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Historic environmental changes and sediment-based condition assessment for Hardy Inlet, Western Australia

Ralf R Haese, Craig S Smith, Vanessa Forbes, Mike Macphail, and Gary Hancock

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APPLYING GEOSCIENCE TO AUSTRALIA'S MOST IMPORTANT CHALLENGES

Historic environmental changes and sediment-based condition assessment for Hardy Inlet, Western Australia

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by

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Australian Government
Geoscience Australia

Government of Western Australia
Department of Water
Looking after all our water needs

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Executive Summary

This project was conducted by Geoscience Australia in collaboration with the Water Science Branch of the Department of Water, Western Australia, to acquire baseline information supporting the condition assessment for Hardy Inlet. The project contributes to the Estuarine Resource Condition Indicators project funded by the Strategic Reserve of the National Action Plan for Salinity and Water Quality / National Heritage Trust and forms part of the Resource Condition Monitoring endorsed under the State (Western Australia) Natural Resource Management framework.

Two surveys were undertaken in Hardy Inlet in September 2007 and April 2008 with the aim to develop an understanding of the historical environmental changes and current nutrient and sediment conditions for the purpose of developing sediment indicators to characterise estuary condition.

Hardy Inlet is situated 320 km south of Perth and flows alongside the town of Augusta, east of Cape Leeuwin. The Inlet consists of a shallow basin with an average water depth less than 1 meter. The basin varies in width along a 5 km long axis from the mouth to the confluence of its two main tributaries at Molloy Island; the Blackwood River and the Scott River. The approximate area of Hardy Inlet is 9 km^2 which remains microtidal through its permanent entrance channel that discharges into Flinders Bay on the Southern Ocean.

The September 2007 survey took place when Hardy Inlet was receiving the first major river flows for the year, and its most significant flow since June 2005. Consequently, surface and bottom waters were fresh and well oxygenated in both the seawater zone (lower basin, west bay and estuary channel) and the typically stratified mixing zone (the upper basin, Molloy Island, Blackwood River and Scott River).

The April 2008 survey took place at the end of the seasonal dry period. In the seaward zone salinities were close to marine and well oxygenated. In the mixing zone salinities were still high (>25) but there was evidence of the salt wedge and stratification. Dissolved oxygen concentrations were also reduced in the bottom waters further indicating stratified conditions.

The key findings of this study include:

1. The large shallow areas predominantly consist of coarse (silt to sand) sediment and the total organic carbon concentration correlates linearly with grain size, i.e. high concentrations of organic matter are found in fine sediments. These areas do not release significant amounts of nutrients, they have small nutrient pool sizes and show high rates of benthic primary production mainly because of sufficient light availability at the sediment surface.

2. In contrast to the shallow areas, deep channel areas west and north of Molloy Island become temporarily stratified and the bottom water turns anoxic leading to significantly increased rates of nutrient release. At a deep channel site north of Molloy Island high rates of nutrient and dissolved inorganic carbon release was measured despite low concentrations of organic matter. This is observation is possibly related to groundwater discharge. It is recommended to further investigate the cause of high nutrient release in the deep channel, particularly near Molloy Island where housing development may have lead to increased nutrient levels in the groundwater.

3. The rate of organic matter decomposition and the sediment phosphorous binding capacity measured as the benthic dissolved inorganic carbon and phosphate flux under dark

conditions, respectively, appear to be the most robust sediment-based condition indicators. The rate of organic matter decomposition is a direct reflection of the organic matter loading, which has been successfully used to classify the trophic status, i.e. the degree of eutrophication. The sediment phosphorous binding capacity is most sensitive to bottom water oxygen concentrations and has been shown to control phosphate levels and N/P nutrient ratios in the water column with implications for phytoplankton abundance and composition. High phosphate concentrations and low N/P ratios have been associated with nuisance (toxic) algae blooms.

4. Sedimentation rates have increased more than 10 times since land management by Europeans commenced at the end of the 19th century. An abrupt increase in sedimentation rate and change from fine to coarse sediment marks the initial stage of land clearance. Deep soil erosion in the catchment must have been associated with initial land clearance. Top soils have gradually re-established over the last century as can be seen by the current deposition of fine sediments. However, sedimentation rates are still an order of magnitude higher compared to pre-European land use.

Acknowledgements

The authors wish to thank Sarah Evans and Bronwyn Rennie from the Department of Water (WA), Matt Carey, John Jaycock, Jodie Smith and Emma Murray from Geoscience Australia for their invaluable assistance during the field sampling programs.

We would also like to acknowledge the good collaboration with staff from the Bunbury office from the Department of Water (WA), who made their boat and boat driver available for the surveys.

Sample analysis for this project was extensive and we thank the National Measurement Institute in Perth, CSIRO and Geoscience Australia laboratories in Canberra, and Environmental Isotopes Pty Ltd in Sydney for their expertise in performing quality analysis in a timely manner. We thank Jodie Smith for preparing maps in ArcGIS.

Finally, we would like to thank Malcolm Robb from the Department of Water (WA) for his continued support of this work over many years.

Contents

1. Introduction

1A. THE NEED FOR SEDIMENT AND WATER QUALITY INFORMATION

Estuaries in the south of Western Australia are typically characterised by a large, shallow central basin and a sand bar separating the estuary from the ocean. The sand bar can be closed for months to years inhibiting water exchange with the ocean. Mediterranean-type climate conditions lead to episodic freshwater inflow during the winter and early spring and high evaporation during the dry and hot summer period. Estuarine sediments play a key role in regulating water quality under such conditions. Therefore, understanding the drivers for changes in sediment deposition and biogeochemical processes affecting the release of nutrients from sediments is important for the management of estuaries. The selection of indicators reflecting changes in water quality and environmental conditions is critical for the design of monitoring programs and a matter of ongoing debate requiring further research.

The recent Hardy Inlet Condition Statement (Department of Water 2006) characterises Hardy Inlet as nutrient enriched showing clear symptoms of poor water quality such as anoxic bottom water, increased algal growth, the occasional occurrence of toxic algae and fish deaths. Of particular concern are the areas around Molloy Island and the estuarine reaches of the Blackwood River (Figure 1). Several causes for the poor water quality are considered in the report, including enhanced nutrient and sediment delivery from the catchment and enhanced nutrient release from sediments within the Inlet. Sediment and water quality data are identified as critical information gaps to develop further management plans including condition targets.

This study contributes to the Estuarine Resource Condition Indicators project funded by the Strategic Reserve of the National Action Plan for Salinity and Water Quality / National Heritage Trust. Indicators are measures of water quality and ecological condition and should be quantifiable, scientifically validated and provide relevant information for management decision making. A selection of indicators and their estuary specific values are increasingly made publicly available through report cards (Department of Water 2008).

1B. OBJECTIVES AND APPROACHES

The aim of this project was to characterise surface sediments in Hardy Inlet in terms of physical-chemical properties and their role as a nutrient source. Based on this new information and existing water quality data from the ongoing monitoring program we wanted to develop an understanding of nutrient dynamics and sediment-related resource condition indicators. Sediment cores were analysed to reconstruct historical environmental changes in the catchment and in the estuary, in particular changes in the estuarine sedimentation rate.

The following specific objectives were addressed:
To identify areas where nutrient concentrations and nutrient release from sediments is particularly high;
To develop sediment-based indicators to assess and monitor estuarine condition. The following parameters were studied as potential indicators:

- Porosity
- Total organic carbon concentration
- Phosphorus binding capacity
- Denitrification efficiency
- Benthic primary production
- Total organic matter decomposition rates

To develop a record of historical changes in sedimentation rate and sediment quality relating to changes in catchment land use patterns, in particular the onset of European land use.

The project provides baseline data on the condition of sediments in Hardy Inlet through experiments in the field and the collection and analysis of sediment samples. This forms part of a broader program which includes a range of estuaries in southern Western Australia and aims to refine the sediment indicators that can best be used to measure changes in estuarine condition over time.

Incubation experiments at 4 sites in the field are used to measure the flux of nutrients from the sediments and to measure sediment metabolism. This component of the study focuses on defining process indicators, such as the organic matter decomposition rate and sediment oxygen demand, denitrification efficiency and phosphorus retention capacity. Those indicators are a measure for the trophic status of an estuary and suggest whether the system will be resilient to further organic matter loading from the catchment.

Sediment cores from 6 sites were collected to characterise the vertical distribution of nutrient concentrations in the porewaters. This provides information of the nutrient and carbon stores in the sediments potentially available for benthic production and bacterial metabolism.

A total of 35 surface sediment samples were collected and analysed for porewater nutrient and dissolved inorganic carbon concentrations, the particulate organic carbon and total nitrogen concentrations, grain size and porosity and carbon and nitrogen stable isotopic composition. These properties characterise the bulk surface sediment, which provide valuable information on the distribution of different sediment types and identify areas of high carbon loading and porewater nutrient storage. The carbon and nitrogen stable isotopic composition potentially indicates the source of organic matter.

Physical, chemical and biological properties of sediments down to 1 meter depth are used to reconstruct changes in catchment conditions, estuarine sedimentation rates and water quality.

1C. GEOGRAPHIC LOCATION AND GEOMORPHOLOGY

Hardy Inlet is situated 320 km south of Perth adjacent the town of Augusta, east of Cape Leeuwin. The catchment of Hardy Inlet includes the catchments of the Blackwood River and the Scott River and extends 330 km from Augusta to Lake Grace in the east and spans an area of 2.8 million ha (28 000 km^2, Figure 1).

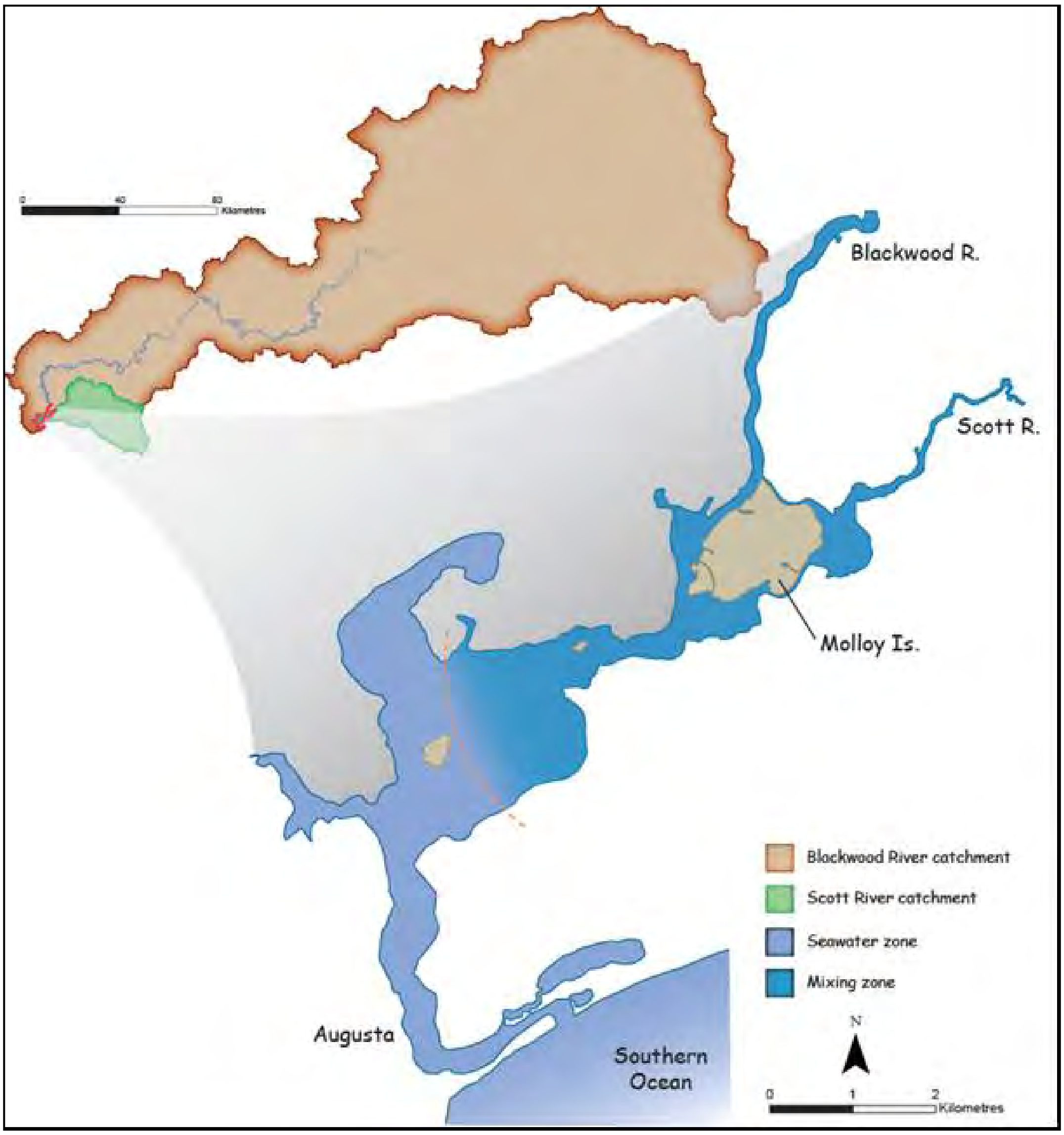

Figure 1: Location map of Hardy Inlet showing the extent of the Blackwood and Scott River catchments that drain into the Hardy Inlet east of Augusta. The Inlet can be separated into a seawater and a mixing zone.

Hardy Inlet is a mature estuary characterised by a large (9 km2), central basin, a channel leading to the permanent opening connecting the Inlet with the ocean and two tributary rivers which meet at the north side just above Molloy Island (Figure 1). Most of the Inlet basin is shallow (<1 m, Figure 2) and characterised by coarse-grained (silt to sand) sediments. The marginal areas have large seagrass meadows. Primary productivity in the seagrass habitat is high and of ecological value as it provides favourable conditions for complex trophic interactions e.g. between microalgae, invertebrates, fish and swans.

The Blackwood River is the main tributary into Hardy Inlet and contributes 80 % of the total river flow. A second tributary, the Scott River enters to the east of the Blackwood River, but flow into the main basin is restricted by narrow channels and the position of Molloy Island. The Scott River only contributes 14 % to the total river flow. The Blackwood River, unlike the Inlet and Scott River, has an extremely uneven depth profile with some areas as deep as 14 m and 22 m; these areas are poorly flushed and almost permanently stratified.

Regular water monitoring data in Hardy Inlet shows the southern parts of the Inlet to be well mixed with salinities resembling marine conditions for most of the year except when river flows are high. This area is here referred to as the seawater zone. Towards the northern parts of the Inlet basin and into the estuarine channel and lower Blackwood River water depths are more varied as are the salinity conditions in the water column. This area is referred to as the mixing zone (Figure 1). The water column in the deep channel, particularly in the Blackwood River is often stratified and bottom waters are frequently anoxic.

