmol m^{-2} d^{-1} at WMP and KMO respectively (Figure 13a). NO_X concentrations were mostly below the limits of reporting; where it was measurable, calculated fluxes were less than 0.5 mmol m^{-2} d^{-1} (Figure 13b). N_2 fluxes were mostly positive at all sites except KMO where negative fluxes were measured (Table 5). Average N_2 fluxes (Figure 13c) were quite large, ranging from 6.13 mmol m^{-2} d^{-1} at SR32 to -4.04 mmol m^{-2} d^{-1} at KMO. A positive N_2 flux generally means the chamber is net denitrifying while a negative flux means a net nitrogen fixing chamber.

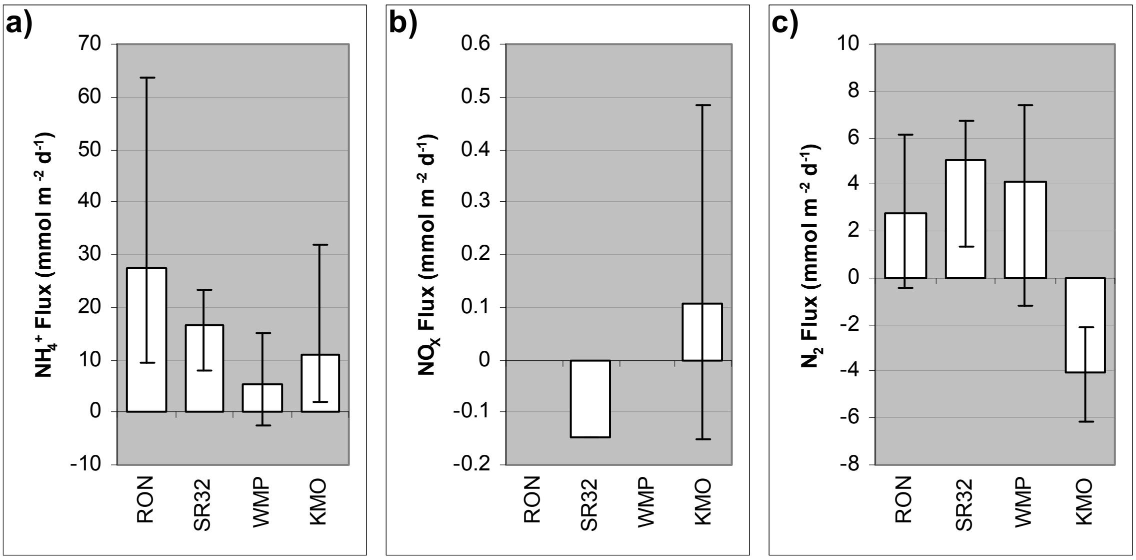

Figure 13 Average and ranges of NH_4^+ (a), NO_X (b) and N_2 (c) fluxes from sites within the upper Swan River estuary.

PO_4^{3-} fluxes (Figure 14a) were strongly correlated with DIC fluxes (r^2 = 0.74) and ranged from 8.85 mmol m^{-2} d^{-1} at RON to -0.19 mmol m^{-2} d^{-1} at KMO. SiO_4^{4-} fluxes (Figure 14b) also showed similar trends to the DIC (Figure 12b) and NH_4^+ (Figure 13a) fluxes with higher fluxes at RON and SR32 and lowest fluxes at WMP and KMO. Average SiO_4^{4-} fluxes ranged from 40.1 mmol m^{-2} d^{-1} at SR32 to 4.9 mmol m^{-2} d^{-1} at KMO.

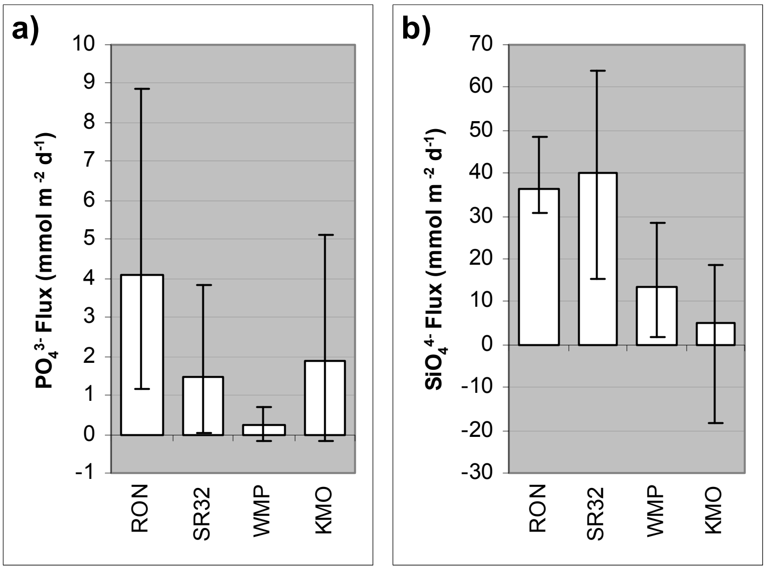

Figure 14 Average and ranges of PO_4^{3-} (a) and SiO_4^{4-} (b) fluxes from sites within the upper Swan River estuary.

