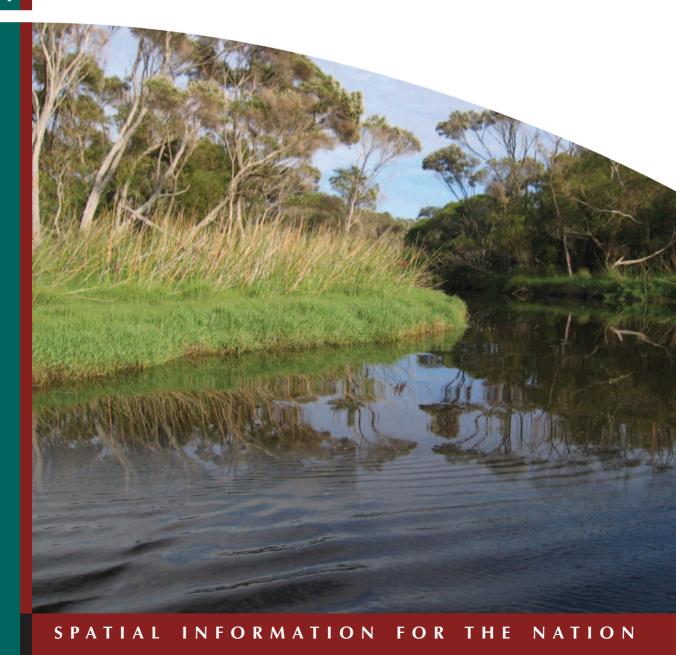


# Nutrient Release from Sediments of the Torbay Drainage System, South-Western Australia

Emma J. Murray, Craig S. Smith, Jodie Smith, Ralf R. Haese, and David T. Heggie

Record

2005/14



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GEOSCIENCE AUSTRALIA RECORD 2005/14

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# **Executive Summary**

In April 2005, Geoscience Australia (GA) conducted a field survey of the waterbodies of the Torbay catchment drainage system. The Torbay Catchment Group and the Western Australian (WA) Department of Environment commissioned this study, through the 'Watershed Torbay' catchment restoration project, in order to address critical knowledge gaps in their understanding of the major components of the nutrient budget in the Torbay catchment waterbodies. In particular, the role of benthic nutrient fluxes, their magnitude, and total benthic nutrient supply to the water column for phytoplankton growth.

The WA Department of Environment considers Torbay Inlet to have the poorest estuarine water quality in the State, and for a number of years toxic blue-green phytoplankton blooms have frequently occurred in Lake Powell, Marbelup Brook, and Torbay Inlet. Progressive nutrient enrichment of these waterways over several decades of catchment land-use practices is certainly a major contributor to lowered water quality and phytoplankton blooms. However, given the shallow nature of waterways within the Torbay drainage system (0.5 m to 1.5 m), and the results of a previous GA study, which found high nutrient concentrations in sediment porewaters, benthic nutrient fluxes were identified as an additional, potentially important control on water quality and phytoplankton growth.

Natural Resource Management agencies work towards the identification of the causes and options to reduce algal blooms, and an overall improvement of water quality. A better understanding of nutrient cycling within these waterways assists achieving these goals.

#### The main objective of this study was to:

Determine the role of estuarine/lake sediments in supplying nutrients to the Torbay catchment waterbodies.

More specifically, this study investigated the four major waterbodies of the Torbay catchment (Torbay Inlet, Lake Powell, Marbelup Brook, and Lake Manarup) in order to determine for each waterbody:

- 1. the magnitude and type of organic matter breakdown in the sediments, and release of nutrients to the water column;
- 2. porewater and water column nutrient pool sizes;
- 3. likely organic matter sources driving benthic nutrient fluxes;
- 4. denitrification efficiencies; and
- 5. overall water quality.

This was achieved by measuring benthic nutrient  $(NH_4^+, NO_X, PO_4^{3-}, SiO_4^{4-})$ , dissolved oxygen  $(O_2)$ , and carbon dioxide  $(TCO_2)$  fluxes using benthic chambers, and determining down core distributions of porewater nutrients  $(NH_4^+, NO_X, PO_4^{3-}, SiO_4^{4-})$ , and  $TCO_2$ .

Immediately prior to the survey, the Albany area experienced an extreme rainfall event, receiving three times the monthly average rainfall in only three days. This rainfall washed a large amount of catchment material into the waterways, and caused a rapid rise in water levels, which was enough to breach the sand bar at the entrance to Torbay Inlet, allowing tidal exchange and marine water to enter the Inlet. It was important to consider the effect of this rainfall event and the resumption of tidal exchange with the ocean when interpreting the results.

### The key findings of this study were:

## 1. Sediments are a major source of nutrients.

This investigation measured significant nutrient fluxes in all four waterbodies. Of particular concern were the extremely high rates of nutrient release from the muddy sediments in the channel of Torbay Inlet, in Marbelup Brook, and in a small area where Marbelup Brook enters Lake Powell. Fluxes measured in the channel of Torbay Inlet were by far the highest ever measured by Geoscience Australia. TCO<sub>2</sub> fluxes in the other 3 waterways were also very high compared to other temperate Australian estuaries, except the sandy sediments in Lake Powell. The significance of sediments as a pool for nutrients was also shown by comparing porewater and water column nutrient pool sizes. In Torbay Inlet and Lake Powell, sediment pool sizes, capturing dissolved nutrients in the top 20 cm of the sediment, were generally more than 5 times larger than the respective pool sizes in the water column.

# 2. Denitrification, nitrogen fixation and benthic photosynthesis are critical processes influencing overall water quality.

Muddy sediments in the channel of Torbay Inlet and Marbelup Brook accumulate nitrogen by converting nitrogen gas  $(N_2)$  into microbial biomass, a process referred to as nitrogen fixation. Nitrogen fixation counteracts the outcome of a process converting  $NH_4^+$  into  $N_2$ , a process referred to denitrification. Denitrification reduces the amount of bioavailable nitrogen and is very efficient in sandy sediments of Torbay Inlet and Lake Powell. Denitrification efficiency was low in Lake Manarup where equal amounts of nitrogen are released as  $NH_4^+$  and  $N_2$ .

Microbenthic algae were identified at the surface of sandy sediments of Torbay Inlet and Lake Manarup. Under light conditions, microbenthic algae assimilate nutrients by photosynthesis and thereby serve as a benthic filter for nutrients.

High rates of benthic nitrogen fixation were found where much  $PO_4^{3-}$  was available, i.e. in Torbay Inlet channel sediments where benthic  $PO_4^{3-}$  fluxes were very high and in Marbelup Brook where  $PO_4^{3-}$  concentrations were very high in the water column. Because nitrogen fixation is carried out by cyanobacteria, a common group of toxic algae in this environment, it is concluded that muddy sediments support the growth of toxic algae.

# **Major Implications**

Muddy sediments in Marbelup Brook, the Torbay Inlet channel, and at the entrance to Marbelup Brook in Lake Powell only constitute a small proportion of the Torbay drainage area, but have the most negative impact on water quality due to a high release of nutrients from sediments into the above waterbody. High fluxes of  $PO_4^{3-}$  support the growth of toxic algae and lead to the accumulation of biomass-bound nitrogen through nitrogen fixation. Plans to reduce nutrient concentrations and the presence of toxic algae in the drainage area must consider the muddy sediments.

The open bar of Torbay Inlet allowed much of the catchment-derived sediment and nutrient load discharged during the rain event to be flushed into the ocean where these compounds were diluted and dispersed within a few days. Subsequent tidal exchange of water reduced nutrients in Torbay Inlet due to the intrusion of nutrient-depleted seawater. Torbay Inlet water is density stratified under open bar conditions, but bottom water anoxia is only expected to occur in the deeper channel areas where water residence time is long and oxygen consumption is high. Even low to moderate wind strength will mix the water of Torbay Inlet counteracting the potential of oxygen depletion. Under the given conditions, the open bar of Torbay Inlet has an overall positive impact on water quality; therefore, it is recommended to keep the bar open for as long as possible.

# Acknowledgements

The authors would like to thank Colin Tindall, Ian Atkinson, and Amy Prendergast from Geoscience Australia, Andrew Maughan, Helen Astill, and Michelle Grassi from the WA Department of Environment, Geoff Bastyan, and Paul Close, for their assistance in field logistics, sampling and analysis. In addition, Helen and Michelle provided excellent sample management, Andrew gave us lots of background information and data, and Geoff provided invaluable information and knowledge about the waterways. We would also like to acknowledge Malcolm Robb and Naomi Arrowsmith for their support, and the WA Department of Environment and the Torbay Catchment Group for commissioning this study. Also thanks to Graham Skyring for his help with data interpretation.

Editing and comments on the final draft by Julie Pech and Andrew Maughan were much appreciated.