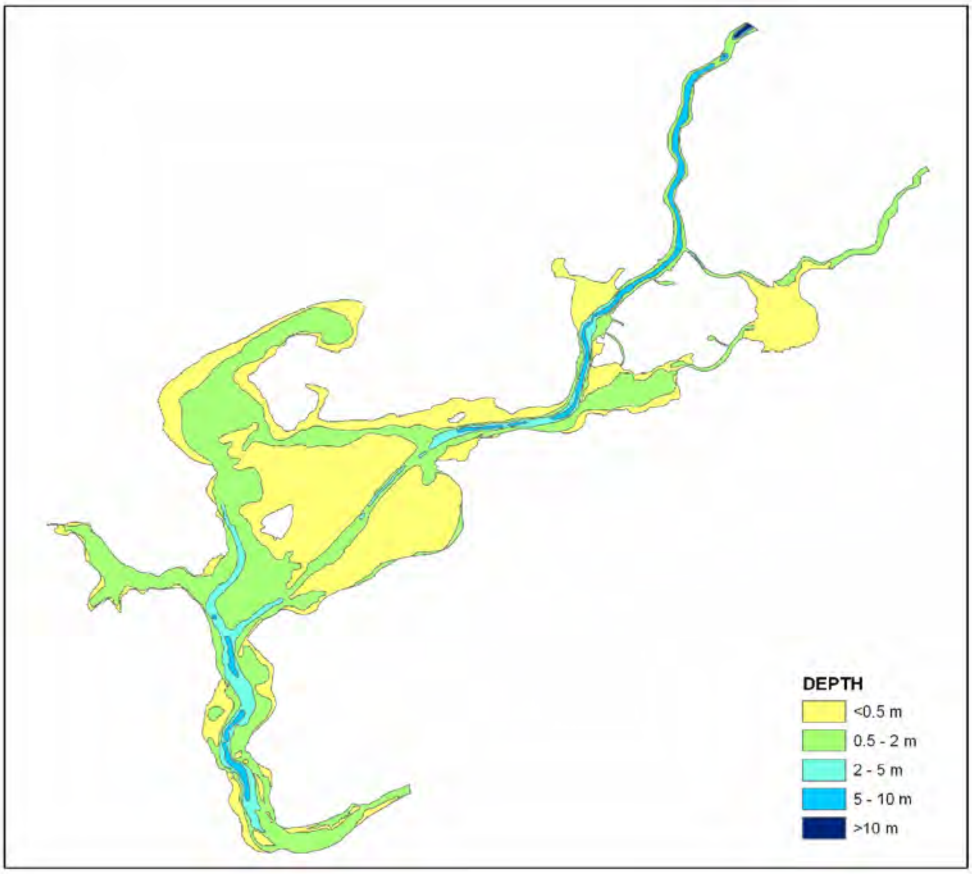

Figure 2: Bathymetry of Hardy Inlet. Note more than 90% of the main basin is shallower than 1 m and Blackwood River flows sustain a deep channel west of Molloy Island.

1D. GENERAL CLIMATE AND ESTUARY CONDITIONS

The south coast experiences a Mediterranean-type climate characterised by high winter rainfall and dry hot summers. Rainfall in the catchment varies from less than 400 mm per annum in the upper catchment to as much as 1400 mm per annum in the lower catchment. It is this lower Blackwood River and Scott River catchment that contributes most of the freshwater discharge to Hardy Inlet.

Generally, highest and lowest rainfall months occur in June and January, respectively (Figure 3), but summer rainfall events are occurring increasingly more frequent. Summer events help maintain the permanent entrance of the Inlet when flows are at a minimum, but they also transport nutrient rich waters from an agricultural catchment into the estuary when it is most productive. This can result in phytoplankton blooms and excessive macroalgal growth which are unfavourable (Department of Water, 2006).

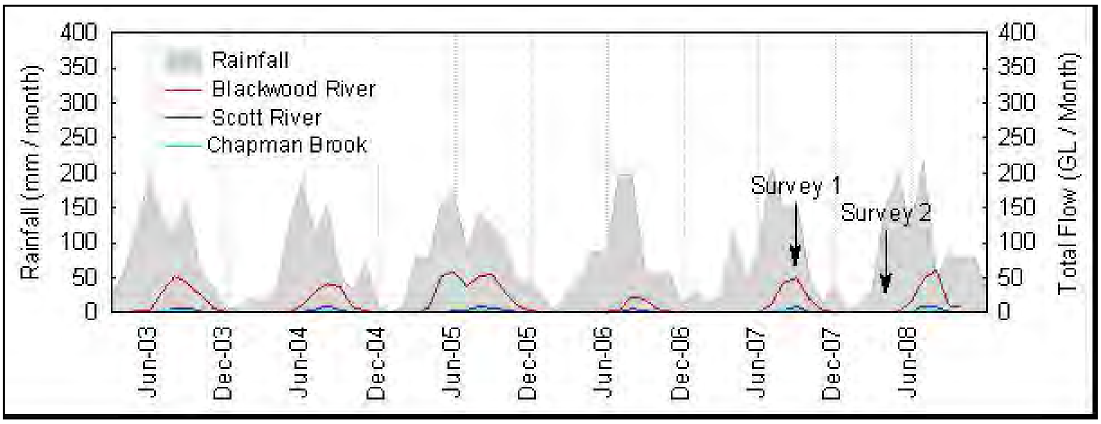

Figure 3: Average monthly rainfall (mm) from the Bureau of Meteorology measurement sites in the Blackwood and Scott River catchments (2003-2009). Total monthly river flow (GL/month) from the Blackwood River, Scott River and Chapman Brook (2003-2009).
Survey 1 – September 2007, Survey 2 – April 2008.

1D1. September 2007 Survey

The September 2007 survey took place when Hardy Inlet was receiving the first major river flows for the year, and its most significant flow since June 2005; the Inlet received very little inflow during 2006 (Figure 3) and there was serious concern that the channel entrance would close.

Consequently, surface and bottom waters were fresh and well oxygenated in both the seawater zone (lower basin, west bay and estuary channel) and the typically stratified mixing zone (the upper basin, Molloy Island, Blackwood River and Scott River) (Figure 4– 7).

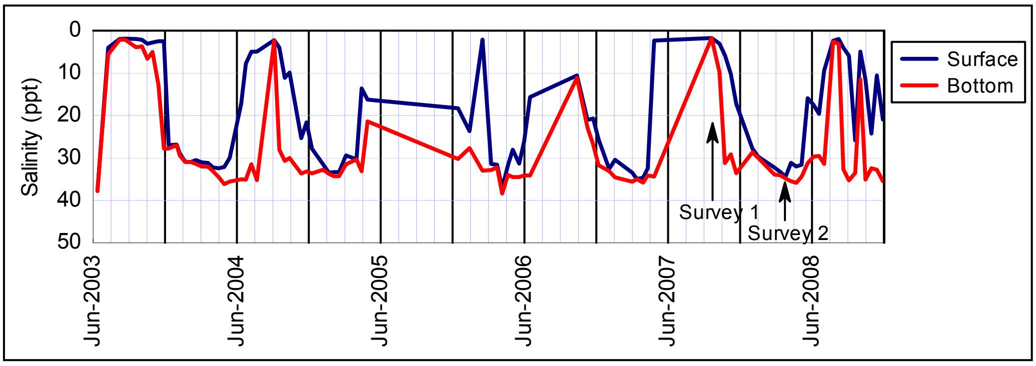

Figure 4: Median surface and bottom salinity across sites in the seawater zone for data collected fortnightly between 2003 and 2009. Survey 1 – September 2007, Survey 2 – April 2008.

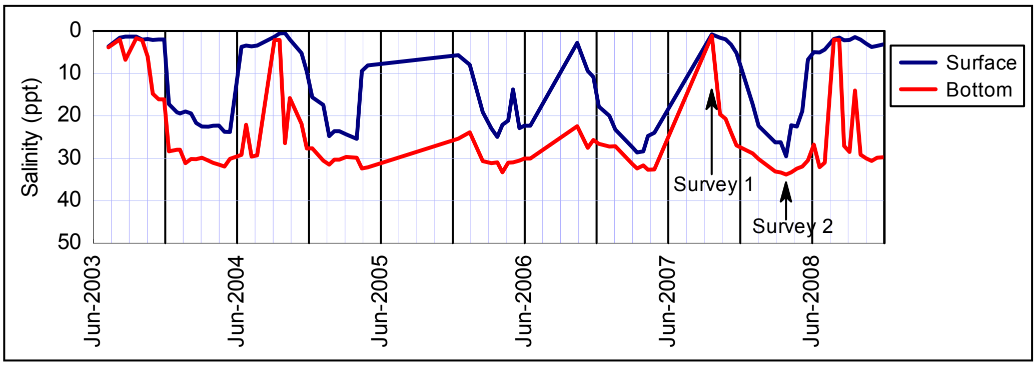

Figure 5: Median surface and bottom salinity across sites in the mixing zone for data collected fortnightly between 2003 and 2009. Survey 1 – September 2007, Survey 2 – April 2008.

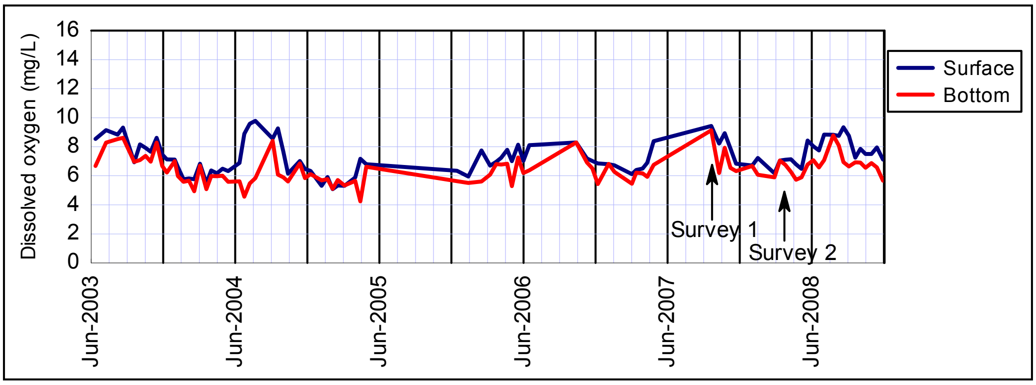

Figure 6: Median surface and bottom dissolved oxygen concentrations (mg/L) across sites in the seawater zone for data collected fortnightly between 2003 and 2009. Survey 1 – September 2007, Survey 2 – April 2008.

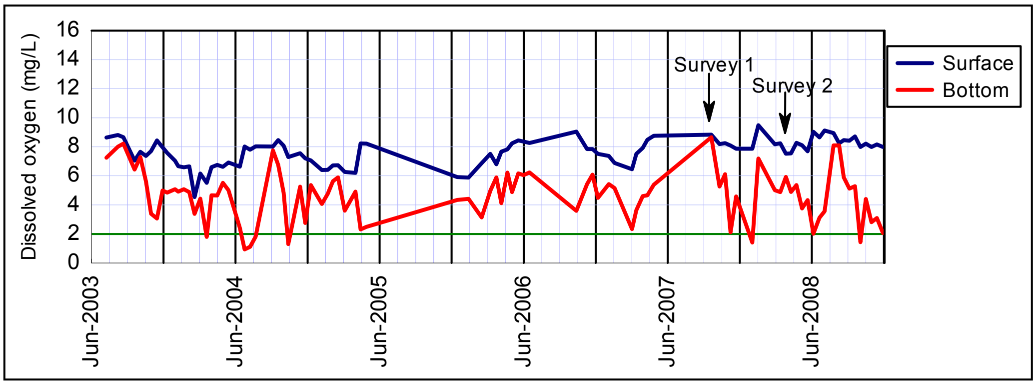

Figure 7: Median surface and bottom dissolved oxygen concentrations (mg/L) across sites in the mixing zone for data collected fortnightly between 2003 and 2009.
Survey 1 – September 2007, Survey 2 – April 2008.

1D2. April 2008 Survey

The survey in April 2008 took place under conditions typical for the end of the summer to early autumn period. In the seawater zone salinities were more marine (~35) and well oxygenated (Figure 4 - 7). There was little difference between surface and bottom waters; this part of the Inlet being shallow and well mixed by wind action.

In the mixing zone salinities were still high (>25) but there was evidence of the salt wedge and stratification with salinities in the bottom waters at 35. Evidence of stratification was also present in the differences between the concentration of dissolved oxygen in the surface and bottom waters; the surface waters were well oxygenated (8 mg/L) while the bottom waters were less (6 mg/L). It should be noted that these values are median values and that the bottom waters at some sites (deep holes) are more frequently <2 mg/L.

2. Methods

This section details the survey methods used to measure nutrient release from sediments, to characterise properties of the bulk surface sediment and to sample and analyse sediments to derive information on paleo-environmental changes.

2A. SAMPLING AND ANALYSIS

2A1. September 2007 survey

The spatial variability in bulk properties of surface sediment was derived by collecting surface sediment samples from 9 sites (HD1 – HD9 in Figure 8, Appendix 1) in September 2007. Sampling sites were selected with the aim to represent different depositional environments: 3 sites were located in the seawater zone, 4 sites were located in the mixing zone and 2 sites were located in the river channels. The following parameters were measured:

- Dissolved inorganic carbon (DIC) and nutrient concentrations in the porewater as a reflection of the intensity of organic matter breakdown
- Nutrient pool sizes,
- Porosity
- Total organic carbon concentration (TOC) and the carbon and nitrogen stable isotopic composition ($\delta^{13}C$, $\delta^{15}N$)

A push corer was used to collect short sediment cores. Sediment from the upper 8 cm of the core was scooped into a 50 mL centrifuge tube and a second sample from the upper 2 cm was scooped into a 20 mL vial. The 50 mL tube was centrifuged immediately for 10 minutes at 4000 rcf (relative centrifugal force) and the supernatant was filtered into 3 mL Labco vials containing 0.02 ml of saturated HgCl solution for DIC analysis and the remaining supernatant was transferred into 50 mL vials for dissolved inorganic nutrient (NH_4^+, NO_X, PO_4^{3-}, SiO_4^{4-}) analysis. The sediment in the 20 mL vial was freeze-dried for later porosity and TOC determination. See Appendix 1 for detailed analytical methods.

Additional short cores were collected at 6 sites (HD1, HD2, HD4, HD5, HD6 and HD9) to describe the vertical distribution of porewater nutrient concentrations. Sediment cores were extruded from the core barrel and cut into depth intervals down to 21 cm. Sediments were transferred into centrifuge tubes and porewater was extracted by centrifugation (see above). The porewater was transferred into 50 ml vials and analysed for dissolved inorganic nutrients (NH_4^+, NO_X, PO_4^{3-}, SiO_4^{4-}). All nutrient analyses were conducted by the National Measurement Institute (NMI). See Appendix 1 for detailed analytical methods.

Water column parameters (temperature, salinity and dissolved oxygen) were also measured at each of the 9 sites at the time of sediment collection. These measurements were taken using a YSI sonde (600XLM).

2A2. April 2008 survey

In April 2008 surface sediment samples, benthic chamber incubations and sediment dating cores were collected to expand the data base collected during the 2007 survey.