4. Discussion

4A. NUTRIENT POOL SIZES

Nutrient pool sizes in the upper Swan River estuary were calculated from surface sediment samples (top 2 cm) collected during the September 2007 survey (Figure 15). The DIC and nutrient pool size in surface sediment are controlled by a number of conditions. Firstly, the rate of organic matter accumulation and the quality ("reactivity") of the organic matter determines the depth-integrated rate of organic matter decomposition, *i.e.* the rate of DIC production (Eyre and Ferguson, 2002). Secondly, many invertebrates living in the sediment enhance the release of DIC and nutrients from the sediment by irrigating their burrows and tubes ("bioirrigation"), which leads to a depletion of dissolved nutrients in the sediment and an enrichment of nutrients in the bottom water (Thibodeaux and Bierman, 2003). Thirdly, phosphate easily adsorbs to the surface of iron-oxyhydroxide, so that the availability of iron-oxyhydroxide also affects the abundance of dissolved phosphate in porewaters (Krom and Berner, 1980).

DIC and nutrient inventories in surface sediments were found to be highly variable (Figure 15), but trends appear to be related to the physiographic setting: Sites RON (SR1) , RCE (SR59), KMO (SR36), SR32 and WMP (SR50, SR51. SR52) consistently have the highest pool sizes in DIC, NH_4^+, PO_4^{3-} and SiO_4^{4-} and are either located in deep water (RON, SR32 and WMP) or are at the confluence of a river (KMO and SR32). It is thus likely that fine sediments enriched with organic matter and associated nutrients accumulate and decompose particularly at sites where water flow slows down, e.g. at river confluences and in deep holes (Kurup and Hamilton, 2002).