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# Abbreviations and Units

ANZECC Australian and New Zealand Environment and Conservation Council

Chl-a Chlorophyll a

C Carbon

cc cubic centimetre cm centimetre CO<sub>2</sub> Carbon Dioxide

DIN Dissolved Inorganic Nitrogen
DIP Dissolved Inorganic Phosphorus

DO Dissolved Oxygen

DoE Department of Environment, Western Australia (formerly the WRC)

Fe Iron

GA Geoscience Australia H<sub>2</sub>S Hydrogen Sulfide

Kd Light Attenuation Coefficient

km kilometre
LP Lake Powell
m meter
m<sup>-1</sup> per metre

mAHD metres above Australian Height Datum

mg/L milligrams per litre
MLB Marbelup Brook
mm millimeters
mL millilitre

mmol m<sup>-2</sup> day<sup>-1</sup> millimoles per metre squared per day

MNL Lake Manarup N Nitrogen N<sub>2</sub> Dinitrogen Gas NH<sub>4</sub><sup>+</sup> Ammonium

NLWRA National Land and Water Resources Audit

NO<sub>2</sub> Nitrite NO<sub>3</sub> Nitrate

 $NO_X$  Nitrate + Nitrite  $O_2$  Oxygen

P Phosphorus

PAR Photosynthetically Active Radiation

PO<sub>4</sub><sup>3-</sup> Phosphate Si Silica SiO<sub>4</sub><sup>4-</sup> Silicate

TCG Torbay Catchment Group Inc.

TCO<sub>2</sub> Total Carbon Dioxide

TI Torbay Inlet

TIN Total Inorganic Nitrogen

TN Total Nitrogen
TOC Total Organic Carbon
TP Total Phosphorus
TSM Total Suspended Matter
WA Western Australia

WRC Water and Rivers Commission, Western Australia (DoE since 2004)

μg/L micrograms per litre

μM micromolar °C degrees Celsius

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# 1. Introduction

# 1A. BACKGROUND

# 1A1. The Importance of Sediment-Water Interactions

Declining water quality is a growing problem in Australian estuaries. This is especially the case along the southeast and southwest coasts where estuaries are predominantly 'modified' (NLWRA 2002), and thus subject to increasing nutrient loads from agricultural, urban, and industrial expansion. Also, most estuaries in these regions are 'wave-dominated' (wave energy is greater than tide and river energy), which are susceptible to eutrophication because they often have a sand bar restricting or blocking the entrance, limiting the estuary's capacity to flush nutrients to the ocean (Ryan *et al.* 2003; Harris and Heap 2003).

Sediments play an important role in controlling eutrophication and water quality in coastal lakes and estuaries. The breakdown of organic matter in sediments, and the resulting exchange (benthic flux) of oxygen, carbon dioxide, and nutrients with the overlying water can influence water column conditions (for example oxygen levels) and also supplement nutrient supply from the catchment (Jørgensen 1996). Plants utilise nutrients available in the water column (Figure 1-1) and when nutrient loads from the catchment and/or the sediments are excessive, eutrophic conditions may develop, involving prolific plant growth and the possibility of toxic blue-green algae blooms.

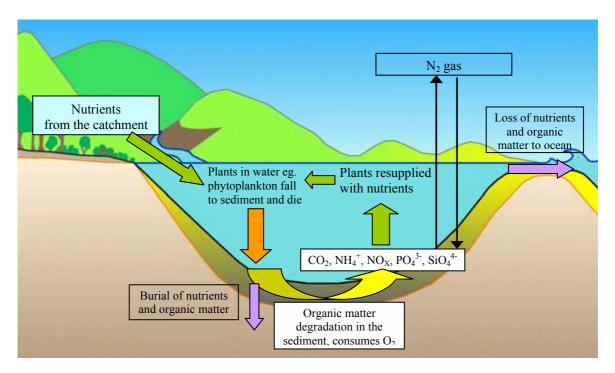


Figure 1-1. Schematic diagram of nutrient cycling in wave-dominated type estuaries. Green arrows indicate supply of nutrients to plants, the orange arrow indicates organic matter supply to the sediment, the yellow arrow represents organic matter breakdown, the black arrows show loss of N through denitrification, and N supply through N fixation, and the purple arrows show loss of nutrients and organic matter to the ocean and burial in the sediments (this is often limited in wave-dominated estuaries such as Torbay Inlet).

The magnitude of benthic fluxes indicates the amount of biological activity and organic matter breakdown in the sediments. Figure 1-1 is a simplified illustration of organic matter breakdown and nutrient cycling in wave-dominated type estuaries. Nutrients in runoff from the catchment can enter an estuary and stimulate plant growth, especially that of phytoplankton and macroalgae. Bacteria subsequently break down these plants when they fall to the bottom sediments and die. The resulting flux of nutrients to the overlying water from organic matter breakdown is a source of nutrients for further plant growth. The bacteria consume oxygen, when available, during respiration to oxidise the organic material.

Denitrification is an important control on eutrophication because this process of organic matter breakdown releases the nutrient nitrogen as  $N_2$  gas, which can be lost from the system into the atmosphere (Figure 1-1; Seitzinger 1990). The degree to which denitrification is occurring in the sediments can indicate the susceptibility of an estuary to eutrophication and associated problems such as water quality decline, low dissolved oxygen levels, and nuisance algal blooms. The capacity for nitrogen removal is limited in systems where ammonification and dissimilatory nitrate reduction dominate nitrogen cycling, which produce bioavailable ammonium as opposed to  $N_2$  gas.

Nitrogen can also be lost through water exchange with the ocean and burial in the sediments (Figure 1-1). However, sedimentation rates are usually not rapid enough to bury a significant fraction of organic material. The restricted entrances of many wave-dominated estuaries, such as Torbay Inlet, limit water exchange with the ocean and consequently the loss of nutrients to the ocean is typically low.

# 1A2. Water Quality Problems in the Torbay Drainage System

Catchment processes strongly influence water quality in Torbay Inlet because it is a 'wave-dominated estuary' (according to the NLWRA classification; NLWRA 2002) with a wave-built sand bar blocking water exchange with the ocean for extended periods (WRC 2002). Progressive nutrient enrichment has, over several decades of catchment land use practices, contributed to lowered water quality of the Torbay Inlet/Lake Powell drainage systems. The water column in parts of the drainage system is often anoxic and nutrient (ammonia and phosphate) levels exceed ANZECC trigger values (ANZECC 2000) for much of the year. The Western Australian (WA) Department of Environment considers Torbay Inlet to have the poorest estuarine water quality in WA.

Toxic blue-green phytoplankton blooms have been recognised as a problem in waterbodies of the Torbay drainage system for a number of years (DoE 2004a). Nutrients from agricultural and urban sources are contributing to the proliferation of algae, which is impacting on recreational and commercial use of these waterways (DoE 2004b). The occurrence of cyanobacterial blooms demonstrate the system has adequate dissolved nutrients and light, and favourable temperatures to allow rapid growth (Adeney 2001).

A combination of cyanophytes (including *Nodularia*), chlorophytes, and diatoms dominated phytoplankton assemblages in Torbay Inlet prior to winter 2002. However, since winter 2002, diatoms have dominated phytoplankton assemblages in Torbay Inlet throughout the year. This change in phytoplankton assemblage may result from a combination of environmental factors, including a change in bar status and frequency of openings, and salinity. Cyanophytes dominate Lake Powell phytoplankton assemblages during summer/autumn and a mix of cyanophytes, chlorophytes, and diatoms persist during winter and spring (DoE 2004a).

During summer 2002, the Water and Rivers Commission found silica was limiting phytoplankton (predominantly diatom) growth in Torbay Inlet, whereas in Lake Powell both silica and nitrogen were limiting phytoplankton growth, along with partial phosphorus limitation (DoE 2004a).

# 1A3. Rationale for this Investigation: Measuring Benthic Fluxes in the Torbay Drainage System

Given the shallow nature of both Torbay Inlet and Lake Powell (0.5 m to 1.5 m), the status of sediment nutrients is possibly an important factor influencing water quality and primary productivity (DoE 2004a). Adeney (2001) highlighted the need to determine nutrient loadings from various sources and the extent of nutrient recycling in the Torbay drainage system. He recommended the assessment of nutrient cycling and the extent of nutrient release from the sediments by collecting sediment cores and using benthic chambers.

In 2002, Geoscience Australia (GA) collected sediment cores and surface sediment samples from Lake Powell and Torbay Inlet to assess sediment nutrient inventories and their potential as a nutrient source (Heggie *et al.* 2003). This study found that average concentrations of nutrients in the porewaters of Lake Powell were within range of other Australian estuaries, but those from Torbay Inlet were significantly higher. Sediment porewater nutrient profiles in both Torbay Inlet and Lake Powell showed higher nutrient concentrations with increasing proximity to the surface sediments, indicating porewater nutrient release to the overlying waters. The study estimated the flux of nutrients from the sediments to the overlying water using the porewater profiles (diffusive flux) of dissolved inorganic nitrogen (DIN) and dissolved inorganic phosphorus (DIP). Diffusive fluxes in Lake Powell were comparable to other temperate Australian estuaries whereas, the fluxes of DIN and DIP in Torbay Inlet were higher than elsewhere. In-situ, directly measured benthic fluxes of solutes often exceed calculated diffusive fluxes by a factor greater than four (Forster *et al.* 1999), therefore, it was expected that actual benthic nutrient fluxes would be significantly higher than those calculated from the porewater profiles.

Porewater nutrients measured by GA in 2002 also indicated that, in contrast to most other temperate Australian estuaries, a significant proportion of labile organic matter in the sediments of Torbay Inlet and Lake Powell is of non-diatomaceous origin. Possibly, under the highly eutrophic conditions, phytoplankton aggregates form and provide a mechanism for non-diatomaceous phytoplankton to settle, or the two waterbodies receive significant labile organic matter directly from the catchment. The DIN result also suggests that there is little denitrification occurring in the sediments, a result which has important implications for 'estuarine health'.