Surface sediments from 26 new sites (Figure 8, Appendix 2) were collected and analysed for porosity and TOC, $\delta^{13}C$ and $\delta^{15}N$ across the Inlet. Surface sediment samples were collected using a Van Veen grab (not a push corer as per the previous survey). The porewater of the sediment was analysed for DIC and the solid phase was analysed for porosity, TOC, $\delta^{13}C$ and $\delta^{15}N$.

Figure 8: Surface sediment site locations in Hardy Inlet. The red circles show sites sampled in September 2007, the yellow circles show sites sampled in April 2008.

Benthic chambers were deployed at four sites (HD1, HD4, HD5a and HD9) representing different depositional environments: Site HD1 is a shallow site with turbid water in the seawater zone, sites HD4 and HD5a are shallow sites with clear water in the mixing zone and site HD9 is a deep channel site. Light and dark chambers were used at the shallow sites (HD1, HD4 and HD5a), while only dark chambers were used at the deeper site (HD9). Note, site HD5a is located on a shallow (0.5 m) muddy flat and is only metres away from the deep (7 m) channel site HD5. Dark benthic chambers measure oxygen consumption and nutrient release from respiration processes alone, whereas light benthic chambers measure fluxes resulting from both respiration and photosynthesis.

The chambers were left with the door open for about an hour to allow any disturbed sediment to settle and the water within the chamber to equilibrate with bottom water. Upon closing the door, 5-6 draws were taken from each of the chambers over an incubation period of approximately 5 hours. Dissolved inorganic nutrients (NH_4^+, NO_X, PO_4^{3-}, SiO_4^{4-}), dissolved oxygen (O_2), dissolved inorganic carbon (DIC), and dissolved di-nitrogen (N_2) were determined in each sample and fluxes calculated from the concentration change over time within the chamber. More details of benthic flux measurements using in situ benthic chambers are given in Haese et al. (2007).

Surface water samples were taken for the analysis of total nitrogen (TN), total phosphorus (TP) and dissolved inorganic nutrients (NH_4^+, NO_X, N_2, PO_4^{3-}, SiO_4^{4-}) and additional bottom water samples were collected for dissolved inorganic nutrient concentrations at each of the benthic chamber sites.

Water column profiles (salinity, dissolved oxygen and temperature) were also taken at each of these sites using a YSI sonde (600XLM).

It proved difficult to find a site with an undisturbed sediment record for paleo-environmental studies. Based on field observations site HD34 appeared the best option. Two cores with a length between 70 to 80 cm were collected from site HD34 to determine sediment ages at different depths and respective sedimentation rates and to derive information on paleo-environmental changes. The cores were sub-sampled and analysed as follows: Core HD34A was kept intact in the field to analyse the dry bulk density of the whole core by the multi-sensor core logger. Afterwards, core HD34A was sub-sampled into 2 cm intervals and samples were prepared for pollen analysis. Core HD34B was sub-sampled into 2 cm intervals in the field and samples were kept frozen for latter sediment dating using radionuclide and OSL analysis and for determining the chemical composition by XRF. For all analytical methods see Appendix 1.

3. Results

This section details the water and sediment quality data, as well as benthic flux data collected during the September 2007 and April 2008 surveys.

3A. SEPTEMBER 2007 SURVEY

3A1. Water quality

The surface and bottom water salinity and dissolved oxygen measured at the 9 sampling sites are shown in Figure 9. Salinity was low throughout most of the Inlet due to high river flows (see General Climate and Estuary Condition). The water column was also well mixed with only HD5 and HD6 (western side of Molloy Island) showing some evidence of salinity stratification.

The water column was generally well oxygenated with dissolved oxygen concentrations ranging between 8.01 mg/L and 9.47 mg/L. There was little difference between the surface and bottom water oxygen concentrations although surface water concentrations were generally higher.

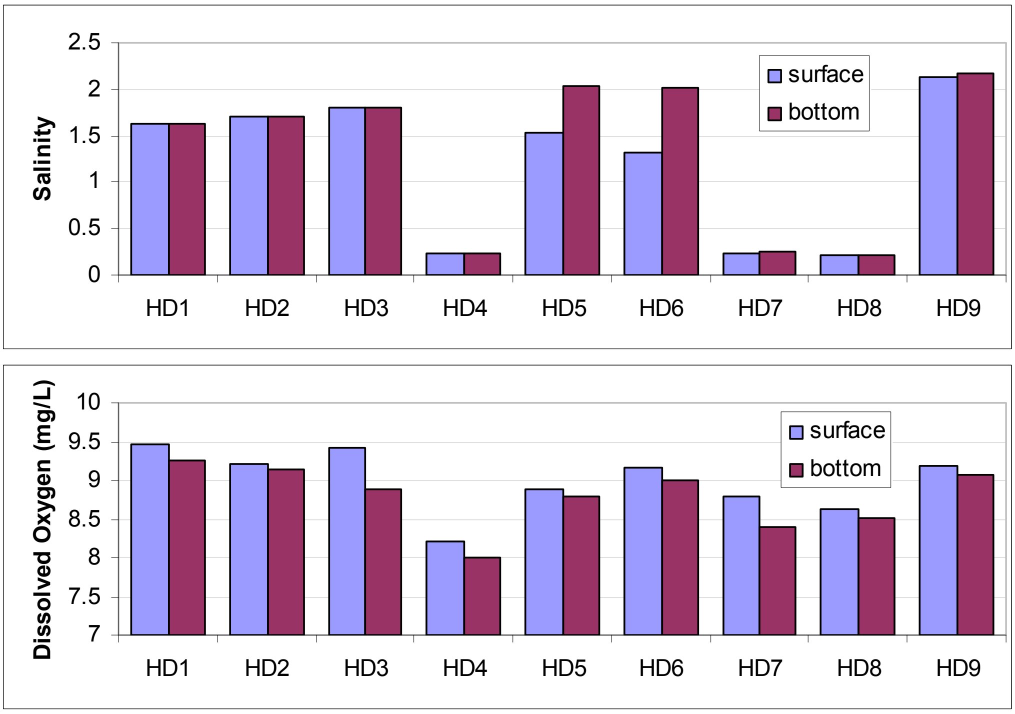

Figure 9: Surface and bottom water salinity and dissolved oxygen measured at sites within Hardy Inlet during the September 2007 survey.

3A2. Sediment Quality

Porosity, TOC, δ^{13}C and δ^{15}N in surface sediments

Porosity, the total organic matter concentration (TOC) and the stable isotopic composition of organic matter carbon (δ^{13}C) and total nitrogen (δ^{15}N) are presented together with the results from the April 2008 survey in section 3B2.

Porewater composition in surface sediments

Concentrations of dissolved inorganic carbon and nutrients (NH_4^+, NO_X, PO_4^{3-}, SiO_4^{4-}) were spatially highly variable in Hardy Inlet (Figure 10 and Appendix 3) and did not correlate with TOC concentrations. Low DIC (22.38 mg/L) and high TOC (5.06 wt%) concentrations were recorded at HD1 (West Arm) while high DIC (73.54 mg/L) but low TOC (0.45%) concentrations were recorded at HD9 in the Blackwood River.

Typically the mixing zone of Hardy Inlet had the highest concentrations of carbon and dissolved nutrients. Sites within the seawater zone (HD1, HD2 and HD3) had low concentrations of NH_4^+ and no detectable NO_X or PO_4^{3-}.

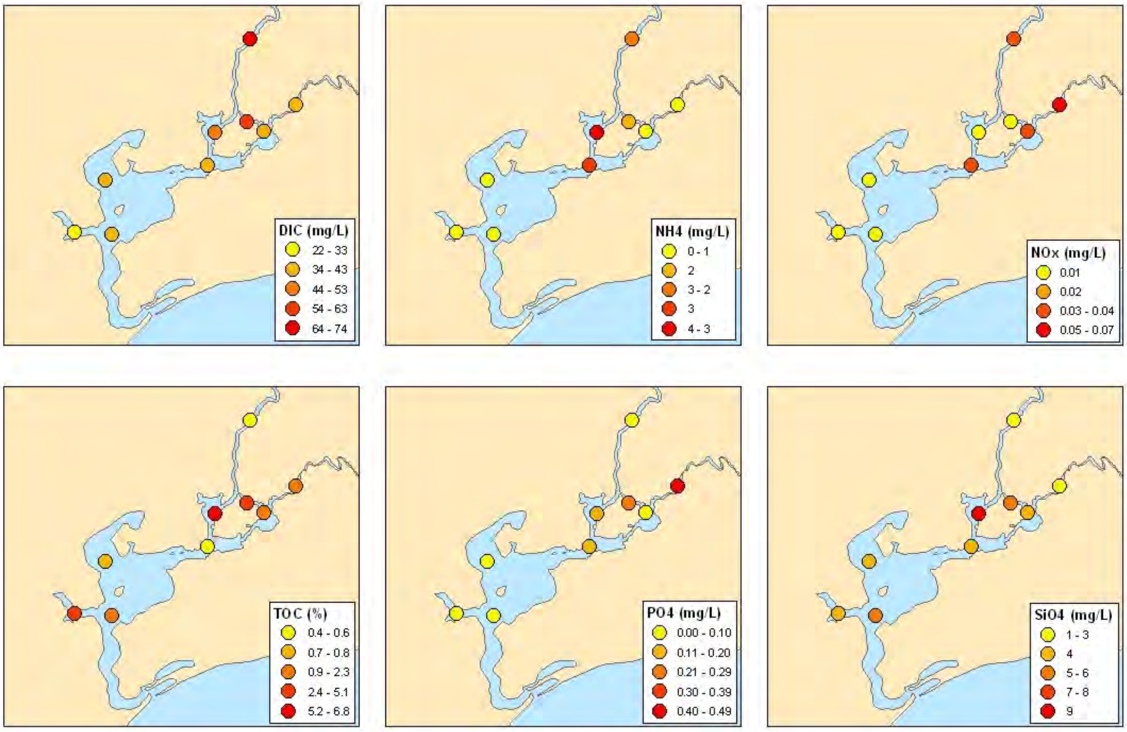

Figure 10: Surface sediment DIC, TOC and Nutrient (NH_4^+, NO_X, PO_4^{3-} and SiO_4^{4-}) concentrations in Hardy Inlet, September 2007.

Porewater depth profiles

The downcore porewater profiles of dissolved nutrients are shown in Figure 11. The NH_4^+ profiles were similar for all sites except HD5, which showed NH_4^+ concentrations throughout the profile to be considerably greater than at other sites. The deeper sediments at HD5 also recorded the only notable concentration of PO_4^{3-} (up to 0.52 mg/L). NO_X concentrations were generally below 0.03 mg/L throughout all the profiles apart from some high concentrations in the surface sediments at HD6 and HD9 (0.17 mg/L and 0.10 mg/L respectively). SiO_4^{4-} concentrations increased with depth most sites reflecting the dissolution of diatom frustules. The highest SiO_4^{4-} concentrations were also measured at HD5 (11 mg/L).

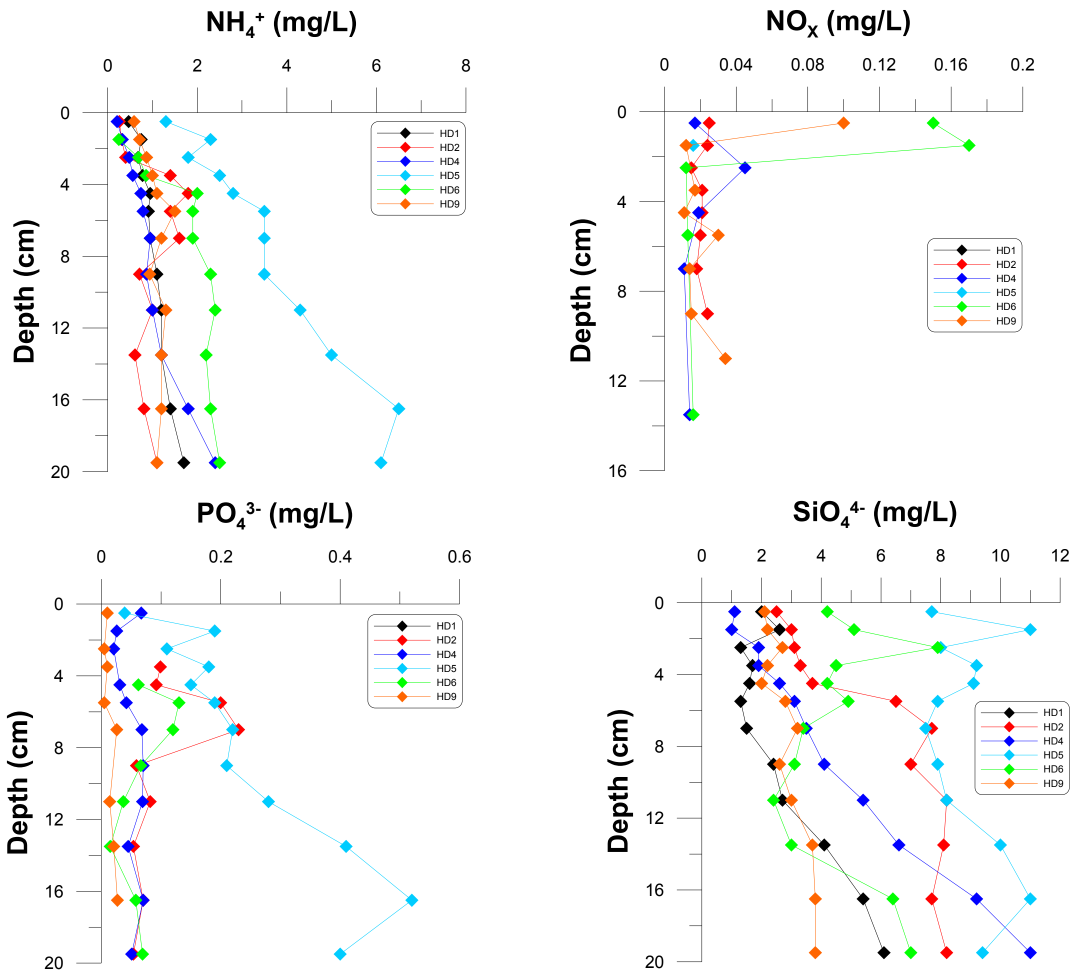

Figure 11: Down core porewater profiles of NH_4^+, NO_X, PO_4^{3-} and SiO_4^{4-} from Hardy Inlet sites, September 2007.

3B. APRIL 2008 SURVEY

3B1. Water quality

Figure 12 shows the interpolated data of the difference between surface and bottom water dissolved oxygen and salinity across 28 sites in Hardy Inlet. The lower Blackwood River, Scott River and West Arm are the main areas of stratification for both salinity and dissolved oxygen. The grey areas in the dissolved oxygen plot show where oxygen concentrations were higher in the bottom waters compared to the surface waters suggesting high rates of benthic photosynthesis and primary production.