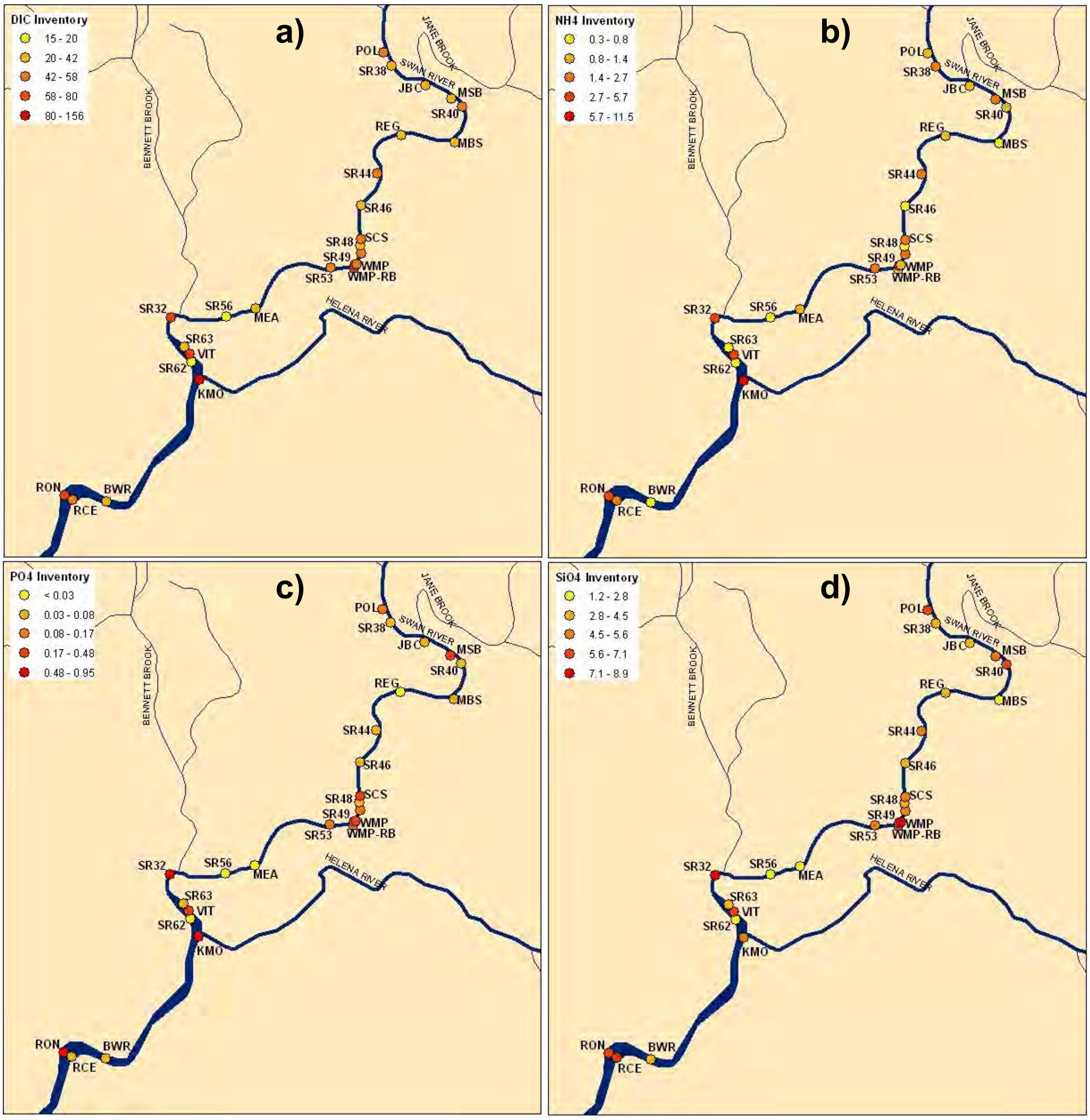

Figure 15 DIC (a) and nutrient (NH_4 (b); PO_4 (c); SiO_4 (d)) pool sizes in the top 2cm of sediments in the upper Swan River estuary. Units: mmol m^{-2}.

DIC and nutrient pool sizes were also calculated from sediment cores collected during the October 2006 (SR32) and May 2008 (KMO, VIT, WMP and REG) surveys (Figure 16). These pool sizes are calculated from concentrations in the top 20 cm of sediment porewater, which is presumably a better representation of DIC and nutrient pool sizes compared to pool sizes derived from the top 2 cm only. Sites SR32 and WMP are the deepest and have the largest pool sizes of DIC and all nutrients of all five sampled sites (Figure 16), which confirms deep sites to be areas of particularly high organic matter accumulation and decomposition.