The GA study concluded that the sediments of Torbay Inlet and Lake Powell are probably a significant source of nutrients for the overlying waters and thereby possibly contribute to the proliferation of phototrophic growth including (toxic) cyanobacteria and nuisance algal blooms. It was identified that future work should focus on in-situ measurements of benthic nutrient fluxes to quantitatively examine the role of sediments as a source of nutrients.

The WA Department of Environment also recognised that in-situ measurements of benthic nutrient fluxes could address a significant knowledge gap in determining the major components of the estuarine nutrient budget in the Torbay drainage system (DoE 2004a). In particular, the magnitude of benthic nutrient fluxes relative to the total nutrient delivery to phytoplankton in the water column remained unknown. The Department also highlighted that benthic nutrient cycling activity is an indicator of ecological function within aquatic ecosystems and that this information is necessary when determining key nutrient sources to water column primary producers and developing effective

nutrient reduction strategies. Management of the problems associated with the Torbay drainage system can therefore benefit from an understanding of sediment processes.

In order to address these knowledge gaps and meet their objectives, the Torbay Catchment Group and the WA Department of Environment commissioned this study, through the 'Watershed Torbay' catchment restoration project, on the storage and release of nutrients in sediments in the Torbay drainage system (incorporating Torbay Inlet, Lake Powell, Marbelup Brook, and Lake Manarup). Benthic chamber studies, sediment cores, and water column sampling were used to provide a better understanding of nutrient fluxes from the bottom sediments into the water column and help quantify the importance of nutrient release from sediments compared to catchment sources. This information aims to help the Torbay Catchment Group and the WA Department of Environment develop effective management and restoration plans to reduce the incidence of algal blooms and improve water quality.

# 1A4. Extreme Rainfall Immediately Prior to Sampling for this Investigation

Field sampling for this study occurred 4-21 April 2005. Albany has a Mediterranean climate and this time of year typically marks the end of the drier summer period, where the Torbay drainage system would have received little recent runoff from the catchment and water column conditions would have been relatively stable for several months. Most of the yearly rainfall usually occurs between May and August. However, immediately prior to field sampling, an extremely large rainfall event occurred. Between 31 March and 2 April, 163.8 mm of rain fell in Albany, and 218 mm at Albany Airport. The average monthly rainfall for Albany in April is only 67.9 mm. Flooding was widespread in the area and water levels rose rapidly in the Torbay drainage system. As a result, the Torbay Inlet sand bar was naturally breached on the 1 April, and much of the water and associated suspended sediment of the run-off event was flushed into the ocean. This led to a temporary large black plume in the ocean immediately adjacent to the mouth of Torbay Inlet. Once the water level in Torbay Inlet equalized with sea level, seawater intruded into Torbay Inlet with the incoming tide. The bar remained open for the duration of the field survey, closing 20 April. During the survey period, a further 10.4 mm of rainfall fell in Albany. The large input of freshwater from the catchment, and the intrusion of saline marine water into Torbay Inlet following opening of the sand bar, significantly influenced water column conditions during the study period. This was an important consideration when interpreting the results.

# 1B. OBJECTIVES

The main objective of this study was to:

Determine the role of estuarine/lake sediments in supplying nutrients to the Torbay drainage system.

More specifically, this study investigated the four major waterbodies of the Torbay drainage system (Torbay Inlet, Lake Powell, Marbelup Brook, and Lake Manarup) in order to determine for each waterbody:

- (1) the magnitude and type of organic matter breakdown in the sediments, and release of nutrients to the water column,
- (2) porewater and water column nutrient pool sizes,
- (3) likely organic matter sources driving benthic nutrient fluxes,
- (4) denitrification efficiencies; and,
- (5) overall water quality.

This was achieved by measuring benthic nutrient (NH<sub>4</sub><sup>+</sup>, NO<sub>X</sub>, PO<sub>4</sub><sup>3-</sup>, SiO<sub>4</sub><sup>4-</sup>), dissolved oxygen (O<sub>2</sub>), and carbon dioxide (TCO<sub>2</sub>) fluxes using benthic chambers, and determining down core distributions of porewater nutrients (NH<sub>4</sub><sup>+</sup>, NO<sub>X</sub>, PO<sub>4</sub><sup>3-</sup>, SiO<sub>4</sub><sup>4-</sup>), and TCO<sub>2</sub>.

# 1C. THE TORBAY DRAINAGE SYSTEM

The Torbay drainage system is located in the lower Torbay catchment, approximately 26 km west of Albany on the south coast of WA. The lower catchment is the most severely altered in the region (DoE 2004a). The Torbay catchment has an area of 330 km², where 51 % is agricultural land, 5 % is commercial timber plantations, 33 % is natural vegetation, and 1.6 % is waterways and wetlands (DoE 2005). Water quality in the Torbay drainage system is often very poor due to inadequate waterways management in the public and private drainage system. Torbay Inlet itself is estuarine. It is a broad, shallow (~0.5 m) lagoon with a deeper (~1.5 m), narrow channel linking it to the ocean (Figure 1-2). The mouth is often closed to the ocean by beach sand, and is artificially breached for drainage control by Water Corporation, the local management authority. Historically, Lake Manarup was also an estuarine body however, it now has flood gates to control saltwater entry from Torbay Inlet (Figure 1-2) and acts as a compensation basin to stop land surrounding Torbay Inlet from flooding prior to preferred bar opening times. Lake Powell is a fresh water system. It was previously about 1 m deep but is now only half that depth (Hodgkin and Clark 1990).

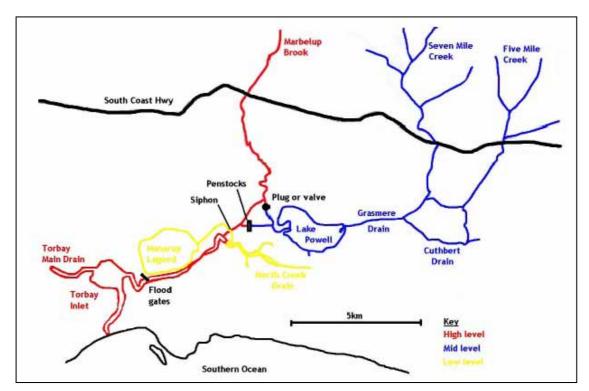


Figure 1-2. The Torbay drainage system showing major streams and drains, and the three different operating levels (from DoE 2004a).

Landuses in the Torbay catchment, which impact on the waterbodies of the drainage system, include horticulture, intensive animal industries (piggeries and dairies), seasonal commercial fishing, and a growing tourism industry. The wastewater treatment plant for the town of Albany previously discharged primary-treated effluent directly into the drainage system. This wastewater is now used

to irrigate a commercial timber plantation at the Irrigated Wastewater Tree Farm, located within the catchment (DoE 2005).

Alterations to the original, natural system of waterways began in 1912 with the construction of floodgates on the narrow channel linking Torbay Inlet with the ocean. Over subsequent decades, extensive changes were made to the waterways with the objective of draining suitable land for agriculture and protecting the rail and road infrastructure from flooding (DoE 2005). The waterways exist today as three interconnected systems operated at three different water levels (Figure 1-2). Farmers initially operated the drainage systems however, the State Government water management agency now controls them with the ability to operate the three different water levels independently (DoE 2005). Each water level affects a different set of stakeholder interests.

Torbay Inlet now receives runoff from four sub-catchments (Figure 1-2; originally described by Hodgkin and Clark 1990):

- (1) Low-lying land west of Torbay Inlet, which drains into Torbay via Torbay Main Drain.
- (2) Marbelup Brook, which now flows directly to Torbay Inlet via Marbelup High Level Drain. A plug blocks the natural channel to Lake Powell however, a pipe through the plug with a sliding flap valve is sometimes opened to allow water to flow, flush the old channel, and regulate water levels.
- (3) Grasmere Drain, which takes flow from Five Mile Creek, Seven Mile Creek and Cuthbert Drain into Lake Powell. Water from the Lake then flows to Torbay Inlet via Marbelup High Level Drain. The water level in Lake Powell can be controlled by penstocks.
- (4) Ewart Swamp and paddocks south of Lake Powell, which drain via North Creek Drain to the old Marbelup Brook (originally from Lake Powell), to a plug in the Brook and a siphon, which takes water under the Marbelup High Level Drain, to Lake Manarup. Floodgates on the outlet from Lake Manarup prevent salt water entering it from Torbay Inlet. The floodgates are sometimes opened to allow water from Torbay Inlet to enter Lake Manarup, rather than opening the sandbar at inopportune times, or to allow water to flood the lake when it dries up.

Surface water runoff from these catchments is a major nutrient and sediment source to the waterways and there are high levels of nutrient enrichment, particularly in Lake Powell and Torbay Inlet (WRC 2002). Torbay Main Drain, Marbelup Brook, and Five and Seven Mile Creeks have been identified in a list of South Coast rivers with the highest nutrient levels (DoE 2004a).

Surface flows into Torbay Inlet and Lake Powell are seasonal, with highest flows occurring in winter months and low flows in summer months. Of the four major Lake Powell tributaries, Seven Mile Creek consistently provides the highest surface flows and the creek currently receives drainage from the upstream Wastewater Irrigated Tree Farm (DoE 2004a). The highest nitrogen and phosphorus concentrations are delivered to Torbay Inlet during the high flow periods associated with winter months (DoE 2004a). In the Lake Powell tributaries, the highest total nitrogen concentrations were measured in Cuthbert Drain although the seasonality of total nitrogen concentrations is variable. Lake Powell receives a variable, yet reliable supply of phosphorus throughout the year from all its tributaries (DoE 2004a).