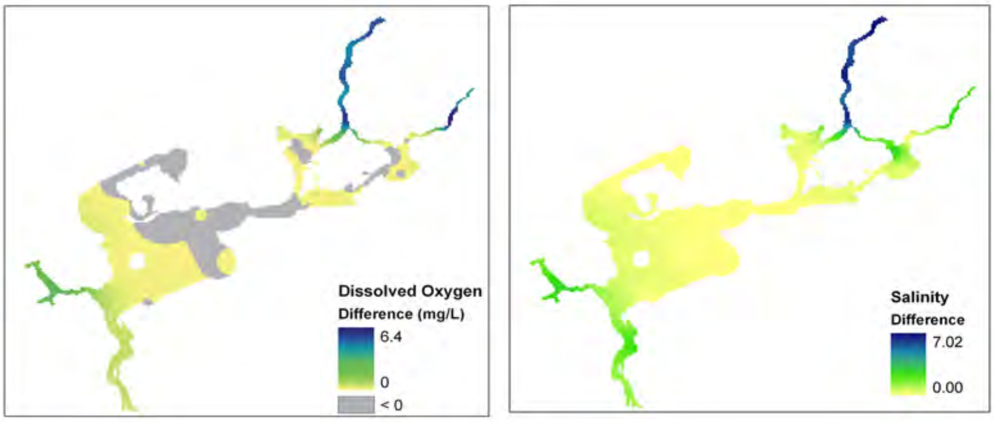

Figure 12: Interpolated data showing the difference between bottom water and surface water dissolved oxygen and salinity in Hardy Inlet, April 2008.

Figure 13 shows the surface and bottom water nutrient concentrations at selected sites in Hardy Inlet. NH_4^+ concentrations were generally around 0.02 mg/L in the surface and bottom waters except for the bottom waters of HD1 and HD9 which had concentrations of 0.70 and 0.41 mg/L respectively. The ANZECC trigger value for NH_4^+ in South-west Australian estuaries is 0.04 mg/L (ANZECC, 2000)

Measurable NO_X concentrations were very low (<0.014 mg/L). PO_4^{3-} was only detected in the bottom waters of HD1 and HD5 where concentrations exceeded the ANZECC trigger value of 0.005 mg/L (0.013 mg/L and 0.007 mg/L respectively). SiO_4^{4-} concentrations were higher in the bottom waters compared to surface waters at all sites. HD1 had the highest bottom water concentration of 0.478 mg/L.

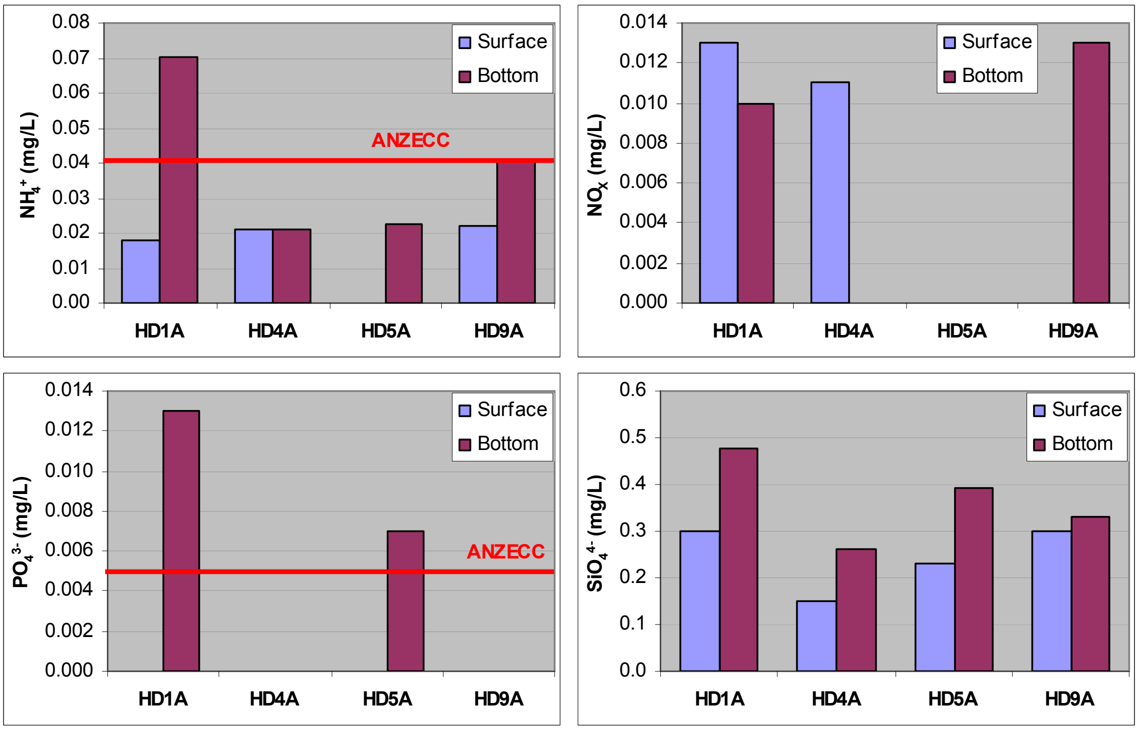

Figure 13: Bottom and surface water nutrient concentrations in Hardy Inlet. The red line represents the ANZECC Trigger Values for South-west Australian estuaries.

3B2. Sediment quality

Porosity in Surface Sediments

Figure 14 shows the interpolated porosity data from Hardy Inlet. The porosity values were obtained from surface sediments collected at 35 sites within Hardy Inlet during the September 2007 and April 2008 surveys. The main basin of the Inlet is shallow and sandy, while muddy sediments are predominant in the West Arm and in the upper mixing zone (Molloy Island, Blackwood River and Scott River). The upper reaches of the Blackwood and Scott Rivers also contain sandier sediments.

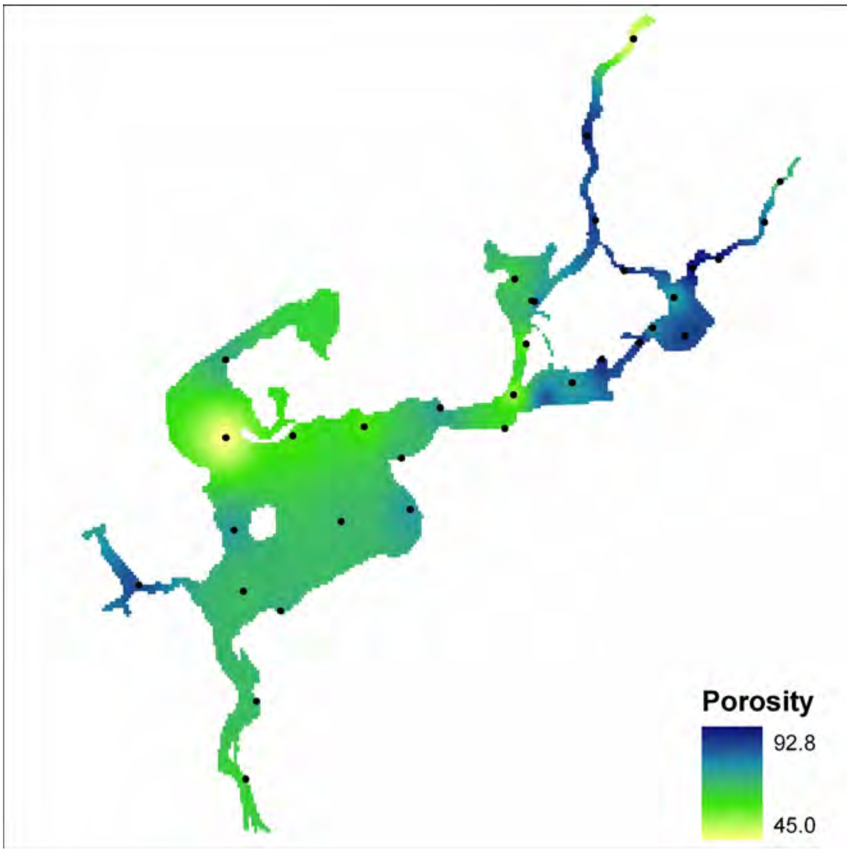

Figure 14: Interpolated porosity data and sampling sites (black dots) in Hardy Inlet.

This porosity distribution reflects sediment- and hydrodynamic conditions in the basin. The central basin south of Molloy Island is shallow (Congdon and McComb, 1979) and well exposed to wind leading to continues resuspension of fine sediments. In contrast, sediments near the entrance of the two major rivers are likely to become episodically scoured through river discharge events and then filled with fine sediments again. This is also documented through the sediment record of HD5 in the northwest of Molloy Island where muddy surface sediments are underlain by sandy sediments.

TOC, $\delta^{13}C$ and $\delta^{15}N$ in surface sediments

TOC concentrations vary between 0.3 and 11.4 wt.% and can be described as a power-function of porosity (Figure 15). Highest TOC concentrations are associated with muds and lowest TOC concentration are associated with sands. The highest TOC concentrations (11.4 wt%) were found at sites HD11 and HD12 where the Scott River converges with Hardy Inlet. High TOC concentrations were also found at the Blackwood River channel sites HD17 and HD18 and in the channel northwest of Molloy Island (HD5). In the main basin south of Molloy Island TOC concentrations are generally very low except for site HD1 in West Arm (Figure 16). All samples from a water depth less than 1.5 m had an average TOC concentration of 1.5 wt.%.

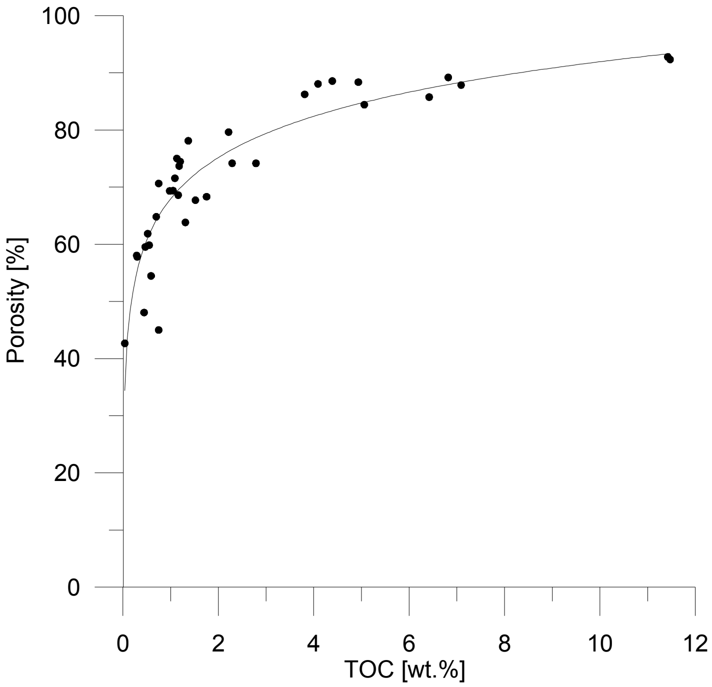

Figure 15: Correlation between total organic carbon concentration (TOC) and porosity.

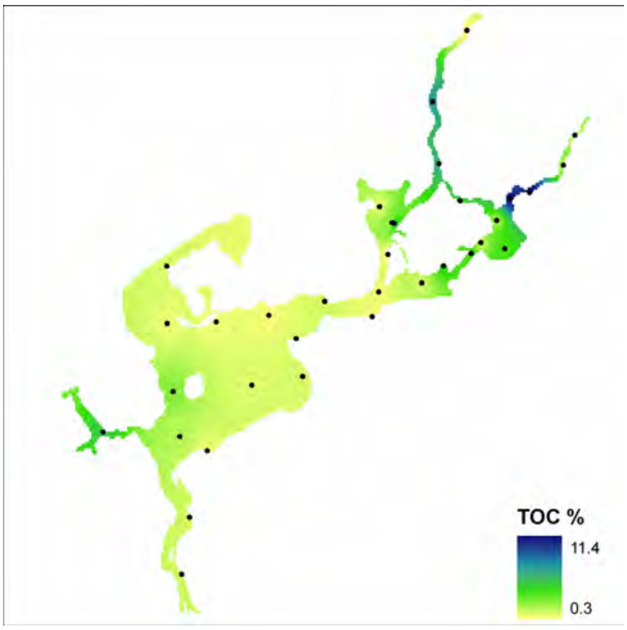

Figure 16: Interpolated total organic carbon concentration data and sampling sites (black dots) in Hardy Inlet.

The stable isotopic composition of organic carbon ($\delta^{13}C$) varies between -27.6 and -20.0 ‰. More positive values are consistently found in the seawater zone, whereas intermediate values are found in the mixing zone and the most negative values are found in the in channel sediments of the Scott and the Blackwood rivers (Figure 17).

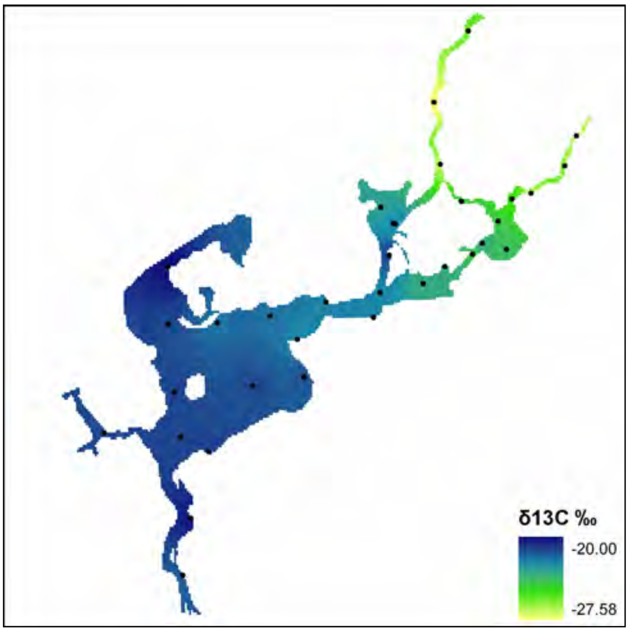

Figure 17: Interpolated stable isotopic composition of organic carbon ($\delta^{13}C$) and sampling sites (black dots) in Hardy Inlet.

The stable isotopic composition of total nitrogen ($\delta^{15}N$) varies between 1.6 and 5.9 ‰. The most negative values (< 2 ‰) are found in channel sediments of Scott River and in the area where the Scott River enters Hardy Inlet. Intermediate $\delta^{15}N$ values are found in the seawater zone, whereas the most positive values are found in the mixing zone and in channel sediments of the Blackwood River (Figure 18).

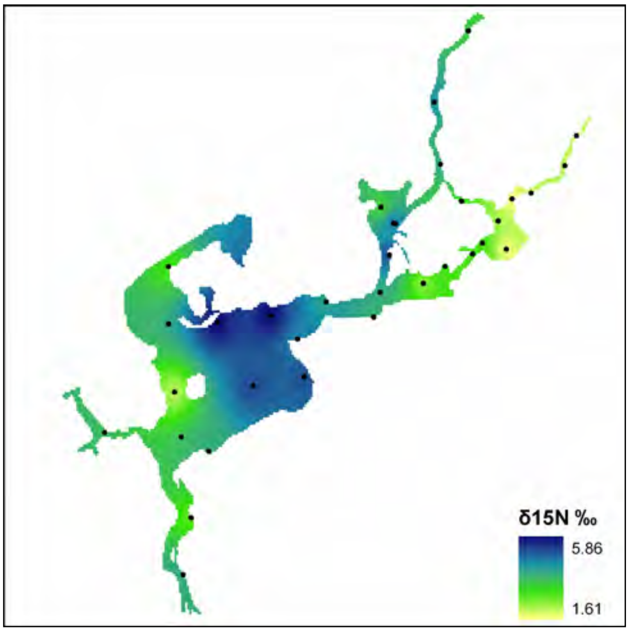

Figure 18: Interpolated stable isotopic composition of total nitrogen ($\delta^{15}N$) and sampling sites (black dots) in Hardy Inlet.