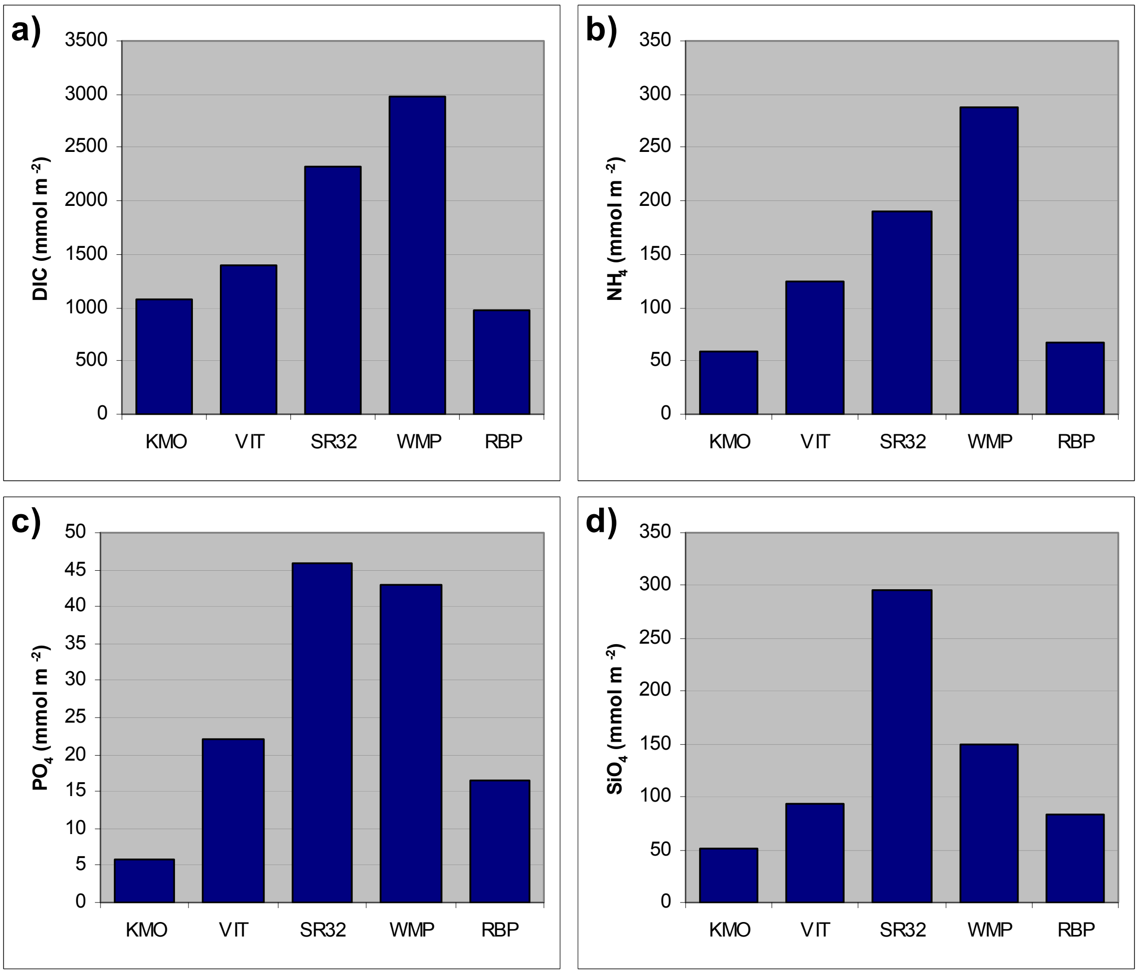

Figure 16 DIC (a) and nutrient (NH_4 (b); PO_4 (c); SiO_4 (d)) pool sizes in the top 20cm of selected sites in the upper Swan River Estuary. Sites ordered from most downstream to most upstream. SR32 collected in October 2006, all other sites collected in May 2008.

4B. OXYGEN AND NUTRIENT EXCHANGE BETWEEN SEDIMENT AND BOTTOM WATER

Given the spatial variability in sediment accumulation and composition in the upper Swan River estuary, it is difficult to derive information on temporal variability of benthic fluxes without extensive sampling through time at the same sites. In this case, sites RON and SR32 were sampled in October 2006 and sites KMO an WMP were sampled in May 2008. Despite the limits of the data, it is worth noting that average benthic fluxes were much larger during October 2006 than in May 2008 (Figure 17). In contrast, water column nutrients were generally much lower in October 2006 than in May 2008 (Figure 4 and Figure 8). This observation is attributed to the different hydrodynamic and water column conditions preceding sampling. Highest river discharge occurs during the winter and early spring (July to September) leading to well mixed, nutrient depleted water column conditions and the delivery of large amounts of labile organic matter from the catchment, which is rapidly decomposed at sites of deposition. In October, despite high rates of organic matter decomposition, the water column is not significantly enriched in nutrients. This is because the initial pulse of nutrient-rich water from the catchment, and any sediment-derived nutrients, are diluted or flushed into the lower Swan River estuary. In contrast, the long no-flow period from late spring, through summer to early winter (November to June) leads to significant enrichment of nutrients in the water column from nutrient release from sediments and the lack of nutrient export. Concurrently, benthic DIC and nutrient fluxes decline following the high flow and sediment deposition period, as the rate of organic matter decomposition decreases exponentially with time (Middelburg 1989).

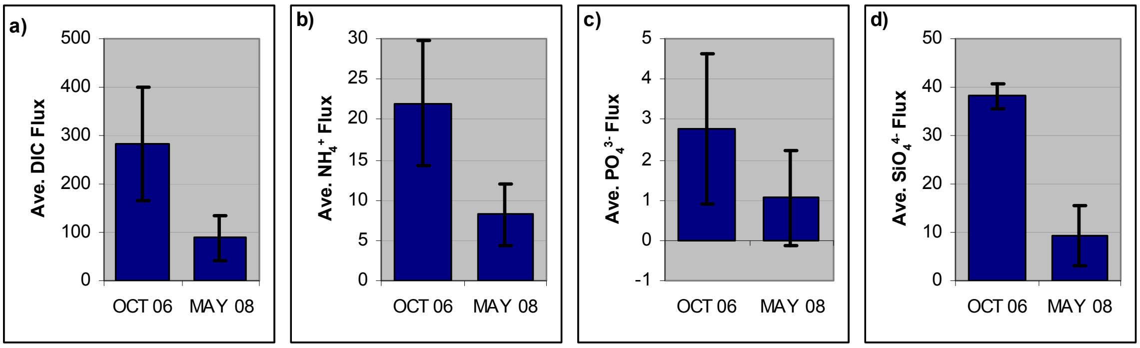

Figure 17 Average DIC (a), NH_4^+ (b), PO_4^{3-} (c) and SiO_4^{4-} (d) fluxes from sites sampled in October 2006 (RON and SR32) and in May 2008 (WMP and KMO). Units: mmol m^{-2} day^{-1}.

The large nutrient pool sizes do not necessarily correlate with a high rate of nutrient release from the sediments. In May 2008, DIC and NH_4^+ pool sizes were the largest at site WMP but benthic fluxes were the smallest. WMP is deep (3.5 m) and regularly experiences long periods of anoxic bottom water conditions. This circumstance is likely to inhibit the establishment of a benthic (invertebrate) community (Forster et al., 1995), which typically enhances nutrient release from sediment significantly through bioirrigation (Haese, 2002; Przeslawski *et al.*, 2009). In the absence of benthic fauna and therefore bioirrigation, benthic fluxes become limited to diffusion only, leading to high sediment nutrient inventories and low benthic fluxes. The example of WMP illustrates why sediment nutrient inventories and benthic fluxes do not necessarily correlate and why the sediment nutrient inventory has a limited application as a potential resource condition indicator.