# 2. Methods

# 2A. SAMPLING STRATEGY

In April 2005, GA conducted an intensive sampling program, which incorporated the four major waterbodies of the Torbay drainage system: Torbay Inlet, Lake Powell, Marbelup Brook, and Lake Manarup (Figure 2-1). The program involved water column sampling, sediment coring, and benthic chamber deployments in each of the four waterbodies (Table 2.1). The rationale for water column, sediment core, and benthic chamber site locations in each of the waterways is described below.

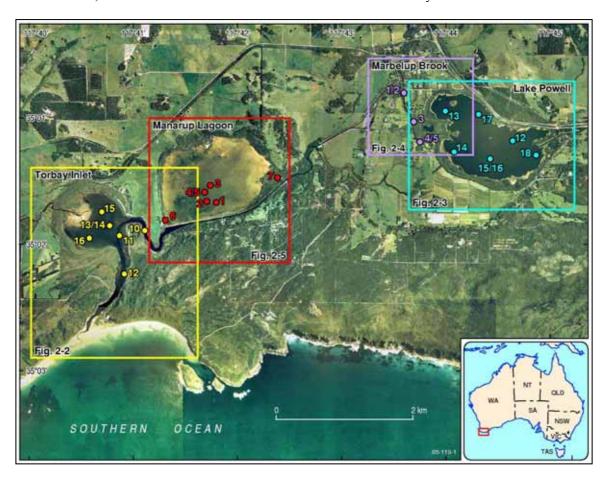


Figure 2-1. The four waterbodies sampled in the Torbay drainage system and sampling sites located within each waterbody. Aerial photo base image source: Department of Land Information, WA Government.

Table 2-1. Site location coordinates and the type of sample (chamber, core, or water column) collected at each site.

Waterway	Site	Lat °S	Long °E	Chamber	Cores	Water Column	Description
	TI_10	-35.03143	117.68542	dark	<b>✓</b>	✓	Upstream of Inlet
	TI_11	-35.03211	117.68138	dark		✓	Muddy Channel
	TI_12	-35.03715	117.68217	dark	<b>✓</b>	✓	Muddy Channel
Torbay Inlet	TI_13	-35.03082	117.67981	dark	<b>✓</b>	✓	Sandy and shallow
	TI_14	-35.03082	117.67981	light			<5 m from TI_13
	TI_15	-35.02900	117.67850			✓	Sandy and shallow
	TI_16	-35.03249	117.67657			✓	Sandy and shallow
	LP_12	-35.01926	117.74416	dark	✓	✓	Sandy and shallow
	LP_13	-35.01537	117.73340	dark	✓	✓	Sandy and shallow
	LP_14	-35.02077	117.73479	dark	✓	✓	Muddy shallow
Lake Powell	LP_15	-35.02165	117.74055	dark		✓	Sandy and shallow
	LP_16	-35.02165	117.74055	light			<5 m from LP_15
	LP_17	-35.01580	117.73866			✓	Sandy and shallow
	LP_18	-35.02100	117.76733			✓	Sandy and shallow
	MLB_1	-35.01303	117.72667	dark	✓	✓	Muddy channel
	MLB_2	-35.01303	117.72667	dark			<5 m from MLB_1
Marbelup Brook	MLB_3	-35.01682	117.72826	dark	✓	✓	Muddy channel
	MLB_4	-35.01949	117.72932	dark	✓	✓	Muddy channel
	MLB_5	-35.01949	117.72932	light			<5 m from MLB_4
	MNL_1	-35.02766	117.69681	dark	✓	✓	Muddy and shallow
	MNL_2	-35.02753	117.69532	dark	✓	✓	Muddy and shallow
	MNL_3	-35.02542	117.69585	dark		✓	Muddy and shallow
Lake Manarup	MNL_4	-35.02632	117.69494	dark	✓	✓	Muddy and shallow
	MNL_5	-35.02632	117.69494	light			<5 m from MNL_4
	MNL_6	-35.03005	117.68871			✓	Muddy and shallow
	MNL_7	-35.02433	117.70657			✓	Muddy channel

# 2A1. Torbay Inlet

Torbay Inlet has two distinct sedimentary environments: a main, shallow (~0.5 m), sandy basin area, and a deeper (~1.5 m), muddy channel (Figure 2-2). In the main basin, the sediment comprises a fine layer (2 mm) of brown organic material overlying brown, organic-rich sand with organic black mud lenses to 10 cm depth. Below this, the sediments consist of light grey sand. In the channel, the upper 5-10 cm of sediment is composed of brown organic muds, overlying fine black mud to at least 50 cm depth.

Two chamber sites were chosen to represent conditions in the deep, muddy channel (TI\_11 and TI\_12; Figure 2-2; Table 2-1). A further two chamber sites were located in the shallow, sandy basin area (TI\_13 and TI\_14) and another site upstream of the Inlet in Marbelup High Level Drain (TI\_10). Sites TI\_13 and TI\_14, in the sandy shallow basin were less than 5 m apart. A light chamber was deployed at site TI\_14, whereas a dark chamber was deployed at site TI\_13 and all other chamber sites (Table 2-1). Section 2B2 explains the difference between 'light' and 'dark' chambers.

Sediment cores were collected from sites TI\_10, TI\_12, and TI\_13 (Table 2-1). Water column samples were collected from all chamber sites (TI\_13 and TI\_14 were considered the same site), and two additional sites in the shallow basin (TI\_15 and TI\_16; Figure 2-2) to provide greater spatial coverage of water column conditions.

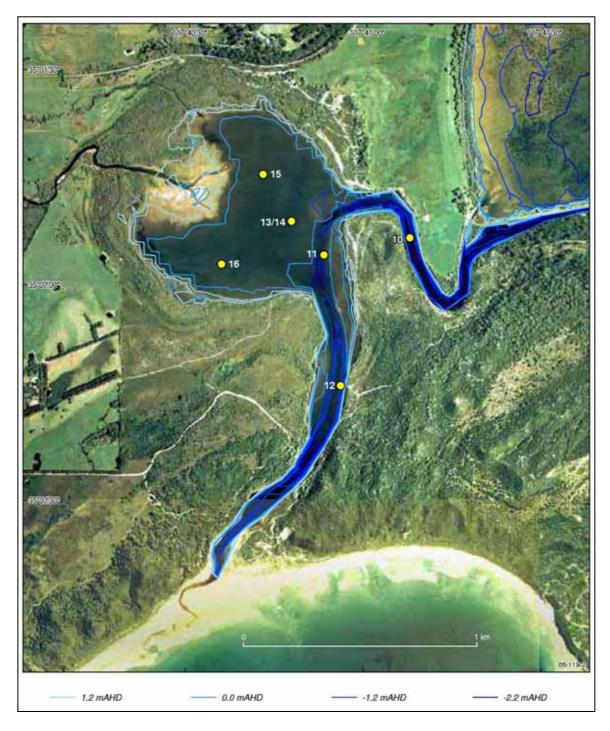


Figure 2-2. Torbay Inlet bathymetry and sampling site locations. mAHD = metres above Australian Height Datum. Aerial photo base image source: Department of Land Information, WA Government.

# 2A2. Lake Powell

Lake Powell is shallow ( $\sim$ 0.5 m) and generally sandy (Figure 2-3). Sediments across most of the Lake comprise a fine surface layer (3 mm) of brown silt on the surface with leaf litter in some areas. The upper sediments (to approximately 15 cm depth) consist of brown sand with black organic

material. Below this are clayey sands and brown clays. Near the entrance to Marbelup Brook, the sediments are brown muds to 10 cm depth, over a thick layer of fine organic dark muds. These muds are mobile, and the area they cover can change in size and location depending on wind direction (Geoff Bastyan personal observation). Occasionally, the muds can extend along much of the southern shoreline but are usually confined to the area near the Brook mouth.

Four chamber sites were chosen to represent the sandy sediments that comprise most of the Lake (LP\_12, LP\_13, LP\_15, and LP\_16; Figure 2-3; Table 2-1) and one chamber site was located within the black organic-rich muds at the entrance to Marbelup Brook (LP\_14). Sites LP\_15 and LP\_16 were less than 5 m apart with a light chamber deployed at LP\_16 and a dark chamber at LP\_15 (Table 2-1). Dark chambers were deployed at all other chamber sites.

Sediment cores were collected from sites LP\_12, LP\_13, and LP\_14 (Table 2-1). Water column samples were collected from all chamber sites (LP\_15 and LP\_16 were considered the same site), and two additional sites (LP\_17 and LP\_18; Figure 2-3). Site LP\_18 was located near the entrance of Grasmere Drain into Lake Powell to allow assessment of inputs from this tributary into the Lake.

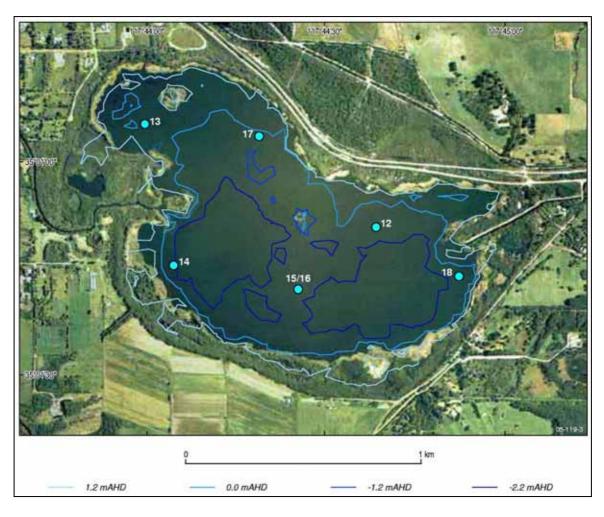


Figure 2-3. Lake Powell bathymetry and sampling site locations. mAHD = metres above Australian Height Datum. Aerial photo base image source: Department of Land Information, WA Government.