Benthic nutrient fluxes

Benthic fluxes are listed in Appendix 5 and the average light and dark benthic fluxes are shown in Figure 19. Positive fluxes indicate a release or production whereas a negative flux indicates an uptake or consumption. Oxygen is consumed and DIC produced during respiration and, vice versa, oxygen is produced and DIC consumed during photosynthesis. Photosynthesis was only evident in the light chambers at HD4 and HD5a with O_2 production rates of up to 69.2 mmol m^{-2} d^{-1} and 112.6 mmol m^{-2} d^{-1} in individual benthic chambers, respectively. HD1 and HD9 had the highest respiration rates as shown by DIC fluxes of up to 120 mmol m^{-2} d^{-1} and 200 mmol m^{-2} d^{-1} in individual benthic chambers, respectively.

The NH_4^+ fluxes were very small at HD4 and HD5a with all fluxes less than 0.2 mmol m^{-2} d^{-1}. NH_4^+ fluxes reached 6.47 mmol m^{-2} d^{-1} at HD1 and 3.98 mmol m^{-2} d^{-1} at HD9. Apart from HD9, all N_2 fluxes were negative, indicating an uptake of N_2. This is usually attributed to nitrogen fixation. N_2 uptake in the light chambers is not considered here due to the possibility of O_2 bubbles stripping the N_2 out of solution and creating a potentially false negative value. N_2 uptake rates in the dark chambers were significant with fluxes of -4.04 mmol m^{-2} d^{-1}, -3.69 mmol m^{-2} d^{-1} and -2.88 mmol m^{-2} d^{-1} recorded at HD1, HD4 and HD5a respectively.

PO_4^{3-} fluxes were either very low or below detection limits at all sites. The only measurable PO_4^{3-} fluxes were found in the dark chambers and ranged from 0.04 mmol m^{-2} day^{-1} at HD9 to -0.07 mmol m^{-2} day^{-1} at HD1. SiO_4^{4-} fluxes were positive at HD1 and HD9 and negative at HD4 and HD5a. SiO_4^{4-} fluxes ranged from 11.91 mmol m^{-2} d^{-1} at HD1 to -3.33 mmol m^{-2} d^{-1} at HD4.

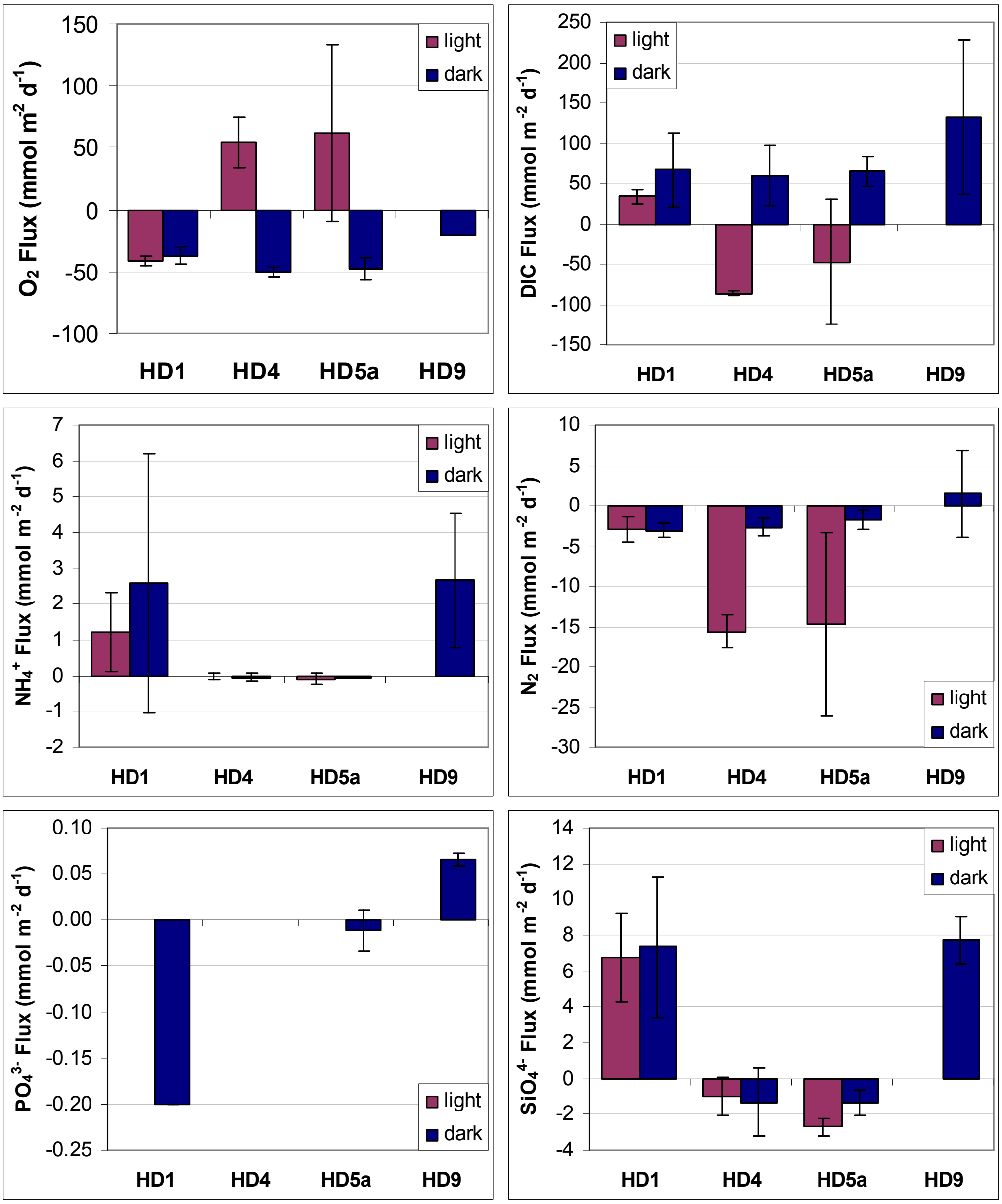

Figure 19: Average light (purple) and dark (blue) benthic fluxes from sites within Hardy Inlet (Note: no light chambers at HD9). Error bars represent standard deviation.

3B3. Sediment cores for paleo-environmental reconstruction

Core HD34A showed an abrupt increase in dry bulk density between 26 and 22 cm sediment depth (Figure 20) suggesting a distinct change in lithology from fine (muddy) to coarse (sandy) sediment at this depth. Above this interval, dry bulk density gradually declined towards the top, i.e. the grain size is becoming finer. In parallel with the abrupt change in dry bulk density, the total number of spores and pollen declined rapidly between 26 and 22 cm sediment depth and remained very low to the sediment top.

The chemical composition of core HD34B revealed an abrupt change from an aluminium-dominated lower section to an silica-dominated upper section between 42 and 32 cm sediment depth. Aluminium-rich sections typically suggest high abundance of clay minerals and fine sediments, while silica-dominated sediments are typically rich in medium to coarse-grained minerals such as quartz and feldspar. Given the prominent and abrupt increase in grain size in cores HD34A and HD34B this marker depth was assumed to correlate and represent the same age of formation, which will be discussed in section 4C.

Very similar $^{210}Pb_{excess}$ activity in the top 6 cm suggested intensive mixing most likely by bioturbation. $^{210}Pb_{excess}$ and ^{137}Cs activity were relatively low in the sediment surface indicating low topsoil inputs to the estuary. $^{210}Pb_{excess}$ decreases linearly between the mixed top layer (0 to 6 cm depth) and a depth of 12 cm. This was also where the deepest detectable ^{137}Cs activity was found (data not shown). ^{137}Cs was introduced to the global environment through nuclear bomb tests during the early 1950. Therefore, the sediment at a depth of 12 cm was presumably deposited at about 1955. By using the half life of ^{210}Pb of 22.3 years, an average sedimentation rate of 0.11 cm y^{-1} was calculated for the depth interval between 6 and 12 cm. This was considered to be the upper limit as bioturbation could extend into this depth interval.

The bottom of core HD34B (79 to 82 cm sediment depth) was dated by OSL and revealed an age of 3,470 ± 500 years.

Pinaceae, *Asteraceae* (including *Liguliflorae* (dandelions) and high spine types) and other probable exotic pollen were found most consistently and abundantly to a depth of 13 cm in core HD34A (MacPhail 2008), which is believed to represent the time after WWI, i.e. the period between approximately 1920 to present. Fossil pollen of the seagrass *Ruppia* were found throughout the core, but the abundance only became frequent (≥ 1% of all spores and pollen) in the top 9 cm. Similarly, the relative abundance of *Leptospermoidae*, a taxon that is presumed to be dominated by riparian paperbarks (*Melaleuca spp.*) and *Casuarinaceae*, were significantly enriched in surface sediments to a depth of 26 cm. These species are typical for low open forest on sand-gravel colluvium.

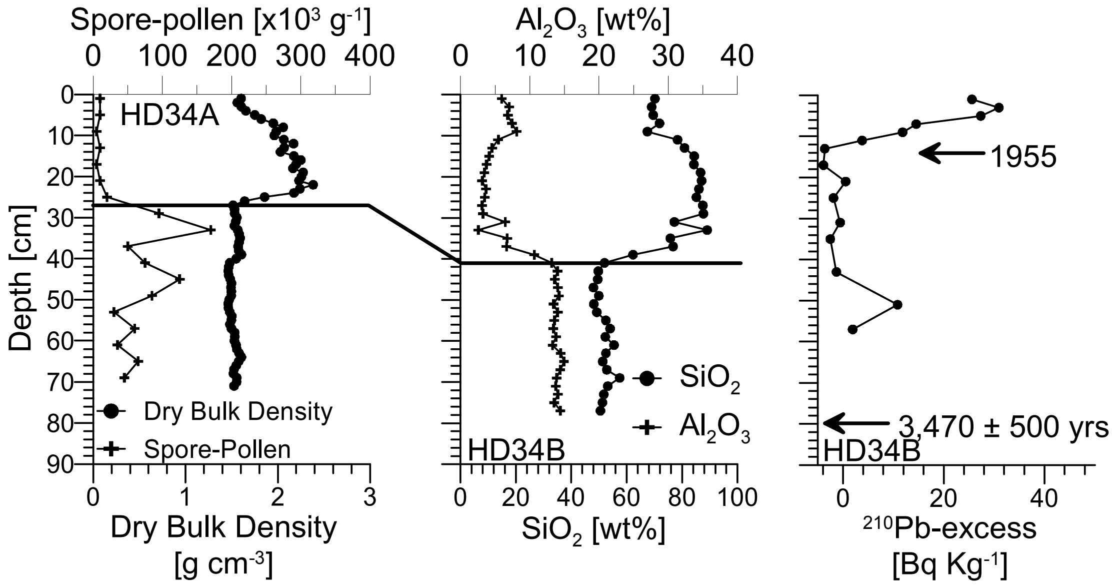

Figure 20: Depth profiles of dry bulk density, total numbers of spores and pollen, the chemical composition (Al_2O_3, SiO_2) and excess ^{210}Pb activity in cores HD34A and B.

4. Discussion

4A. SPATIAL VARIABILITY OF PORE WATER NUTRIENT POOL SIZES AND NUTRIENT RELEASE FROM SEDIMENTS

Porewater nutrient pool sizes (Figure 21) are calculated from the porewater nutrient concentrations in the top 20 cm of the sediment cores and they give an indication of the storage of dissolved nutrients in surface sediments. Site HD5 is located within the channel west of Molloy Island and stands out as having the greatest NH_4^+, PO_4^{3-} and SiO_4^{4-} pool sizes with 56.9 mmol m-2, 1.8 mmol m-2 and 60.5 mmol m-2, respectively. The pore water nutrient pool sizes at HD5 are 2 – 7.2 times the pool sizes at other sites. HD5 was also the deepest site (7 m) and had the highest porosity (89%) and TOC concentration (6.8 wt%) among all sites where pore water pool sizes were calculated. This could suggest that the site has recently served as a depositional site for organic matter rich, fine sediments, leading to the high rates of organic matter decomposition and sediment nutrient concentrations recorded in the pore waters. Due to depth, this site is periodically exposed to hypoxic and anoxic conditions in the bottom waters (Figure 7), There is also evidence of a scouring event given the observation, that sandy sediment was found at HD5 in April 2008, while it was very muddy in September 2007 (see above). Most likely, periods of hypoxic and anoxic bottom water conditions and scouring prevent the establishment of benthic fauna. Benthic fauna have been shown to significantly contribute to the depletion of nutrients from the sediment pore water pool through bioirrigation (Foster et al. 1999), i.e. pore water nutrient pool sizes become particularly large where organic matter rich sediments accumulate and benthic fauna is poorly established or absent.

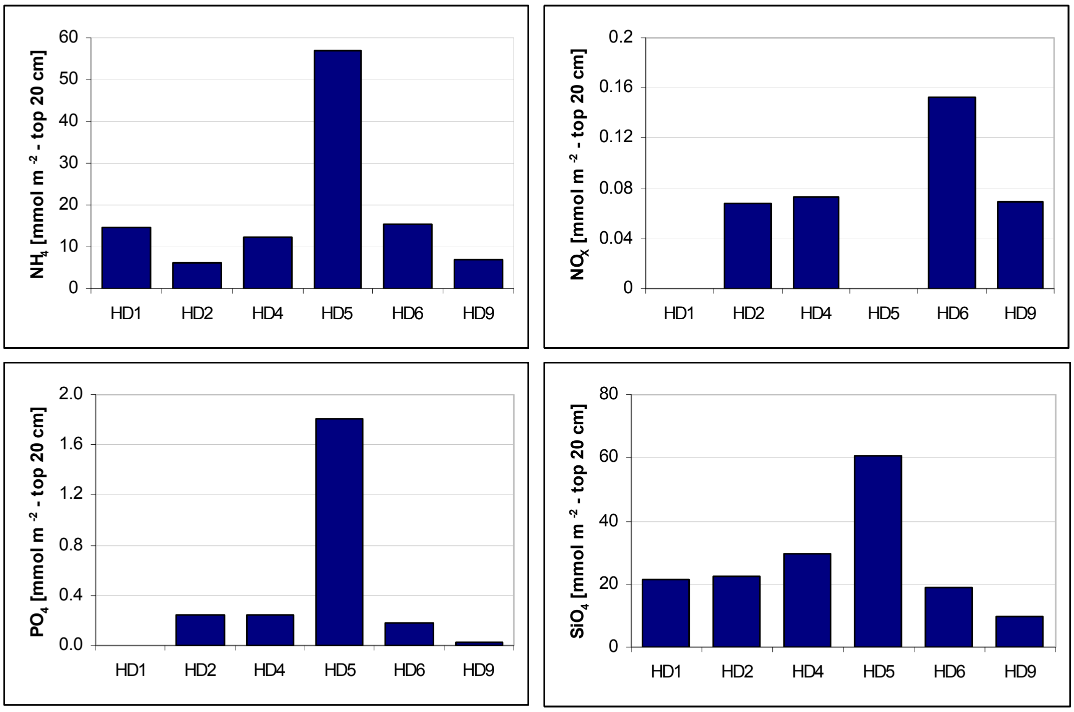

Figure 21: Nutrient pool sizes in the surface (top 20 cm) sediments of Hardy Inlet

Net benthic fluxes were derived from combining the light and dark fluxes into a single 24-hour flux. As conditions can change considerably between night and day, particularly light conditions at shallow sites, the net fluxes are a good representation for nutrient and gas transport across the sediment-water interface over one to several days. The oxygen and DIC net fluxes from Hardy Inlet (Figure 22) show clearly the difference between the two shallow sandy sites HD4 (0.4 m water depth, 74% porosity) and HD5a (0.5 m water depth, 58% porosity) compared to the muddy shallow site HD1 in West Arm (1.2 m water depth, 85% porosity) and the deep sandy site HD9 in the Blackwood River channel (6.5 m water depth, 48% porosity). HD4 and HD5a are net photosynthetic, i.e. more O_2 is produced and DIC is consumed in the light than it is consumed in the dark. In contrast, HD1 and HD9 are net respiratory, i.e. sediment oxygen demand is higher than oxygen production and net DIC fluxes are positive over 24-hours. The West Arm site HD1 appears to be a turbid, depositional site for fine, organic matter rich sediment. Insufficient light reaches the sediment surface which is likely related to high turbidity caused by resuspension and may account for the absence of significant benthic photosynthesis during day time. The deep Blackwood River channel site HD9 appears to be affected by scouring. Sediment data in 2007 recorded muddy sediments at HD9, while the most recent survey in 2008 recorded sandy sediments with low organic matter content (0.45 wt.%TOC).