N_2 fluxes indicate the amount of denitrification (positive fluxes) or nitrogen fixation (negative fluxes) occurring in an estuary. Of the sites sampled, RON, SR32 and WMP showed average positive fluxes whereas KMO showed an average negative flux (Figure 13c). Denitrification efficiencies, calculated as the percentage of dissolved inorganic nitrogen released as N_2 gas, were 9%, 20% and 43% for RON, SR32 and WMP respectively. These rates are small and indicate that most of the nitrogen is remaining in biologically available forms (NH_4^+ and NO_X). The negative N_2 flux at KMO remains unexplained, because N fixation is unlikely given the high concentrations of NH_4^+ in the bottom water (Figure 8). A possible explanation for the observed decrease in N_2 concentrations during the benthic chamber incubations could be the release of CO_2 bubbles from sediments, which leads to stripping of other gases such as N_2. Bubbles rising to the water surface were observed at this site during the benthic chamber deployment and is commonly attributed to exceedingly high concentrations of DIC in sediments.

4C. THE INFLUENCE OF BOTTOM WATER OXYGEN ON BENTHIC FLUXES AND INVERTEBRATE COMMUNITIES

4C1. Nitrogen

The production of di-nitrogen gas (N_2) is a desirable process as it removes biologically available nitrogen from the aquatic systems, however several microbial processes are required as precursors. Firstly, during the breakdown of organic matter, nitrogen in the form of ammonia is released (ammonification), which is then be converted into nitrate in the presence of oxygen (nitrification). The formed nitrate then diffuses into anoxic layers of the sediments, where it is transformed into N_2 gas (denitrification) which is then able to leave the system. Nitrification and denitrification are generally closely linked and known as coupled nitrification-denitrification. The waters of temperate Australian estuaries do not contain significant levels of nitrate, therefore coupled nitrification-denitrification in sediments is the only way to achieve denitrification. Under anoxic bottom water conditions nitrification will be inhibited, thus negatively impacting denitrification (Eyre & Ferguson, 2009).

The positive N_2 flux at WMP in May 2008 is unexpected, because the bottom water was depleted in nitrate and oxygen at the time. One possible source of nitrate for the subsequent formation of N_2 through denitrification could be groundwater seepage at this relatively deep site. However, no independent evidence for an aquifer carrying nitrate-rich water and intersecting the estuary at WMP is currently known.

A good correlation (r^2=0.77) between the DIC and NH_4^+ flux was found (Figure 18a) suggesting that the rate of organic matter decomposition has the biggest control over the NH_4^+ release. In contrast, the correlation between the NH_4^+ flux and the bottom water oxygen concentration is poor (Figure 18b). Low benthic NH_4^+ fluxes under low oxygen bottom water conditions were found in May 2008 when the water column was stratified and the catchment-derived organic matter had lost its initial high reactivity after decomposing for several months (see 4B).

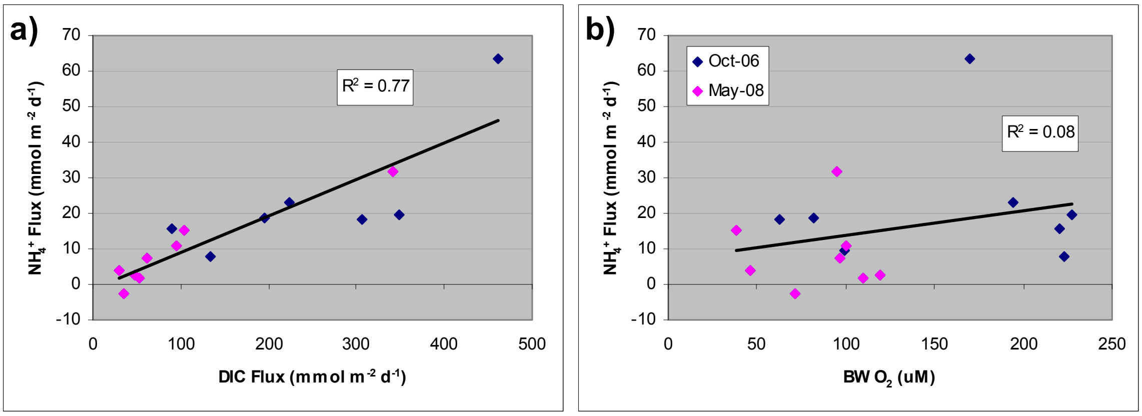

Figure 18 DIC flux versus NH_4^+ flux (a) and Bottom water O_2 concentration versus NH_4^+ flux (b) from benthic chambers deployed in the upper Swan River estuary.