### 2A3. Marbelup Brook

The portion of Marbelup Brook included in this study is a stagnant section of the original channel, downstream of an earth bund installed in the 1950s to divert the main channel flow directly to Torbay Inlet rather than via Lake Powell. This section of Marbelup Brook has a deep (~1.5 m), narrow channel with dark, tannin-coloured waters (Figure 2-4). The Brook contains woody debris and leaf litter along much of its length and algal scum was observed on the water surface near the plug at the time of sampling. The sediments are predominantly black organic-rich muds containing plant and leaf material.

Chambers were deployed at five sites along the length of Marbelup Brook between the plug and the entrance to Lake Powell (Figure 2-4; Table 2-1). Three chamber sites were located upstream of the outlet to the penstocks; two of these were less than 5 m apart and positioned near the plug (MLB\_1 and MLB\_2), and one was further downstream, nearer the outlet to the penstocks (MLB\_3). Two chambers were deployed between the outlet to the penstocks and the entrance to Lake Powell (MLB\_4 and MLB\_5). These two sites were less than 5 m apart, with a light chamber at MLB\_5 and a dark chamber at MLB\_4 (Table 2-1). However, it is unlikely the chamber deployed at MLB\_5 functioned as a 'light' chamber because the extremely dark waters would have prevented light from penetrating to the bottom.

Cores were collected from all chamber sites (MLB\_1, MLB\_3, and MLB\_4; Table 2-1). For coring and water column sampling purposes, MLB\_1 and MLB\_2 were considered the same site, and MLB\_4 and MLB\_5 were considered the same site. The upper section of the cores from MLB\_1 and MLB\_3 comprised loose black plant and leaf material, and soft mud. At MLB\_1, this organic material extended to 10 cm depth, below which there was clean, grey sand. At site MLB\_3, the organic material extended to approximately 20 cm depth, below which there was dark brown organic mud. The top 16 cm of sediment from site MLB\_4 consisted of black organic mud. Below this, there was a thin (2 cm) layer of clean grey sand and then dry, grey, hard mud to at least 40 cm depth. Water column samples were collected from sites MLB\_1/2, MLB\_3, and MLB\_4/5 (Table 2-1).

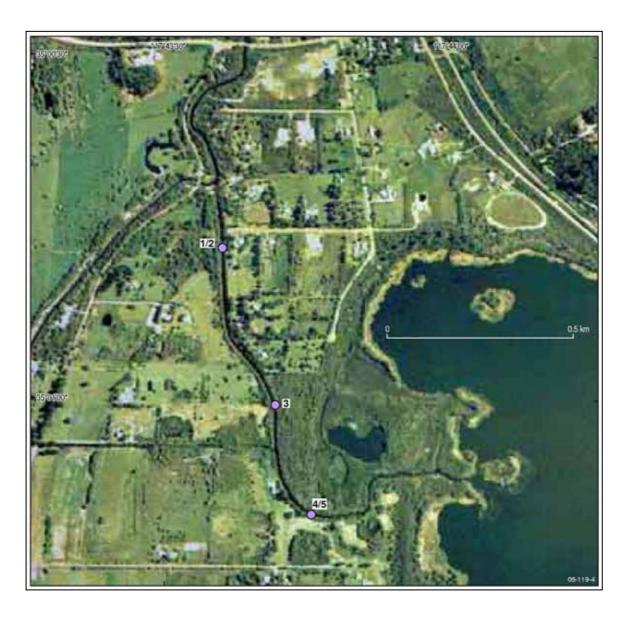


Figure 2-4. Marbelup Brook sampling site locations. mAHD = metres above Australian Height Datum. Aerial photo base image source: Department of Land Information, WA Government.

## 2A4. Lake Manarup

Lake Manarup is broad, shallow ( $\sim$ 0.7 m) and muddy (Figure 2-5). The sediment is mainly light brown organic muds with small sand lenses and muddy sands in some parts. Grey clays underlie these organic muds.

Chambers were deployed at five sites in the central part of the lake (Figure 2-5). Dark chambers were deployed at sites MNL\_1, MNL\_2, MNL\_3, and MNL\_4, whereas a light chamber was deployed at MNL\_5 (less than 5 m from MNL\_4; Table 2-1).

Sediment cores were collected from MNL\_1, MNL\_2, and MNL\_4 (Table 2-1). Water column samples were collected at the chamber sites (MNL\_4 and MNL\_5 were considered the same site) as well as two additional sites (MNL\_6 and MNL\_7; Figure 2-5). Site MNL\_6 was downstream near the floodgates separating the lake from Torbay Inlet, and site MNL 7 was in the drain feeding Lake

Manarup, which flows from Ewart Swamp via a siphon that diverts water underneath Marbelup High Level Drain (Figure 1-2).

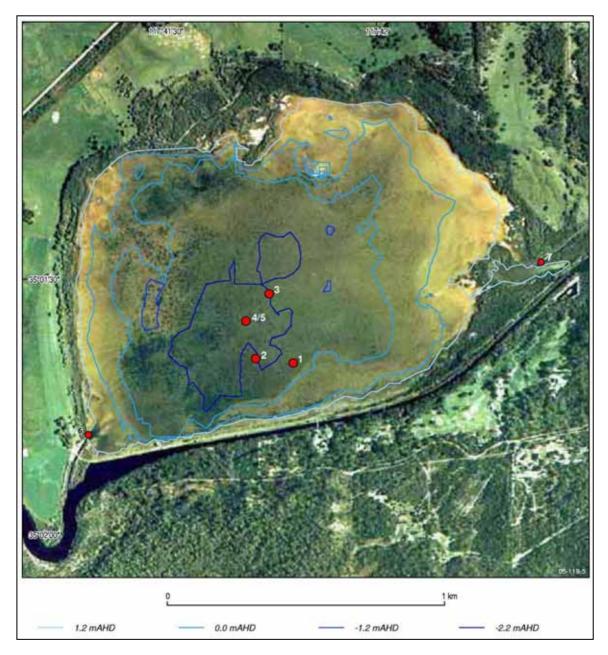


Figure 2-5. Lake Manarup bathymetry sampling site locations. mAHD = metres above Australian Height Datum. Aerial photo base image source: Department of Land Information, WA Government.

# **2B. SAMPLING METHODS**

Water column, benthic chamber, and sediment core sampling methods are briefly described below. See Appendix 1 for more detail regarding benthic chamber operations, and Appendix 2 for detailed sediment core sampling procedures. Appendix 3 outlines the analytical methods for determining ammonia ( $NH_4^+$ ), nitrate + nitrite ( $NO_X$ ), phosphate ( $PO_4^{3-}$ ), silicate ( $SiO_4^{4-}$ ), total carbon dioxide ( $TCO_2$ ), chlorophyll a (Chl-a), and total suspended matter (TSM) concentrations. Appendix 4 gives the methods for calculating benthic fluxes and denitrification efficiencies.

# 2B1. Water Column

Water column sampling was performed at each benthic chamber site (Table 2-1). Several additional sites were also sampled to provide a greater spatial representation of water column conditions in each waterbody. Water column sampling aimed to determine water column conditions at the time of benthic chamber experiments and core collections, that is, whether the water column was well mixed or stratified in relation to salinity, dissolved oxygen and/or temperature, as well as determine if any of the tributaries were distinct sources of nutrients.

Water column temperature, salinity, and dissolved oxygen (DO) was measured at the surface and bottom of the water column using a YSI 600 XLM sonde. Photosynthetically active radiation (PAR) was measured at several depth intervals throughout the water column using a quantum sensor LICOR light meter (LI-250A) and the average vertical light attenuation coefficient ( $K_d$ ) was calculated from the PAR profiles.

Discrete surface water samples were collected in 1L plastic bottles. At deep sites, bottom waters were also collected using a Niskin bottle. Both surface and bottom water samples were analysed for nutrients ( $NH_4^+$ ,  $NO_X$ ,  $SiO_4^{4-}$ ,  $PO_4^{3-}$ ; see Appendix 3 for methods). These were filtered using 0.45  $\mu$ m filters and refrigerated until analysed within 48 hours at the NMI laboratories in Perth. Surface water samples from each site were also analysed for TSM and Chl-a (Appendix 3). These were vacuum filtered using 0.45  $\mu$ m filters and analysed within 24 hours. The filters used for Chl-a analysis were kept frozen until extraction in 20 mL of 90 % acetone. The extracted samples were shaken vigorously, placed in an ultrasonic bath, centrifuged and analysed by fluorometry.

#### 2B2. Benthic Chambers

Nutrient (NH<sub>4</sub><sup>+</sup>, NO<sub>X</sub>, SiO<sub>4</sub><sup>4-</sup>, PO<sub>4</sub><sup>3-</sup>), DO, and TCO<sub>2</sub> fluxes were measured at the sediment-water interface using benthic chambers (Figure 2-6) according to the methods of Berelson *et al.* (1998). Fluxes were calculated from the change (either positive or negative) in metabolite concentrations over time inside each benthic chamber (see Appendix 4 for calculation). Five chambers were deployed within each waterway. Four of these were blacked out to stop sunlight entering (dark chambers), and one was transparent to sunlight (light chamber). The dark chambers recorded oxygen consumption and nutrient release from respiration processes, whereas light chambers recorded *net* oxygen flux (production minus consumption) and nutrient release from both respiration and photosynthesis.