Given the sandy, organic matter poor sediments it was surprising to note the highest net DIC, NH_4^+, PO_4^{3-} and SiO_4^{4-} fluxes at the deep Blackwood River site (HD9) (see above). This may be indicative of an aquifer releasing metabolites from organic matter decomposition into the estuary.

The shallow sites HD1, HD4 and HD5a show net N_2 uptake, indicating nitrogen fixation is occurring at these sites. Nitrogen fixation is the conversion of di-nitrogen gas (N_2) into a biologically available form of nitrogen (NH_4^+) and is an additional pool of nitrogen to a system. Nitrogen fixation in Hardy Inlet is possibly associated with the rhizosphere of seagrass or epiphytic microalgae attached to the seagrass leaves, and is therefore presumably restricted to the shallow areas where seagrass is growing. HD9 was the only site that recorded a net N_2 release. Again, this may be related to the possible aquifer intersection (see above).

By combining the information on pore water pool sizes, benthic fluxes, porosities and TOC concentrations it becomes clear that sediments at shallow sites (< 1.5 m water depth) are typically coarse grained (silt to sand) and depleted in organic matter, and that their pore water nutrient pool sizes and benthic fluxes are small. Given the wide distribution of shallow, coarse grained sediment throughout the main basin of Hardy Inlet (> 90 % is shallower than 1 m) nutrient release from sediments in these shallow parts of the basin is considered of minor importance compared to other estuaries with a deeper basin, e.g. St. Georges Basin in NSW (Haese et al. 2007) and Wilson Inlet in WA (Haese and Pronk submitted).

Areas of particular interest in Hardy Inlet include the deeper sections in the channels around Molloy Island (> 6 m water depth) and the lower Blackwood River. Firstly, deep channel areas experience temporal stratification and hypoxic to anoxic bottom water conditions and episodic scouring during high flow events prevent the establishment of benthic fauna. As a consequence, these areas build up large porewater nutrient pools during periods of fine sediment accumulation, which are eventually released into the water column of the estuary. Secondly, exceptionally high release of DIC and nutrients from sandy sediments with little organic matter suggest a possible nutrient source from an aquifer intersecting the estuary in the lower reaches of the Blackwood River.

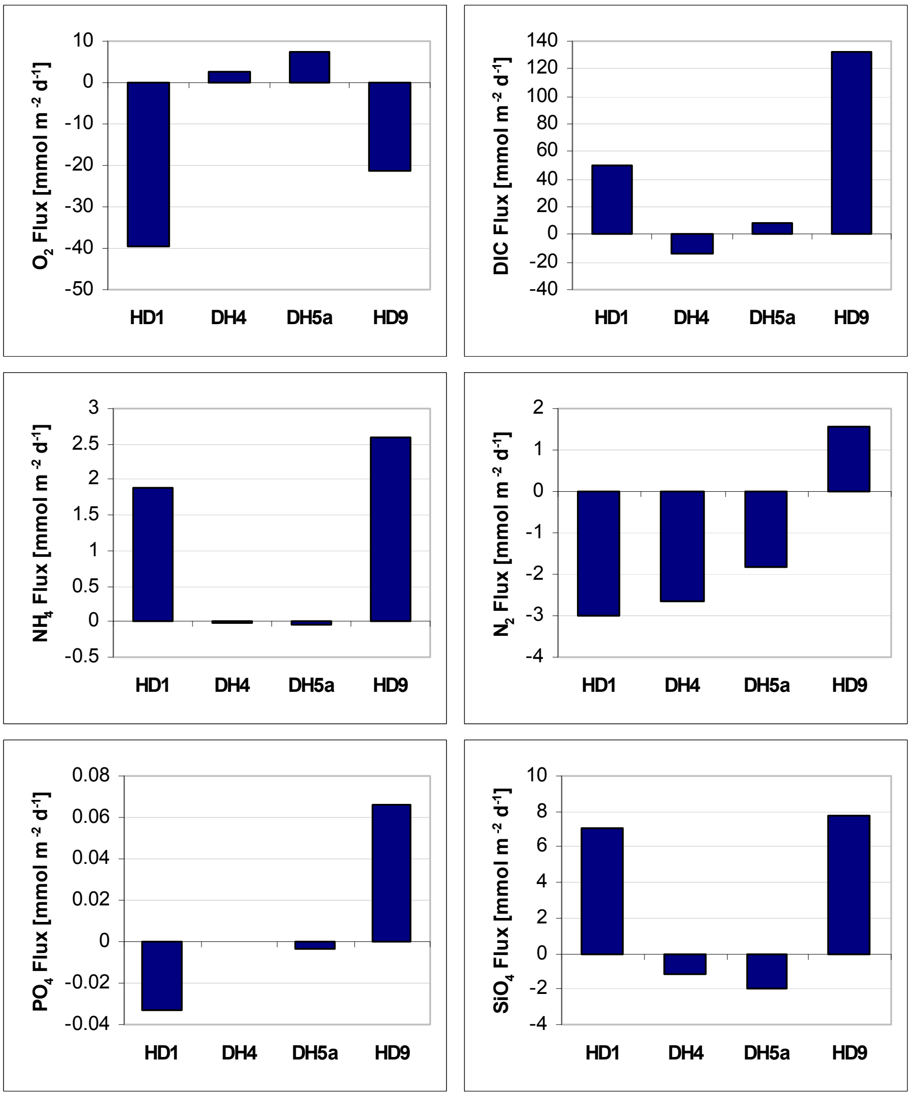

Figure 22: Net benthic fluxes from Hardy Inlet, April 2008
(Note: only dark fluxes used for N_2 flux)

4B. SPATIAL DISTRIBUTION OF SEDIMENT TYPES

Surface sediment types are characterised by their physical (porosity) and chemical properties (TOC, $\delta^{13}C$, $\delta^{15}N$). The main basin south of Molloy Island is very shallow, i.e. the water depth is less than 1 m except along the channel connecting the upper Inlet with the opening to the ocean. In this shallow environment only coarse sediment is permanently deposited, because wind-driven wave energy keeps fine sediments in suspension. The coarse sediment is very poor in TOC with an average concentration of 1.5 wt.%. In contrast, deep channel sediments can be very fine and rich in TOC, e.g. in the lower Scott River sediment porosity is about 90% and the TOC concentration is greater than 10 wt.%. The transition areas between river channels and the shallow, open basin west and east of Molloy Island form an intermediate sediment type. Properties of sediments of the transition areas and channels are temporarily highly variable as they experience sediment erosion and deposition related to highly variable river flow and sediment discharge. This makes the selection of suitable sites for the collection of cores with fine, undisturbed sediments for the reconstruction of paleo-environmental conditions particularly difficult.

The stable isotopic composition of organic carbon ($\delta^{13}C$) is sometimes used to show the mixing of two sources of organic matter, terrestrial and marine derived biomass. Soil, terrestrial woody and freshwater phytoplankton biomass typically has a $\delta^{13}C$ composition in the range from -24 to -29 ‰, whereas $\delta^{13}C$ of estuarine-marine phytoplankton and microphytobenthos biomass is in the range from -19 to -24 ‰ (Cloern et al. 2002). The mixing of marine and terrestrial derived organic matter is well reflected in the distribution of $\delta^{13}C$. The seawater zone is characterised by values between -20 and -22, whereas river channel sediments have $\delta^{13}C$ values between -25 and -27.6 ‰. This distribution gives evidence that catchment-derived fine sediments and associated organic matter are not deposited in the main basin of the Inlet, but are likely flushed out to the ocean during river run-off events.

The stable isotopic composition of total nitrogen ($\delta^{15}N$) can be an indicator for the presence of organic matter formed by nitrogen-fixing organisms. According to Cloern et al. (2002) estuarine-marine and terrestrial biomass without biomass from nitrogen-fixing organisms have typically $\delta^{15}N$ values ranging from 6 to 9 and 3 and 6.6 ‰, respectively. In contrast, nitrogen-fixing cyanophytes have $\delta^{15}N$ values less than -1 ‰. The Scott River channel sediment and the area where the Scott River enters the Inlet have $\delta^{15}N$ values less than 2 ‰ suggesting biomass from nitrogen-fixing organisms is contributing to total biomass. This could be detrital biomass from the catchment or biomass formed in the lower reaches of the Scott River and the adjacent Inlet area. The latter possibility is likely as toxic algal (cyanophyte) blooms have been observed in the lower Scott River and northeast of Molloy Island. The Scott River is known for its high phosphorous loads and low nitrogen-to-phosphorous ratio in the river water providing suitable conditions for blooms by nitrogen fixing algae.

4C. SEDIMENT-BASED CONDITION INDICATORS

A range of sediment-based condition indicators are currently considered nationwide and further research is currently underway to identify the most robust parameters to consistently assess and monitor estuarine condition. In this study, the following parameters are assessed and discussed as indicators:

- Organic matter decomposition rate and oxygen consumption / production measured as benthic DIC and O_2 fluxes, respectively
- Sediment porosity and TOC concentration in surface sediments
- Denitrification
- Phosphorous binding capacity

Given the important role of sediments as a site of organic matter accumulation and decomposition in basin-shaped estuaries benthic nutrient (mainly NH_4^+, PO_4^{3-}, SiO_4^{4-}) and gas (DIC, O_2, N_2) fluxes have been recognised as sensible indicators for the carbon loading and nutrient status ("eutrophication") in Australia since the Port Phillip Bay study (Harris et al. 1996).

The benthic DIC flux under dark conditions is a measure of the rate of organic matter decomposition and appears to be a robust indicator of estuarine condition. This particular variable is not affected by secondary processes. It is an accurate measure for **the rate of organic matter decomposition** in sediments, which reflects quantitatively the deposition of labile organic matter to the sediment (Haese et al. 2007) with little seasonal variability (Haese and Pronk submitted). Average dark DIC fluxes at shallow sites in Hardy Inlet (< 1.5 m water depth) are between 60 to 70 mmol m-2 d-1 (Figure 19), which is similar to DIC fluxes measured in Wilson Inlet under dark conditions at shallow to intermediate water depths. It is important to note that the highest dark benthic DIC fluxes were measured at the deep channel site HD9, where sandy, organic matter poor sediments were found. This unusual observation is leading to the hypothesis that an aquifer enriched in metabolites from organic matter decomposition intersects and releases these metabolites into the estuary here.

Differences in **sediment oxygen consumption and production** is less useful as an indicator of estuarine condition. Usually observed at shallow sites under dark and *in situ* light conditions, respectively, sediment oxygen consumption and production is a measure for benthic photosynthesis which can be converted into a measure of benthic primary production. When light and dark benthic oxygen fluxes are combined to calculate net 24-hours fluxes net sediment oxygen demand is often found for deeper sites. The degree of net oxygen demand can be seen as a measure for potential bottom water anoxia, particularly when the water column is poorly mixed and may become stratified. The two shallow sites with much light penetration to the sediment surface, HD4 and HD5a, show large differences (~100 mmol m-2 d-1) between light and dark oxygen fluxes suggesting high benthic photosynthesis and primary production. In contrast, HD1 in West Arm is only insignificantly deeper, but the difference between light and dark oxygen fluxes is negligible, which is attributed to the turbid water conditions. Perhaps the biggest limitation of this approach is the dependence of benthic photosynthesis by the availability of light. Variable degrees of cloud cover immediately affect benthic photosynthesis, which leads to bias when sites are compared and these sites were measured under different light conditions. Consequently, the measurement of benthic oxygen production and consumption represents a snapshot in time and much depends on the prevailing water turbidity and solar radiation conditions. Oxygen is utilised in the sediment not only for the decomposition of organic matter (aerobic respiration), but also for the oxidation of reduced species such as sulphide and ferrous iron. When organic matter loading increases the supply of oxygen to the sediment becomes insufficient and anaerobic parthways, particularly sulfate reduction, become the dominant way of organic matter decomposition. Consequently, the proportion of oxygen consumption due to bacterial respiration decreases and the proportion of anoxic decomposition of organic matter increases as can be seen for site HD9 (Figure 23).

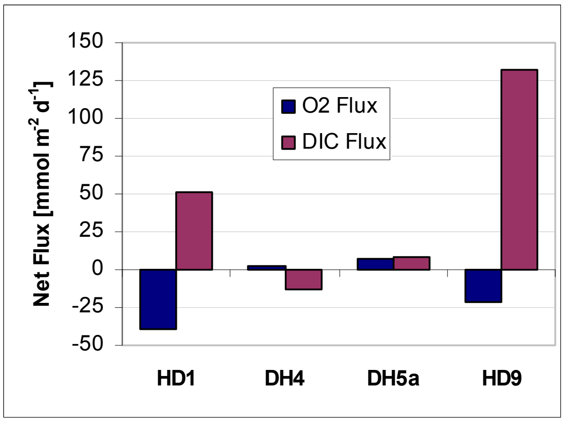

Figure 23: Net O_2 and DIC fluxes from Hardy Inlet, April 2008

Sediment porosity and TOC concentration cannot be used as a surrogate indicator for sediment reactivity. If the quality and thus the reactivity of organic matter would always be the same, then we would expect a correlation between TOC concentration and the rate of organic matter decomposition measured as benthic DIC flux under dark conditions. This is, however, not the case. Benthic DIC fluxes under dark conditions are very similar between sites HD1, HD4 and HD5a (Figure 19) even though porosities and TOC concentrations range from 59 to 84% and between 0.3 to 5.0 wt%, respectively.