4C2. Phosphorus

Phosphate has a high tendency to adsorb to the surface of iron-oxyhydroxides (Rozan *et al.*, 2002), which typically form a coating on detrital minerals. Most iron-oxyhydroxides in surface sediments becomes enriched over years to geological time scales, because reducing redox conditions below the oxic surface layer induces the reduction of solid phase Fe^{3+} to produce dissolved Fe^{2+} and the latter then diffuses back into the oxic zone, where it precipitates as oxyhydroxide again. If the bottom water becomes anoxic, the sediment binding capacity diminishes, because the iron in the iron-oxyhydroxide becomes reduced and the produced Fe^{2+} either escapes into the bottom water or precipitates as FeS, which has no phosphate binding capacity.

A good correlation (r^2=0.74) was found between the rate of organic matter decomposition, as represented by the benthic DIC flux, and the PO_4^{3-} flux (Figure 19a), suggesting that the rate of organic matter decomposition has the biggest control over the PO_4^{3-} release as was also found for NH_4^+. Importantly, the slope of the correlation shows a benthic flux C:P ratio of ~100 (similar to the Redfield ratio), which indicates no phosphate is retained in these sediments irrespective of the instantaneous bottom water oxygen concentration (Figure 19b). This is due to the regular and long exposure of sediments to anoxic bottom water conditions at the four sites, which inhibits the accumulation of iron-oxyhydroxides and limits the binding capacity for phosphate.

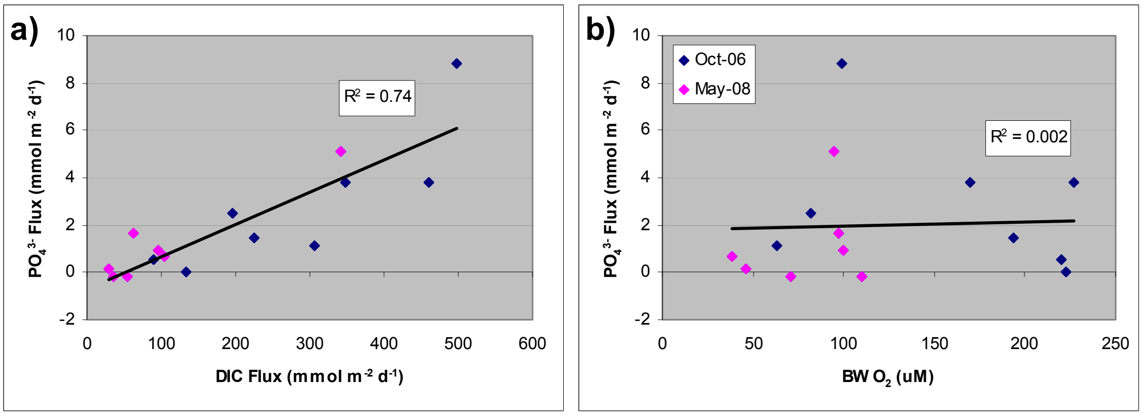

Figure 19 DIC flux versus PO_4^{3-} flux (a) and Bottom water O_2 concentration versus PO_4^{3-} flux (b) from benthic chambers deployed in the upper Swan River estuary.

4C3. Benthic Communities

Seasonal bottom water anoxia over several months at the study sites has not only led to a very poor phosphate binding capacity as discussed in section 4C2, but also to discontinuous conditions that hinder benthic invertebrates to establish. Intermittent periods of anoxia have been shown to result in steady impoverishment in species composition (Rachor 1980) and to a significant delay in the re-establishment and successive stages in the benthic assemblages following a perturbation event (Rhodes *et al.* 1978). Bioirrigation by benthic invertebrates is a particularly important ecosystem process ("service") for water quality as it leads to a much higher oxygen uptake by sediments (Jørgensen *et al*., 2005) enhancing denitrification (Gilbert *et al*., 1998) and the formation of oxyhydroxides required to retain phosphorous in sediments (Boers *et al*., 1998). Bioirrigation also enhances nutrient fluxes across the sediment-water interface, which avoids the build-up of excessive nutrients in porewaters.

In the upper Swan River estuary, it is believed that the absence of benthic invertebrate communities are responsible for the reduction in benthic fluxes, decreased denitrification efficiency and P-binding capacity, and the build-up of nutrients in the sediment porewaters, as observed at WMP.

5. Conclusion

The release of nutrients from the sediments to the overlying water column in the upper Swan River estuary is controlled primarily by the rate of organic matter decomposition in the sediments. The most reactive sediments were found at the deeper sites (>2.5 m) and at the confluence of rivers into estuary. Fine sediments enriched in labile organic matter accumulate at these locations because the water velocity decreases and fine particles settle out of suspension. During high-flow events these areas are likely to be eroded and fine sediments are transported to the lower estuary or even into the ocean. However, historical records and the modelling of future scenarios suggest that larger flushing events are likely to decrease in frequency in the Swan estuary (Kelsey *et. al.*, 2009), which makes the upper estuary more prone to long-term deposition of fine sediments and increased release of nutrients from sediments.