Timing of sample draws from each chamber involved: an initial water sample representing ambient conditions (bottom water) taken immediately before lid closure; a sample draw taken 30 minutes after lid closure; then, a sample drawn every 0.5 to 1.5 hours, with the last sample taken up to 8 hours after lid closure. Appendix 1 describes chamber specifications in more detail, as well as sample draw, sample handling, and sub-sampling procedures. Sample draws from each chamber

were analysed for NH<sub>4</sub><sup>+</sup>, NO<sub>X</sub>, nitrogen gas (N<sub>2</sub>), pH, alkalinity, PO<sub>4</sub><sup>3-</sup>, and SiO<sub>4</sub><sup>4-</sup> using the procedures outlined in Appendix 3. TCO<sub>2</sub> concentrations were calculated using the alkalinity and pH measurements, also described in Appendix 3. YSI data loggers recorded DO concentrations, salinity, and temperature both inside and outside each chamber. Appendix 4 explains how benthic fluxes and denitrification efficiencies were calculated from the raw benthic chamber data.

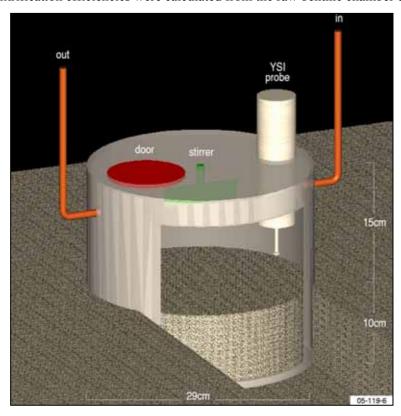


Figure 2-6. Schematic diagram of a benthic chamber experimental set-up.

#### 2B3. Cores

Three sediment cores were collected within each waterway for porewater and sediment analysis (Table 2-1). These were all located at benthic chamber sites. We collected these cores using a manually operated corer (Figure 2-7), which we pushed into the soft sediment using a long pole (pole corer; see Appendix 2 for more detail). The depth of sediment collected varied between 20 and 50 cm depending on how far the core barrel could be pushed into the sediment. Cores were sliced into depth intervals and centrifuged to separate porewaters from the solid phase. Porewaters were analysed for PO<sub>4</sub><sup>3-</sup>, NO<sub>x</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, SiO<sub>4</sub><sup>4-</sup>, and TCO<sub>2</sub> using the methods outlined in Appendix 3. Note that TCO<sub>2</sub> was measured by means of conductivity rather than the alkalinity titration method used for the lower concentration benthic chamber samples. We also measured the sediment porosity of each depth interval (see Appendix 2).

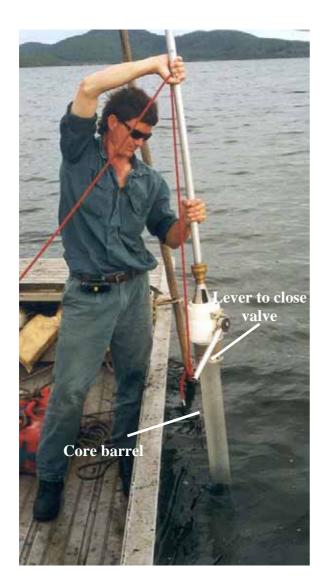


Figure 2-7. Collecting a sediment core using a pole corer.

# 3. Results

# 3A. WATER COLUMN

Water column conditions at the time of the survey differed significantly between the four different waterways (Table 3-1), and were greatly influenced by the extreme rainfall event that immediately preceded the survey (see Section 1A4 for details). The channel in Torbay Inlet and the site in Lake Manarup near the floodgates to Torbay Inlet were subject to tides and the intrusion of marine water following opening of the sand bar. Sites in these areas had high salinities, whereas all sites in Lake Powell and Marbelup Brook, and remaining sites in Lake Manarup and Torbay Inlet had low (fresh to brackish water) salinities.

Marbelup Brook stands out as having very low DO, and generally the highest nutrient concentrations. Surface water nutrient concentrations in Lake Powell and Torbay Inlet were also very high, probably representing nutrient-rich runoff from the catchment associated with the recent rainfall event. Water column conditions in each waterway are described in detail below.

Table 3-1 Water column properties and nutrient concentrations (Temp=temperature; DO=dissolved oxygen; Sal.=salinity;  $NH_4^+$ =ammonia;  $NO_X$ =oxidised nitrogen;  $PO_4^{3-}$ =phosphate;  $SiO_4^{4-}$ =silicate; Chl-a=chlorophyll a; TSM=total suspended matter;  $K_d$ =average vertical light attenuation coefficient)

Site	Depth (m)	Temp.	<b>DO</b> (%)	Sal.	<b>NH</b> <sub>4</sub> <sup>+</sup> (μΜ)	<b>NO</b> <sub>X</sub> (μΜ)	<b>PO</b> <sub>4</sub> <sup>3-</sup> (μΜ)	<b>SiO<sub>4</sub><sup>4-</sup></b> (μΜ)	Chl-a (µg/l)	TSM (mg/l)	<b>K</b> <sub>d</sub> (m <sup>-1</sup> )
TI_10	Surface 1.5	19.4 19.5	82 94	1.7 35.3	85.7 25.7	9.3 3.1	3.6 0.9	107.1 16.1	6.7	14.4	5.9
TI_11	Surface 0.9	21.1 19.8	115 118	28.1 37.2	42.1 15.7	12.1 1.1	1.5 0.7	39.3 3.9	3.4	15.6	4.1
TI_12	Surface 2.0	22.0 19.9	122 118	28.0 37.4	33.6 14.3	7.1 0.8	1.2	27.9 2.9	3.3	22.8	1.5
TI_13/14	Surface	21.3	107	7.2	71.4	8.6	2.6	82.1	5.5	14.0	5.5
TI_15	Surface	23.6	112	4.4	59.3	10.0	2.2	60.7	3.5	12.8	3.5
TI_16	Surface	23.5	110	9.7	37.9	9.3	1.5	35.7	3.9	23.2	4.1
LP_12	Surface	17.9	88	0.9	100.0	7.1	4.8	57.1	3.1	7.3	6.0
LP_13	Surface	17.7	76	0.9	107.1	7.9	4.5	64.3	4.1	7.3	5.1
LP_14	Surface	18.5	74	0.9	114.3	5.7	4.8	71.4	6.2	13.3	6.9
LP_15/16	Surface	17.9	78	8.0	100.0	7.9	4.5	75.0	5.0	10.5	7.2
LP_17	Surface	17.7	82	8.0	92.9	10.7	4.8	67.9	2.5	6.0	5.5
LP_18	Surface	17.4	49	0.7	78.6	4.6	4.5	185.7	7.4	20.0	7.8
MLB_1/2	Surface 1.5	16.1 16.5	11 3.5	0.8 1.2	85.7 135.7	1.7 1.1	2.6 4.8	107.1 135.7	2.3	7.6	8.2
MLB_3	Surface 1.5	16.6 16.0	40 10	0.9 0.9	142.9 128.6	4.8 4.4	5.8 7.4	96.4 107.1	3.6	12.0	6.3
MLB_4/5	Surface 1.0	16.0 15.3	50 47	0.9 0.9	171.4 164.3	6.6 7.9	5.8 5.5	96.4 89.3	9.3	18.4	7.7
MNL_1	Surface	15.4	83	9.3	3.9	0.0	0.4	6.8	4.4	7.2	3.1
MNL_2	Surface	15.7	78	9.1	2.9	0.0	0.4	5.7	3.9	2.2	1.4
MNL 3	Surface	15.9	84	8.9	4.1	0.0	0.4	4.6	5.9	13.5	1.9
MNL_4/5	Surface	16.0	80	9.0	2.7	0.0	0.4	4.6	4.0	9.3	2.9
MNL_6	Surface	18.6	53	24.9	2.4	0.0	0.4	4.6	2.6	5.2	1.8
MNL_7	Surface	16.5	138	2.4	5.4	3.0	0.9	225.0	116.5	23.0	5.4

# 3A1. Torbay Inlet

The sand bar that usually blocks water exchange between Torbay Inlet (Figure 2-2) and the ocean was naturally breached by the large amount of runoff from the heavy rainfall that occurred immediately prior to sampling. This allowed tidal exchange with the ocean to commence and the intrusion of marine water into the Inlet. The marine water entered as a salt wedge and moved up the channel, remaining under the fresher water entering from the catchment. Water column properties at site TI\_10 strongly reflected this situation (Table 3-1), where surface water salinities were fresh (1.7) and bottom waters were marine (35.3). The shallow sandy sites (TI\_13/14, TI\_15, and TI\_16) were relatively fresh (salinities ranging from 4.4 to 9.7), indicating runoff from Torbay Main Drain was a greater influence at these sites than the marine intrusion.

Sites TI\_11 and TI\_12 showed slight thermal stratification (temperatures decreased from 21.1 to 19.8 and 22.0 to 19.9 °C respectively). All sites in Torbay Inlet were well oxygenated, except site TI\_10, where bottom waters were more oxygenated (94 %) than surface waters (82 %), probably reflecting the presence of the salt wedge comprising more oxygenated marine water.