Sediment porosity and TOC themselves correlate over a large range of sediment types, i.e. from sandy to muddy sediments (Figure 15). This can be explained with the attachment of organic matter onto the surface of grains leading to a higher TOC concentration in sediments with a higher specific surface area per volume, which are fine-grained sediments.

The phosphorous binding capacity is a measure for the release of phosphorous from sediments, which overall, is a reliable measure for the capacity of sediments to retain and bury phosphorous. Only three out of the 16 benthic chamber deployment experiments showed measurable benthic phosphorous fluxes. This results gives evidence for very effective retention of phosphorous in sediments. The one negative flux was found at HD1 and suggests a very high uptake rate, which is very unusual and remains unexplained. Positive phosphorous fluxes were measured at HD9 (Figure 24) and suggest moderate phosphorous release. Phosphorous release at HD9 has two likely reasons: The sediment is very coarse-grained (sandy) and therefore the sediment is poor in iron oxides, which means the sediment does not have much capacity to adsorb phosphate. Secondly, other benthic fluxes at HD9 were also exceptionally high indicating possible groundwater discharge at this particularly deep site. Except for HD9 sediments in Hardy Inlet have a high capacity to retain phosphorous even though sediments are mostly sandy. This leads to undetectable phosphate concentrations and contributes to nutrient limitation for primary productivity in the water column.

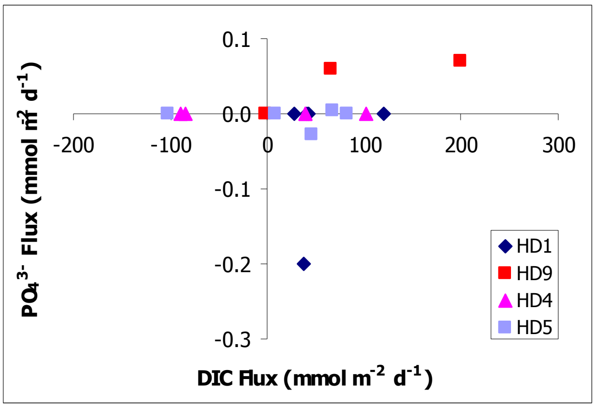

Figure 24: PO_4^{3-} versus DIC flux from benthic chambers deployed in Hardy Inlet

Denitrification efficiency is the percentage of nitrogen released from sediments as di-nitrogen gas relative to the sum of di-nitrogen gas and dissolved inorganic nitrogen. Denitrification efficiency has been proposed as a condition indicator (Berelson et al. 1998), because the microbial process of denitrification is the only pathway to remove bioavailable nitrogen from the system. Since then, denitrification has been implemented as a function of the organic matter decomposition rate in water quality models (Murray and Parslow 1997, Webster 2001) and, more recently, empirical correlations between the denitrification efficiency and the organic matter decomposition rate have been presented (Eyre et al. 2009). The latter study has shown that a very large deviation from the average of denitrification efficiency prevails across oligotrophic to hypertrophic conditions. For example, the average denitrification efficiency for mesotrophic conditions (50 – 100 mmol m^{-2} d^{-1}) is 40%, but individual observations range between 5 and 95% denitrification efficiency.

Given the large variability of denitrification efficiency observed in this study under the same trophic conditions and the unexplained nature of N2 uptake observed, we conclude that processes affecting denitrification efficiency are poorly understood and a poor predictor for the assessment of estuarine condition. N2 uptake rather than N2 release from sediments was observed under dark conditions at all sites except for HD9. This is indicative of nitrogen fixation, which means bioavailable nitrogen is added to the system. The denitrification efficiency at HD9 is less than 40%, which means that most of the nitrogen is released into the bottom water as ammonia at this site. The negative benthic fluxes observed at the shallow sites under dark conditions may be attributed to the presence of the seagrass Ruppia. It has been argued that biogeochemical processes by seagrass rhizomes create unfavourable conditions for coupled nitrification-denitrification (Risgaard-Petersen 2004) and favourable conditions for nitrogen fixation (Welsh 2000). The observed nitrogen fixation at shallow sites cannot be attributed to an artefact referred to ‘gas stripping’, which may occur when oxygen becomes supersaturated during the incubation due to benthic photosynthesis under light conditions.

4D. HISTORICAL CHANGES IN SEDIMENTATION RATE AND SEDIMENT COMPOSITION

The most prominent feature in the downcore profiles of total number of spores and pollen, dry bulk density representing grain size and bulk chemical composition is an abrupt change at 26 and 42 cm sediment depth in cores HD34A and AD34B, respectively. A pulse of sediment deposition from the catchment as observed in Stokes Inlet (Murray et al. 2008) can be ruled out as most sediment properties remain fairly constant and the linear $^{210}Pb_{excess}$ gradient in the upper section suggests quasi-continuous deposition in recent decades. Similarly, this unconformity could not be formed by a meandering channel, because the infilling of a channel frequently experiences deposition and erosion events, which is disproved by the linear decrease in $^{210}Pb_{excess}$ activity in surface sediments.

Instead, the rapid change to coarser sediment followed by a slight return to finer sediment is believed to be caused by the initial land clearance with much subsoil erosion and gradual re-establishment of a new vegetation cover including exotic plants *(Pinaceae, Asteraceae)* and plant groups thriving on sand-gravel colluvium *(Casuarinaceae)*. The low 210Pb and 137Cs activity at the sediment surface also suggests low inflow of top soil supporting poor conditions for soil formation in the catchment. The continuously low numbers of total spore and pollen in the upper sediment section also suggests much less pollen and spore production in the catchment than before the change.

Land clearance occurred during successive episodes starting in the late 1870's to 1913 with timber cutting and milling, which played a significant role in the area's economy and resource utilisation. Post World War I and II land development schemes were leading to further land clearing to help facilitate an expanding population (Hodgkin 1978). It is believed that the initial land clearing at about 1880 resulted in the abrupt change in estuarine sediment composition at a sediment depth of 26 and 42 cm in cores HD34A and HD34B, respectively.

Using the $^{210}Pb_{excess}$ profile between 6 and 12 cm and the 1955 marker at a depth of 12 cm leads to a calculated recent sedimentation rate of 0.11 cm y^{-1} in core HD34B. Assuming the unconformity at a depth of 42 cm was formed in 1880 and using the 1955 marker depth at 12 cm in core HD34B, an average sedimentation rate of 0.4 cm y^{-1} is calculated for the interval between 42 and 12 cm. Using the derived age of sediment at a depth of 80 cm of the core HD34B (4370 ± 500 years) and the derived age of the unconformity at a depth of 42 cm (128 years) an average sedimentation rate of 0.01 ± 0.02 cm y^{-1} is calculated for the period proceeding land clearing by European settlers.

The derived record of sedimentation rates at HD34 is very similar to two sedimentation records derived for Stokes Inlet (Murray et al. 2008): Firstly, all three records show about 10-times lower sedimentation rates during pre-European time compared to current sedimentation rates. Secondly, catchment erosion and sediment deposition in the estuary was particularly high during the initial phase of land clearing, i.e. sedimentation was 2 to 5 times higher in Stokes Inlet and about 4 times higher in Hardy Inlet compared to current sedimentation.

It remains speculative why seagrass pollen is most abundant in the top 9 cm, but the rapid infilling of the Hardy Inlet basin between 1880 and WWII has probably increased the shallow water area suitable for seagrass. In addition, the reduction in sediment loads after WWII has probably improved water clarity contributing to better growth conditions for seagrass.

5. Conclusion

Sediment analysis and benthic flux measurements have shown that the shallow areas in Hardy Inlet are typically characterised by coarse grain sediments that have low nutrient pools sizes and nutrient fluxes, and do not serve as a major source of nutrients. In contrast, deep channel sites with finer sediments were generally also rich in organic matter and had higher nutrient pools. Nutrient fluxes at these sitres were influenced by the bottom water oxygen status and the presence of benthic producers. One exception was the deep channel site in the lower Blackwood River which had high nutrient concentrations in the pore water and high benthic release rates of dissolved inorganic carbon and nutrients despite coarser sediment and little organic matter content. Groundwater discharge at the bottom of the deep channel may provide some explanation for this observation. Further investigation into the contribution of nutrients and metabolites from groundwater are recommended, in particular, along the western side of Molloy Island where nutrient enriched groundwater from residential and commercial developments on Molloy lsland and along the foreshore of the Blackwood River near the caravan park can be expected.

The rate of organic matter decomposition measured as benthic dissolved inorganic carbon flux under dark conditions has proven to be the most robust indicator for estuarine condition. It effectively measures the organic carbon loading to the sediment which has been proposed as a measure to group coastal water bodies into oligotrophic, mesotrophic and eutrophic. The phosphorous retention capacity of sediments measured as the benthic phosphate flux is also a useful indicator and clearly identifies sites where sediment serves as a major source of phosphorous. Other tested indicators such as total organic carbon concentration , rate of benthic photosynthesis and denitrification efficiency are less reliable for a range of reasons.

The site selection for extracting a long core for paleo-environmental reconstruction studies was difficult, because deep (channel) sites become frequently scoured during high flow periods and shallow sites are too much exposed to wave action so that fine sediments do not settle. The chosen site for paleo-studies south of Molloy Island, however, showed continuous deposition of fine sediments judging by radionuclides depth profiles. A high resolution sediment age record was derived revealing an abrupt and major increase in sedimentation rate during the initial phase of European land clearance at the beginning of the 20th century. Pre-European sedimentation rate was about 0.01 cm y^{-1}, which changed to about 0.4 cm y^{-1} with the land clearance. The catchment-derived sediment composition also changed from a fine, clay mineral rich sediment to a coarse, quartz and feldspar rich sediment documenting the deep erosion of soil once the native vegetation is cleared. With the establishment of a new vegetation cover the sedimentation rates have decreased and the sediments have become finer again during the last century, but conditions have not yet returned to pre-European times, e.g. the current sedimentation rate is still 4 times higher than during pre-European times.

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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 1A).

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 method

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 1A. Limits of reporting (and associated measurement uncertainty to 95 % confidence intervals) as stated 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 δ^{13}C-OM and δ^{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, δ^{13}C-OM, and δ^{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.

A1E. SEDIMENT DATING

Gamma-ray spectrometry was used to measure the activity of natural and man-made radioisotopes ^{210}Pb and ^{137}Cs respectively. With the appropriate validation using chronological markers, ^{210}Pb geochronology is a well established technique for dating recent sediments (Robbins 1978) because the short half life of ^{210}Pb (22.3 years) provides high temporal resolution. ^{137}Cs is a useful chronological marker since it was introduced to the global environment in the early 1950's with the beginning of nuclear bomb testing. The total ^{210}Pb gamma radiation results from the sum of ^{210}Pb deposition with the settling sediment plus the in situ formation of ^{210}Pb through the decay of U decay products. Therefore, ^{210}Pb excess ($^{210}Pb_{exc}$) was determined by subtracting the in situ ^{210}Pb formation, estimated from its parent ^{226}Ra, from the total decay rate. For older sediments, i.e. for samples from the bottom of each core, sediment ages were derived from the optically stimulated luminescence (OSL) of individual quartz grains as described by Olley and colleagues (2004).

The data quality from gamma-ray spectrometry and OSL dating was generally very good with a typical standard error of < 5 and < 0.4 Bq kg^{-1} for $^{210}Pb_{exc}$ and ^{137}Cs, respectively, and with a standard deviation of < 15 % for OSL ages.

The deepest sample in each core with a ^{137}Cs activity exceeding the standard error (0.4 dpm g^{-1}) was taken as a marker for the beginning of nuclear testing in the year 1955.

A1F. POLLEN AND SPORE SAMPLE PREPARATION AND ANALYSIS

A tablet containing known numbers of *Lycopodium clavatum* spores (Stockmarr 1971) was added to approximately 15 g of wet sediment sample. The sample was pre-treated with 15vol.% HCl before the standard chemical processes using hydrofluoric acid digestion followed by acetolysis was applied (e.g. Eshet and Hoek 1996). Spores and pollen were extracted from residual sediment by heavy liquid separation using sodium polytungsten. Floating residue was mounted on slides using polyvinyl alcohol. Pollen magnification using bright field light microscopy typically allowed identification to genus or family level. In cases where only one species of parent plant occurs within the pollen source area, identification at species level was possible. Pollen and spores were identified using a comprehensive modern pollen herbarium prepared by Mike McPhail.

Relative abundances of pollen and spores are expressed as a percentage of the total dryland pollen and spore count. The latter excludes pollen produced by aquatic angiosperms and spores produced by hornworts, liverworts, and fungi, as well as reworked Cretaceous and tertiary pollen types. Absolute concentrations of carbonized particles per gram sediment are reported using known concentrations of Lycopodium spores as a reference. This approach assumes that the microfossils and Lycopodium spores are evenly distributed on the strew mount.

A1G. BULK GEOCHEMICAL ANALYSIS (X-RAY FLUORESCENCE (XRF) SPECTROMETRY)

Sediment samples from cores ST9 and WE11 were analysed by X-ray fluorescence at the Geoscience Australia laboratories to determine major, minor, and some trace elements. These were determined using a Philips PW2404 4kW Sequential Spectrometer with a Rh tube and according to a modified version of Norris and Hutton's (1969) methods. The instrument was calibrated using a range of international standards from United States Geological Survey (USGS) and South African Reference Material (SARM). Approximately 1 gm of ground sample was combined with flux material and 0.5 ml of 20% LiNO3. The mixture was heated at 400 ºC for 10 minutes then at 1100 ºC for a further 10 minutes during which time a tablet of Ammonium Iodide was added. The resulting melt was poured into moulds, cooled, and then introduced to the XRF. The reported precision was better than 5%.