Time series data of nutrient release from sediment sites in the upper Swan River estuary is not available, so the study of temporal variability in benthic nutrient fluxes is based on the comparison of different sites at different times. This bears the risk of introducing bias due to spatial variability. Differences in nutrient fluxes were measured and it is possible that this is due to seasonal differences associated with organic matter delivery from the catchment. The largest benthic fluxes were recorded in October 2006 following the annual winter to early spring high river discharge period, most likely due to the recent deposition of catchment-derived reactive organic matter. Once river flow ceases, a salt wedge migrates upstream and stratification develops in the upper estuary. The rate of organic matter decomposition decreases over time and, consequently, low benthic nutrient fluxes were measured in May 2008 after the long, no-flow period from late spring to autumn. Because of the anoxic bottom water imposed by stratification, the sediment is likely to be devoid of benthic invertebrates leading to lower benthic nutrient fluxes despite very high porewater nutrient inventories. This observation illustrates the limitations of pore water inventories as a resource condition indicator.

The phosphorus retention capacity of sediments in the upper Swan River estuary is minimal because iron-oxydydroxide do not accumulate in surface sediments given the seasonal bottom water anoxia. As a consequence, a linear correlation between benthic DIC and phosphate fluxes was found. The seasonal bottom water anoxia also inhibits the permanent establishment of benthic invertebrates, which if present would have the capacity to significantly enhance the sediment oxygen uptake and thereby enhance denitrification and phosphate retention.

In order to improve water quality in the upper Swan River estuary long-term management actions should be directed to

a. reduce the amount of catchment-derived nutrient and organic carbon in order to reduce organic matter decomposition and associated nutrient release from sediments.
b. establish permanent oxygenated bottom water conditions to establish benthic invertebrate communities supporting denitrification and phosphate retention.

6. References

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Appendix 1 Analytical Methods

A1A. DIRECT CARBON DIOXIDE BY DISSOLVED INORGANIC CARBON ANALYSER

Total dissolved inorganic carbon (TCO_2) was analysed without any sample pre-treatment with the dissolved inorganic carbon (DIC) analyser AS-C3 (Apollo SciTech), which includes an infrared-based CO_2 detector (LiCor 7000). Certified sea water was used as a standard (A.G. Dickson, UC San Diego). The precision of the measurements were typically 0.1 %, i.e. differences of 2 µmol/l on a background of 2000 µmol/l were detectable. Benthic chamber samples had a volume of 0.5 ml, whereas the highly concentrated porewater samples had volumes between 0.05 and 0.1 ml. A memory effect was found when samples with large concentration differences were measured one after another, which was accounted for by analysing each sample 3 times and the first two sample results were discarded.

A1B. DISSOLVED INORGANIC NUTRIENTS

Ammonia (NH_4^+), nitrate + nitrite (NO_X), phosphate (PO_4^{3-}), and silicate (SiO_4^{4-}) were determined at the National Measurement institute (NMI) laboratories (Cottesloe, WA). A table of limits of reporting and associated measurement uncertainty to a 95 % confidence interval for various levels is shown below (Table 6A).

NH_3-N/NH_4-N (sol): Automated phenate method

Ammonia nitrogen was determined by an automated flow injection analyser with a spectrophotometer that included a flow-through-cell, used at 640 nm (for UV-vis detection). An intensely blue compound indophenol is formed by the reaction of ammonia hypochlorite, and phenol catalysed by sodium nitroprusside. There is no interference from other trivalent forms of nitrogen. Interfering turbidity was removed by filtration through a 0.45 mm cellulose nitrate filter paper. The lowest limit of reporting was 0.01 mg L^{-1}.

NO_x-N: Automated cadmium reduction method

Total oxidised nitrogen was determined by an automated flow injection analyser with a spectrophotometer that included a flow-through-cell, used at 540 nm (for UV-vis detection). Nitrate is reduced quantitatively to nitrite in the presence of cadmium. The sample is passed through a column containing granulated copper-cadmium to reduce the nitrate to nitrite. The nitrite (originally present plus reduced nitrate) is determined by diazotising with sulphanilamide and coupling with a-naphthylethylenediamine dihydrochloride to form a highly coloured azo dye that is measured colorimetrically at 540 nm. Concentrations of Fe, Cu or other metals above several mg L^{-1} lowers reduction efficiency. Oil and grease will coat cadmium surface. Interfering turbidity was removed by filtration through a 0.45 mm cellulose nitrate filter paper. The lowest limit of reporting was 0.01 mg L^{-1}.

PO_4-P (sol react): Automated ascorbic acid reduction method

Soluble reactive phosphorus (SRP) or PO_4-P was determined by an automated flow injection analyser with a spectrophotometer that included a flow-through-cell, used at 880 nm (for UV-vis detection). Ammonium molybdate and potassium antimonyl tartrate react in acid medium with orthophosphate to form a heteropoly acid that is reduced to intensely coloured molybdenum blue by ascorbic acid. Arsenates react to produce a similar colour. Interfering turbidity was removed by filtration through a 0.45 mm cellulose nitrate filter paper. The lowest limit of reporting was 0.005 mg L^{-1}.