The contribution of nutrients by surface water runoff was clearly evident in the water column concentrations for Torbay Inlet. Nutrient concentrations were all higher in surface waters compared to bottom waters and were strongly related to salinity. The highest  $NH_4^+$ ,  $PO_4^{3-}$ ,  $SiO_4^{4-}$ , and Chl-a concentrations were measured at sites  $TI\_10$  and  $TI\_13/14$ , which are the sites closest to the catchment inputs of Marbelup Brook and Torbay Main Drain respectively. In the surface waters,  $NH_4^+$  concentrations decreased from 85.7  $\mu$ M at site  $TI\_10$  to 33.6  $\mu$ M at  $TI\_12$ , where there was a stronger marine influence. Bottom water concentrations ranged from 14.3 to 25.7  $\mu$ M. Surface water  $SiO_4^{4-}$  concentrations ranged from 27.9 to 107.1  $\mu$ M and bottom water concentrations ranged from 2.9 to 16.1  $\mu$ M.

Freshwater inputs also appeared to influence light attenuation, with the highest  $K_d$  values measured at sites TI\_10 and TI\_13/14 ( $K_d = 5.5$  and  $5.9 \text{ m}^{-1}$  respectively). The lowest  $K_d$  value (1.5 m<sup>-1</sup>) was measured at site TI\_12. Chl-a concentrations were >3 µg/L with the highest concentrations at sites TI\_10 and TI\_13/14. TSM values were greatest at sites TI\_12 and TI\_16 and did not appear to be related to the other parameters, suggesting that Chl-a and/or coloured dissolved organic matter was discharging into the estuary and limiting light penetration in the water column.

#### 3A2. Lake Powell

Lake Powell sampling sites (Figure 2-3) all had similar water column characteristics (Table 3-1), indicating the lake, at the time, was fully mixed. Salinities were low (~0.85) and temperatures ranged from 17.4 to 18.5 °C. At site LP\_18, the salinity was slightly lower than other sites (0.72), showing the influence of freshwater runoff from Grasmere Drain. The waters were depleted in oxygen at all sites, with concentrations from 49 % at LP 18 to 88 % at LP 12.

Nutrient concentrations in Lake Powell were much higher than in Torbay Inlet, probably because of nutrient-rich runoff from the catchment from the preceding rainfall event. All sites had similar nutrient concentrations except LP\_18. At sites LP\_12 to LP\_17,  $NH_4^+$  concentrations ranged from 92.9 to 114.3  $\mu$ M,  $NO_X$  from 5.7 to 10.7  $\mu$ M,  $PO_4^{3-}$  from 4.5 to 4.8  $\mu$ M and  $SiO_4^{4-}$  from 57.1 to 75.0  $\mu$ M. Interestingly, at site LP\_18,  $NH_4^+$  and  $NO_X$  concentrations were much lower than other sites (78.6  $\mu$ M and 4.6  $\mu$ M respectively). However, the  $PO_4^{3-}$  concentration was similar to other sites (4.5  $\mu$ M) and the  $SiO_4^{4-}$  concentration was significantly larger (185.7  $\mu$ M). The highest  $NH_4$  concentration measured was at site LP\_14 where the sediments comprise black, organic-rich muds.

The waters of Lake Powell were turbid and  $K_d$  values were >5 m<sup>-1</sup> at all sites. Chl-a concentrations ranged from 2.5 to 7.4  $\mu$ g/L and TSM ranged from 6 to 20 mg/L. Site LP\_18 had the highest TSM and Chl-a concentrations and the highest light attenuation, possibly a result of its proximity to Grasmere Drain.

## 3A3. Marbelup Brook

Dissolved oxygen in Marbelup Brook (Figure 2-4) was extremely depleted in the surface waters at all sites (11 to 50 % saturation) and almost totally depleted in the bottom waters at sites MLB\_1/2 and MLB\_3 (4 and 10 % respectively). Dissolved oxygen in the bottom water at site MLB\_4/5 was only slightly lower than the surface water (47 %). Salinities were low at all sites (0.8 to 1.2) and sites MLB\_3 and MLB\_4/5 were fully mixed with respect to salinity. At site MLB\_1/2, salinity was slightly higher in the bottom waters than the surface waters. Temperatures were similar at all sites (15.3 to 16.6 °C).

Nutrient (NH<sub>4</sub><sup>+</sup>, PO<sub>4</sub><sup>3-</sup> and SiO<sub>4</sub> <sup>4-</sup>) concentrations in Marbelup Brook were in general the highest out of all four waterbodies sampled. Moving upstream from site MLB\_4/5 to MLB\_1/2, surface water NH<sub>4</sub><sup>+</sup> concentrations decreased from 171.4  $\mu$ M to 85.7  $\mu$ M, NO<sub>X</sub> concentrations decreased from 6.6  $\mu$ M to 1.7  $\mu$ M, and PO<sub>4</sub><sup>3-</sup> concentrations decreased from 5.8  $\mu$ M to 2.6  $\mu$ M, whereas surface water SiO<sub>4</sub><sup>4-</sup> concentrations increased from 96.4 to 107.1  $\mu$ M.

Bottom water nutrient concentrations were also high with  $NH_4^+$  ranging from 128.6 to 164.3  $\mu$ M,  $NO_X$  from 1.1 to 7.9  $\mu$ M,  $PO_4^{3^-}$  from 4.8 to 7.4  $\mu$ M, and  $SiO_4^{4^+}$  from 89.3 to 135.7  $\mu$ M. At site  $MLB_1^{-1/2}$ , surface water  $NH_4^+$ ,  $PO_4^{3^-}$  and  $SiO_4^{4^-}$  concentrations were lower than bottom water concentrations. At site  $MLB_3^-$ , surface water  $NH_4^+$  concentrations were lower than in the bottom waters, and surface water  $PO_4^{3^-}$  and  $SiO_4^{4^-}$  concentrations were lower than in the bottom waters. At site  $MLB_4^-$ 5, surface water  $NH_4^+$ ,  $PO_4^{3^-}$  and  $SiO_4^{4^-}$  concentrations were all larger than bottom water concentrations.

High concentrations of NH<sub>4</sub><sup>+</sup>, PO<sub>4</sub><sup>3</sup>-, and SiO<sub>4</sub><sup>4</sup>- in the bottom waters at all sites suggest that the sediments contribute large amounts of nutrients to the water column. However, nutrient-rich floodwaters from Lake Powell flowing through Marbelup Brook to the penstocks and into Marbelup High Level Drain (see Figure 1-2) have resulted in higher surface water nutrient concentrations at MLB\_4/5. Water column conditions at MLB\_1/2 suggested that floodwaters from Lake Powell had not reached this site, as surface water nutrient concentrations were lower than bottom water nutrient concentrations and the water in this section of the creek was stagnant.

The water column in Marbelup Brook was very dark and tannin-coloured. Chl-a concentrations were relatively low at sites MLB\_1/2 and MLB\_3 (2.3 and 3.6  $\mu$ g/L respectively), and much higher at site MLB\_4/5 (9.3  $\mu$ g/L). TSM values increased with proximity to Lake Powell, ranging from 7.6 mg/L at site MLB\_1/2 to 18.4 mg/L at site MLB\_4/5.  $K_d$  values were generally higher than the other waterways and ranged from 6.3 to 8.2 m<sup>-1</sup>. Chl-a and TSM concentrations did not correlate well with  $K_d$  values, indicating that it is likely coloured dissolved matter contributing to the high light attenuation measured in the water column. Such high light attenuation in the water column would stop light reaching the bottom sediments and therefore prevent benthic photosynthesis from occurring.

# 3A4. Lake Manarup

The water column of Lake Manarup (Figure 2-5) was the clearest of all the waterways sampled. Water column properties were similar at all sites within the central part of the basin (MNL\_1 to MNL\_4/5), indicating this part of the waterway was well mixed. Temperatures ranged from 15.4 to 16.0 °C, salinity from 8.9 to 9.3, and DO was slightly depleted, ranging from 78 to 84 %. Water column conditions downstream near the floodgates (MNL\_6) and in the upstream drain (MNL\_7), differed significantly to the main body of the lake. At MNL\_6, the temperature was higher (18.6 °C), and DO was significantly depleted (53 %). Salinity was also much higher (24.9), possibly due to marine water leaking through the floodgates from Torbay Inlet. At MNL\_7, salinity was 2.4, indicating freshwater was entering the lake from the catchment (North Creek Drain; Figure 1-2). DO at this site was high (138 %), corresponding to extremely high Chl-a (116.5 μg/L).

Water column nutrient concentrations at the main basin sites were the lowest of all four waterways sampled.  $NH_4^+$  concentrations ranged from 2.7 to 4.1  $\mu$ M,  $NO_X$  was below detection limits,  $PO_4^{3-}$  was 0.4  $\mu$ M at all four sites, and  $SiO_4^{4-}$  ranged from 4.6 to 6.8  $\mu$ M. Nutrient concentrations at MNL\_6 were similar to the rest of the lake. However at site MLB\_7, nutrient concentrations were all high  $(NH_4^+ = 5.4 \,\mu\text{M}, NO_X = 3 \,\mu\text{M}, PO_4^{3-} = 0.9 \,\mu\text{M})$ , particularly  $SiO_4^{4-}$  (225  $\mu$ M).