Appendix 2 Site Locations and Details

SITE	LAT	LONG	WATER DEPTH (M)	CHAMBERS	CORES	SURFACE SEDIMENT
HD1	-34.29551	115.15246	1.2	4/2008	9/2007	Yes
HD2	-34.28006	115.16383	0.7		9/2007	Yes
HD3	-34.29637	115.16568	1.5			Yes
HD4	-34.26577	115.22070	0.8	4/2008	9/2007	Yes
HD5	-34.26621	115.20338	7.0		9/2007	Yes
HD5a	-34.26614	115.20313	0.5	4/2008		
HD6	-34.27608	115.20062	1.8		9/2007	Yes
HD7	-34.26316	115.21496	2.8			Yes
HD8	-34.25830	115.23299	3.0			Yes
HD9	-34.23863	115.21667	6.5	4/2008	9/2007	Yes
HD10	-34.25401	115.23506	3.5			
HD11	-34.26215	115.22705	1.7			Yes
HD12	-34.26296	115.22373	1.6			Yes
HD13	-34.26925	115.21844	0.5			Yes
HD14	-34.27250	115.21192	1.2			Yes
HD15	-34.27075	115.21673	1.7			Yes
HD16	-34.27015	115.22261	0.8			Yes
HD17	-34.25776	115.21144	6.5			Yes
HD18	-34.24882	115.21053	6.0			Yes
HD19	-34.26380	115.20099	0.5			Yes
HD20	-34.27071	115.20234	0.4			Yes
HD21	-34.27488	115.20808	1.0			Yes
HD22	-34.27961	115.19939	0.5			Yes
HD23	-34.27731	115.19122	0.5			Yes
HD24	-34.27916	115.18149	0.5			Yes
HD25	-34.27999	115.17239	0.6			Yes
HD26	-34.27182	115.16398	0.8			Yes
HD27	-34.28986	115.16467	1.6			Yes
HD28	-34.28255	115.18615	1.0			Yes
HD29	-34.28799	115.18718	0.5			Yes
HD30	-34.28915	115.17834	0.5			Yes
HD31	-34.29847	115.17041	0.7			Yes
HD32	-34.30800	115.16713	1.0			Yes
HD33	-34.31620	115.16563	1.0			Yes
HD34	-34.27663	115.20466	2.0		4/2008	

Appendix 3 Surface Sediment Data

Site	Sampling Time	Porosity	DIC [uM]	NH4 [uM]	NOX [uM]	PO4 [uM]	SiO4 [uM]	TOC [wt.%]	$\delta^{13}C$ [‰PDB]	$\delta^{15}N$ [‰air]
HD1	25/09/2007	84.42	1865.15	58.54	bdl	bdl	99.70	5.06		
HD2	25/09/2007	44.99	3505.32	31.41	bdl	bdl	121.06	0.75		
HD3	25/09/2007	68.31	3415.56	44.26	bdl	bdl	181.59	1.76		
HD4	25/09/2007	74.18	2836.19	52.83	1.14	2.36	117.50	2.29		
HD5	25/09/2007	89.19	4066.03	235.60	bdl	5.17	334.69	6.82		
HD6	26/09/2007	54.46	2890.98	171.35	1.43	5.17	128.18	0.59		
HD7	26/09/2007	88.37	4467.58	92.81	bdl	8.39	199.39	4.94		
HD8	26/09/2007	79.63	3316.21	51.40	5.07	15.82	32.40	2.22		
HD9	26/09/2007	48.05	6128.04	114.23	2.43	1.90	60.53	0.45		
HD5a	19/04/2008	57.80	2662.15					0.30	-22.45	4.62
HD8	19/04/2008	67.71	5279.85					1.52	-26.70	1.99
HD11	19/04/2008	92.33	3138.74					11.47	-26.41	2.08
HD12	19/04/2008	92.77	2745.13					11.42	-24.98	1.61
HD13	19/04/2008	78.10	2733.73					1.37	-23.38	2.94
HD14	19/04/2008	88.56	2410.60					4.39	-23.27	2.91
HD15	19/04/2008	88.05	2449.55					4.09	-24.19	2.93
HD16	19/04/2008	86.23	2497.54					3.81	-23.89	1.71
HD17	19/04/2008	85.75	2767.36					6.42	-26.58	3.95
HD18	19/04/2008	87.85	5134.00					7.09	-27.58	4.36
HD19a	19/04/2008	42.66	2143.96					0.04	-23.65	
HD19b	19/04/2008	64.81	2574.16					0.70	-23.00	3.31
HD20	19/04/2008	58.04	2964.53					0.29	-21..8	5.08
HD21	19/04/2008	74.46	2563.52					1.20	-23.38	2.55
HD22	18/04/2008	61.85	3144.92					0.52	-22.26	3.91
HD23	18/04/2008	73.68	2997.76					1.18	-22.23	4.18
HD24	18/04/2008	59.52	3028.86					0.47	-21.98	5.86
HD25	18/04/2008	59.84	2748.69					0.55	-22.03	5.82
HD26	18/04/2008	71.55	2755.56					1.09	-20.00	3.03
HD27	18/04/2008	74.17	2591.12					2.79	-21.17	2.21
HD28	19/04/2008	69.38	2941.02					1.05	-22.40	4.58
HD29	19/04/2008	75.01	2772.03					1.13	-21.44	5.07
HD30	19/04/2008	69.32	2623.35					0.98	-21.19	5.14
HD31	19/04/2008	70.64	3841.00					0.75	-21.12	3.93
HD32	19/04/2008	68.60	3035.06					1.16	-20.28	2.87
HD33	19/04/2008	63.82	2578.26					1.31	-21.69	4.00

Appendix 4 Porewater Data

Sample ID	Base Depth [m]	Top Depth [m]	Ave Depth [m]	Porosity [%]	DIC [uM]	NH4 [uM]	NOX [uM]	PO4 [uM]	SiO4 [uM]
HD1A_0-1	0	0.01	0.005	84.42		33.56			71.21
HD1A_1-2	0.01	0.02	0.015			53.55			92.57
HD1A_2-3	0.02	0.03	0.025			48.55			46.29
HD1A_3-4	0.03	0.04	0.035			55.69			60.53
HD1A_4-5	0.04	0.05	0.045			67.82			56.97
HD1A_5-6	0.05	0.06	0.055			64.97			46.29
HD1A_6-8	0.06	0.08	0.07			67.82			53.41
HD1A_8-10	0.08	0.1	0.09			78.53			85.45
HD1A_10-12	0.1	0.12	0.11			85.67			96.14
HD1A_12-15	0.12	0.15	0.135			85.67			145.98
HD1A_15-18	0.15	0.18	0.165			99.95			192.27
HD1A_18-21	0.18	0.21	0.195			121.37			217.19
HD2A_0-1	0	0.01	0.005	44.99		18.56	1.78		89.01
HD2A_1-2	0.01	0.02	0.015			22.13	1.71		106.82
HD2A_2-3	0.02	0.03	0.025			28.56	1.07		110.38
HD2A_3-4	0.03	0.04	0.035			99.95	1.50	3.20	117.50
HD2A_4-5	0.04	0.05	0.045			128.51	1.50	2.97	131.74
HD2A_5-6	0.05	0.06	0.055			99.95	1.43	6.46	231.44
HD2A_6-8	0.06	0.08	0.07			114.23	1.29	7.43	274.16
HD2A_8-10	0.08	0.1	0.09			50.69	1.71	1.90	249.24
HD2A_10-12	0.1	0.12	0.11			71.39		2.65	291.97
HD2A_12-15	0.12	0.15	0.135			43.55		1.74	288.41
HD2A_15-18	0.15	0.18	0.165			57.83		2.26	274.16
HD2A_18-21	0.18	0.21	0.195			78.53		1.74	291.97
HD4A_0-1	0	0.01	0.005	70.00		14.99	1.21	2.16	39.17
HD4A_1-2	0.01	0.02	0.015			23.56		0.84	35.61
HD4A_2-3	0.02	0.03	0.025			34.27	3.21	0.68	67.65
HD4A_3-4	0.03	0.04	0.035			39.98			67.65
HD4A_4-5	0.04	0.05	0.045			52.83	1.36	1.00	92.57
HD4A_5-6	0.05	0.06	0.055			55.69		1.29	110.38
HD4A_6-8	0.06	0.08	0.07			67.82	0.79	2.20	124.62
HD4A_8-10	0.08	0.1	0.09			62.11		2.26	145.98
HD4A_10-12	0.1	0.12	0.11			71.39		2.23	192.27
HD4A_12-15	0.12	0.15	0.135			85.67	1.00	1.45	235.00
HD4A_15-18	0.15	0.18	0.165			128.51		2.26	327.57
HD4A_18-21	0.18	0.21	0.195			171.35		1.65	391.66
HD5A_0-1	0	0.01	0.005	89.19		92.81		1.26	274.16
HD5A_1-2	0.01	0.02	0.015			164.21	1.14	6.13	391.66
HD5A_2-3	0.02	0.03	0.025			128.51		3.55	284.84
HD5A_3-4	0.03	0.04	0.035			178.49		5.81	327.57
HD5A_4-5	0.04	0.05	0.045			199.90		4.84	324.01
HD5A_5-6	0.05	0.06	0.055			249.88		6.13	281.28
HD5A_6-8	0.06	0.08	0.07			249.88		7.10	267.04
HD5A_8-10	0.08	0.1	0.09			249.88		6.78	281.28
HD5A_10-12	0.1	0.12	0.11			299.86		9.04	277.72
HD5A_12-15	0.12	0.15	0.135			356.97		13.24	356.06
HD5A_15-18	0.15	0.18	0.165			464.06		16.79	391.66
HD5A_18-21	0.18	0.21	0.195			435.50		12.91	334.69
HD6A_0-1	0	0.01	0.005	54.46			10.71		149.54
HD6A_1-2	0.01	0.02	0.015			17.85	12.14		181.59
HD6A_2-3	0.02	0.03	0.025			49.26	0.86		281.28
HD6A_3-4	0.03	0.04	0.035			61.40			160.23
HD6A_4-5	0.04	0.05	0.045			142.79		2.00	149.54
HD6A_5-6	0.05	0.06	0.055			135.65	0.86	3.55	167.35
HD6A_6-8	0.06	0.08	0.07			135.65		3.87	121.06
HD6A_8-10	0.08	0.1	0.09			164.21		2.13	110.38
HD6A_10-12	0.1	0.12	0.11			171.35		1.19	85.45
HD6A_12-15	0.12	0.15	0.135			157.07	1.14	0.48	106.82
HD6A_15-18	0.15	0.18	0.165			164.21		1.87	227.88
HD6A_18-21	0.18	0.21	0.195			178.49		2.23	249.24

HD9A_0-1	0	0.01	0.005	48.05		42.12	7.14	0.32	74.77
HD9A_1-2	0.01	0.02	0.015			50.69	0.86		78.33
HD9A_2-3	0.02	0.03	0.025			62.11		0.16	96.14
HD9A_3-4	0.03	0.04	0.035			71.39	1.21	0.32	78.33
HD9A_4-5	0.04	0.05	0.045			78.53	0.79		71.21
HD9A_5-6	0.05	0.06	0.055			107.09	2.14	0.16	99.70
HD9A_6-8	0.06	0.08	0.07			78.53			81.89
HD9A_8-10	0.08	0.1	0.09			67.11	1.07		92.57
HD9A_10-12	0.1	0.12	0.11						
HD9A_12-15	0.12	0.15	0.135			85.67		0.68	131.74
HD9A_15-18	0.15	0.18	0.165			85.67		0.87	135.30
HD9A_18-21	0.18	0.21	0.195			78.53			135.30
HD4B_0-1	0	0.01	0.005	62.34	2791.77	15.71	4.00		8.55
HD4B_1-2	0.01	0.02	0.015	60.45	2855.45	14.99	4.14		14.95
HD4B_2-3	0.02	0.03	0.025	58.99	2618.57	19.99	3.86		29.55
HD4B_3-4	0.03	0.04	0.035	59.88	2579.72	40.69	3.28		60.53
HD4B_4-6	0.04	0.06	0.05	62.72	2494.68	31.41	3.93		96.13
HD4B_6-8	0.06	0.08	0.07	58.48	2454.76	39.27	4.07		121.06
HD4B_8-10	0.08	0.1	0.09	59.52	2514.66	39.98	4.78		113.94
HD4B_10-13	0.1	0.13	0.115	61.29	2450.47	40.69	4.78		160.22
HD4B_13-16	0.13	0.16	0.145	63.57	2290.80	48.55	5.21		217.19
HD4B_16-19	0.16	0.19	0.175	54.16	2332.49	60.68	1.07	1.42	170.90
HD4B_19-22	0.19	0.22	0.205	49.57	2367.39	92.81	1.00	1.36	192.27
HD4B_22-25	0.22	0.25	0.235	52.48	2397.45	135.65	0.86	1.65	234.99
HD4C_0-1	0	0.01	0.005	83.05	3288.03	46.41			49.85
HD4C_1-2	0.01	0.02	0.015	73.99	3114.91	29.99	0.93		39.17
HD4C_2-3	0.02	0.03	0.025	67.46	3326.65	57.11	1.14		64.09
HD4C_3-4	0.03	0.04	0.035	67.51	3880.23	71.39	5.50	0.48	113.94
HD4C_4-6	0.04	0.06	0.05	62.27	4316.95	62.83	1.86	1.36	124.62
HD4C_6-8	0.06	0.08	0.07	58.57	5114.13	60.68	3.78	1.03	188.71
HD4C_8-10	0.08	0.1	0.09	60.92	5519.60	44.98	6.64	0.77	277.72
HD4C_10-13	0.1	0.13	0.115	62.19	5433.82	44.26	3.36		324.01
HD4C_13-16	0.13	0.16	0.145	62.93	4949.49	27.84	0.86	0.29	391.66
HD4C_16-19	0.16	0.19	0.175	59.77	5614.68	40.69	1.14	0.48	427.26
HD4C_19-22	0.19	0.22	0.205	52.01	6040.74	51.40		0.61	427.26
HD4C_22-25	0.22	0.25	0.235	62.83	6674.44	107.09	1.50	0.68	534.08

Appendix 5 Benthic Flux Data

Site	Chamber	Type	O_2	DIC	Err	NH_4^+	Err	NO_x	Err	PO_4^{3-}	Err	SiO_4^{4-}	Err	N_2	Err
HD1	4	dark	-44.4	37.84	16.08	-0.70	0.24			-0.200	0.04	5.12	1.72	-2.83	0.38
	5	light	-44.4	27.73	8.22	0.43	0.04					5.01	0.44	-3.98	0.49
	6	light	-39.1	40.15	2.10	2.00	0.38					8.50	1.84	-1.80	0.50
	7	dark	-35.7	43.32	1.37	1.95	0.24					5.10	0.69	-4.04	1.55
	8	dark	-31.3	120.70	1.35	6.47	0.33					11.91	0.74	-2.36	0.25
HD9	1	light	-21.4	199.91	101.44	3.98	1.63	-0.10	0.07	0.071	0.03	6.80	2.15	-2.30	6.53
	2	light	-20.9	65.11	66.53	1.34	1.29	0.31	0.29	0.060	0.04	8.64	2.52	5.30	2.86
	~~3~~	~~light~~													
HD4	4	dark	-54.0	102.47	6.48	-0.17	0.05					-3.33	0.32	-2.61	0.50
	5	light	69.2	-89.23	4.09	0.04	0.03					-1.73	0.59	-14.17	2.73
	6	light	40.4	-84.94	12.58	-0.07	0.05					-0.26	1.21	-17.07	2.87
	7	dark	-46.2	39.07	0.52	0.04	0.22					0.48	0.15	-1.64	1.25
	8	dark	-49.7	38.85	2.75	-0.02	0.03	-0.01	0.08			-1.08	0.14	-3.69	0.50
HD5a	4	dark	-42.3	45.66	16.01	-0.05	0.05			-0.027	0.02	-0.53	1.01	-0.50	1.35
	5	light	112.6	-102.6	13.69	0.01	0.04					-2.39	0.77	-22.68	0.64
	6	light	11.3	7.28	2.29	-0.19	0.05	0.01	0.13			-3.03	0.86	-6.58	1.01
	7	dark	-41.7	67.96	3.60					0.004	0.02	-1.82	0.29	-2.88	0.11
	8	dark	-57.4	82.74	2.77							-1.65	0.31	-2.05	0.27