Silica as SiO_2-Si: Automated method for molybdate-reactive silica

Silica as SiO_2-Si was determined by an automated flow injection analyser with a spectrophotometer that included a flow-through-cell, used at 810 nm (for UV-vis detection). Silica in solution as silicic acid or silicate reacts with an acidified ammonium molybdate solution to form (β)-molybdosilicic acid. The complex acid is reduced by ascorbic acid to form molybdenum blue (which is a blue dye). This absorbance is measured at 810 nm. Oxalic acid is added to avoid phosphate interference. Interfering turbidity was removed by filtration through a 0.45 mm cellulose nitrate filter paper. The lowest limit of reporting was 0.001 mg L^{-1}.

Table 6A. Limits of reporting (and associated measurement uncertainty to 95 % confidence intervals) for the methods used for analysis of nutrients by NMI (Cottesloe, WA).

Analyte	**Method Number**	**Level 1 (LOR)**	**Level 2**	**Level 3**	**Level 4**	**Level 4** (expressed as %)
Ammonia as NH_3-N - High Level	WL119	1 ± 0.4 mg/L	2 ± 0.5 mg/L	5 ± 0.8 mg/L	10 ± 1.6 mg/L	>10 mg/L ± 16%
Ammonia as NH_3-N - Low Level	WL239	0.01 ± 0.010 mg/L	0.05 ± 0.012 mg/L	0.20 ± 0.028 mg/L	0.50 ± 0.067 mg/L	>0.50 mg/L ± 13%
Nitrite as NO_2-N - High Level	WL119	0.3 ± 0.36 mg/L	3 ± 0.45 mg/L	6 ± 0.69 mg/L	12 ± 1.3 mg/L	>12 mg/L ± 10%
Nitrite as NO_2-N - Low Level	WL239	0.01 ± 0.005 mg/L	0.02 ± 0.006 mg/L	0.05 ± 0.007 mg/L	0.20 ± 0.018 mg/L	>0.20 mg/L ± 9%
Nitrate as NO_3-N - High Level	WL119	0.2 ± 0.24 mg/L	1 ± 0.26 mg/L	5 ± 0.53 mg/L	10 ± 1.2 mg/L	>10 mg/L ± 11%
Nitrate as NO_3-N - Low Level	WL239	0.01 ± 0.007 mg/L	0.05 ± 0.011 mg/L	0.10 ± 0.018 mg/L	0.20 ± 0.035 mg/L	>0.20 mg/L ± 17%
Silica as SiO_2	WL239	0.001 ± 0.0038 mg/L	0.020 ± 0.0040 mg/L	0.10 ± 0.065 mg/L	0.40 ± 0.022 mg/L	>0.40 mg/L ± 5%
ortho-Phosphate as PO_4-P - High Level	WL119	0.1 ± 0.06 mg/L	0.2 ± 0.07 mg/L	0.5 ± 0.09 mg/L	1.0 ± 0.14 mg/L	>1.0 mg/L ± 14%
ortho-Phosphate as PO_4-P - Low Level	WL239	0.005 ± 0.007 mg/L	0.020 ± 0.013 mg/L	0.10 ± 0.018 mg/L	0.50 ± 0.049 mg/L	>0.50 mg/L ± 10%

A1C. DISSOLVED NITROGEN GAS

Dissolved N_2 was measured in benthic chamber samples using a Membrane Inlet Mass Spectrometer as described by Kana *et al*. (1994). Gases were detected with a Balzers QMS422 quadrupole mass spectrometer and a water bath (± 0.01 °C) was used to stabilize sample temperature in the water line upstream of the membrane.

A1D. TOTAL ORGANIC CARBON, TOTAL NITROGEN AND STABLE ISOTOPES

Total organic carbon (TOC) and total nitrogen (TN) concentrations, and the respective stable isotopic compositions $\delta^{13}C$-OM and $\delta^{15}N$-OM, were analysed after the samples were pre-treated with acid and washed with demineralised water to remove carbonate and residual acid. TOC, TN, $\delta^{13}C$-OM, and $\delta^{15}N$-OM were analysed using an elemental analyser (EA), attached to an isotope ratio mass spectrometer (IRMS Fry et al. 1992). At Geoscience Australia, a Thermo Finnigan Flash EA is coupled to a Finnigan Mat 252. The oxidation furnace of the Flash EA was packed with copper oxide and silvered cobaltous oxide and operated at 900°C. The reduction furnace was packed with pure copper and operated at 600°C. Combustion products were separated on a packed GC column run isothermally at 40°C. We conducted carbon and nitrogen analysis separately to improve analytical performance. The precision of sample analysis was better than 10% for TOC and better than 5% for TN.