Chl-a concentrations at the main basin sites ranged from 3.9 to 5.9  $\mu$ g/L, however TSM was more variable, ranging from 2.2 to 13.5 mg/L. This is likely due to disturbance of the water column and bottom sediments during sampling. Light attenuation was the lowest of all waterways sampled, with  $K_d$  values ranging from 1.4 to 3.1 m<sup>-1</sup> in the main body of the lake. The Chl-a concentration (2.6  $\mu$ g/L), TSM (5.2 mg/L), and light attenuation ( $K_d = 1.8 \text{ m}^{-1}$ ) were all low at MNL\_6. At MNL\_7, TSM was elevated (23 mg/L) and light attenuation was higher than in the central part of the lake ( $K_d = 5.4 \text{ m}^{-1}$ ).

# 3A5. Summary of Water Column Conditions

Water column nutrient concentrations in the Torbay drainage system were generally very high, and NH<sub>4</sub><sup>+</sup> concentrations in all sites in all waterways (except the central part of Lake Manarup) greatly exceeded the ANZECC water quality trigger values for southwestern Australian aquatic ecosystems (NH<sub>4</sub><sup>+</sup> = 2.86  $\mu$ M; ANZECC 2000). All sites also exceeded the guidelines for PO<sub>4</sub><sup>3-</sup> (FRP = 0.16  $\mu$ M). The surface waters in Torbay Inlet, all sites in Lake Powell, sites MLB\_3 and MLB\_4/5, as well as MNL\_7, exceeded the guidelines for NO<sub>X</sub> (3.2  $\mu$ M). Although there are no guideline values recommended for SiO<sub>4</sub><sup>4-</sup>, very high concentrations were recorded at all sites, except in Lake Manarup, and it is likely these are also cause for concern. Overall, Marbelup Brook had the highest water column nutrient concentrations of all studied waterways.

DO was generally depleted in all the waterways, except Torbay Inlet. Light attenuation was high at most sights, particularly in Marbelup Brook and Lake Powell, and light availability may be an important control on primary productivity. Chl-a concentrations were similar in all waterways and were generally close to the ANZECC trigger value of 3  $\mu$ g/L. However, several sites had high Chl-a concentrations, particularly site MNL\_7 (116.5  $\mu$ g/L).

# **3B. BENTHIC FLUXES**

Biogeochemical processes occurring within the sediments control the rate of exchange of nutrients (NH<sub>4</sub><sup>+</sup>, NO<sub>X</sub>, PO<sub>4</sub><sup>3</sup>-, and SiO<sub>4</sub><sup>4</sup>-), O<sub>2</sub>, and TCO<sub>2</sub> between the sediment and overlying water. The microbially mediated breakdown of organic matter within the sediments results in the consumption and release of these metabolites at the sediment-water interface and any changes in the nature of this process can influence water quality and primary production within the estuary.

All benthic chamber experiments were successful except for two in Marbelup Brook (MLB\_1 and MLB\_3), where the chambers failed to seal adequately. Table 3-2 presents the benthic fluxes determined for all successful chamber incubations conducted within the Torbay drainage system. These fluxes were calculated based on the change in solute concentrations within each chamber over time (refer to methods in Appendix 4).

The magnitude of fluxes varied greatly both within and between the four waterways. Sites TI\_11 and TI\_12, both located in the channel of Torbay Inlet, had by far the largest fluxes for most solutes (TCO<sub>2</sub>, NH<sub>4</sub><sup>+</sup>, PO<sub>4</sub><sup>3-</sup>, and SiO<sub>4</sub><sup>4-</sup>). All three sites in Marbelup Brook, and the muddy site in Lake Powell (LP\_14), recorded the next highest fluxes. The remaining sites in Torbay Inlet and Lake Powell, and all sites in Lake Manarup, had relatively lower fluxes.

Following is an outline of the benthic flux results for each waterway. Note the graphs have different scales for each waterway to account for the large range in flux values.

Table 3-2. Benthic fluxes for all sites (all in mmol  $m^{-2}$  day<sup>-1</sup>). Positive values represent a flux out of the sediment whereas negative values represent a flux into the sediment. n/a = not available due to oxygen probe failure. bdl = below detection limits.

Site	DO	TCO <sub>2</sub>	$NH_4^+$	NO <sub>X</sub>	$N_2$	PO <sub>4</sub> <sup>3-</sup>	SiO <sub>4</sub> <sup>4-</sup>
TI_10	-65.0	-40.6	-5.5	-0.4	-0.3	-0.1	0.1
TI_11	-78.7	789.5	122.5	-1.8	-6.4	14.1	37.5
TI_12	-70.8	1104.3	110.7	-0.9	-12.5	20.0	31.4
TI_13	-67.3	149.2	-3.3	3.4	3.4	0.1	-0.3
TI_14	67.9	-77.6	-12.8	3.8	-1.1	0.1	-3.0
LP_12	-69.6	53.1	0.0	-1.0	4.0	-0.2	0.0
LP_13	-66.4	32.8	-0.2	0.0	4.8	-0.3	-3.7
LP_14	-102.3	180.8	17.7	-0.8	7.3	-0.4	3.2
LP_15	-78.8	62.5	-9.4	-1.0	1.6	0.0	0.1
LP_16	-69.3	97.2	0.0	-1.0	3.4	-0.6	-8.0
MLB_2	n/a	643.3	22.0	2.4	-115.5	-0.2	16.1
MLB_4	-111.4	210.7	31.6	-1.6	-49.9	2.6	1.7
MLB_5	-88.9	106.1	10.8	-2.3	-25.3	-0.3	-3.5
MNL_1	n/a	145.4	4.1	bdl	4.3	bdl	14.0
MNL_2	n/a	83.0	3.7	bdl	3.4	bdl	9.2
MNL_3	n/a	90.1	2.4	bdl	2.3	bdl	9.6
MNL_4	-98.0	97.8	1.7	bdl	2.1	bdl	7.5
MNL_5	-70.9	43.0	1.1	bdl	2.4	bdl	5.0

# 3B1. Torbay Inlet

All fluxes were derived from dark benthic chambers except for Site TI\_14, which was a light chamber and located at the same site as TI\_13. The fluxes measured in the lower channel sites (TI\_11 and TI\_12) were consistently higher for all metabolites except NO<sub>X</sub> compared to the upper channel (TI\_10) and the shallow sandy sites (TI\_13 and TI\_14; Figure 3-1 to Figure 3-3).

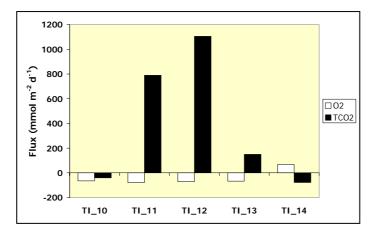


Figure 3-1. O<sub>2</sub> and TCO<sub>2</sub> fluxes from Torbay Inlet

Apart from site TI\_10, oxygen consumption rates in Torbay Inlet were all less than TCO<sub>2</sub> production rates. The light chamber at site TI\_14 showed signs of photosynthetic production with oxygen produced (67.9 mmol m<sup>-2</sup> day<sup>-1</sup>) and TCO<sub>2</sub> consumed (-77.6 mmol m<sup>-2</sup> day<sup>-1</sup>). The lower channel sites (sites TI\_11 and TI\_12) have extremely high TCO<sub>2</sub> fluxes (789.5 and 1104.3 mmol m<sup>-2</sup> day<sup>-1</sup> respectively).

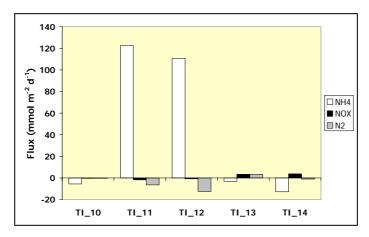


Figure 3-2.  $NH_4^+$ ,  $NO_X$ , and  $N_2$  fluxes from Torbay Inlet

The lower channel sites had very high  $NH_4^+$  fluxes (122.5 and 110.7 mmol m<sup>-2</sup> day<sup>-1</sup> respectively), whereas the remaining sites all had  $NH_4^+$  uptake (ranging from -3.3 to -12.8 mmol m<sup>-2</sup> day<sup>-1</sup>). The shallow sandy sites (sites  $TI_13$  and  $TI_14$ ) are the only sites with  $NO_X$  release (3.4 and 3.8 mmol m<sup>-2</sup> day<sup>-1</sup> respectively). There were significant  $N_2$  uptake rates in the lower channel sites (-6.4 and -12.5 mmol m<sup>-2</sup> day<sup>-1</sup>)

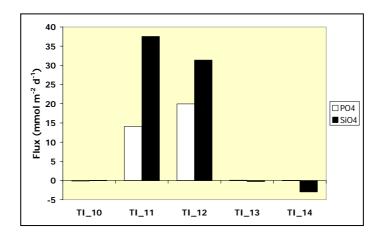


Figure 3-3. PO<sub>4</sub><sup>3-</sup> and SiO<sub>4</sub><sup>4-</sup> fluxes from Torbay Inlet

 $PO_4^{3-}$  and  $SiO_4^{4-}$  fluxes are low or negative for all sites except the lower channel sites.  $PO_4^{3-}$  fluxes are very high at these sites (14.1 and 20.0 mmol m<sup>-2</sup> day<sup>-1</sup>) as are  $SiO_4^{4-}$  fluxes (37.5 and 31.4 mmol m<sup>-2</sup> day<sup>-1</sup>).

## 3B2. Lake Powell

Figures 3-4 to 3-6 show the benthic nutrient fluxes for Lake Powell. All fluxes were derived from dark benthic chambers except for Site LP\_16, which was a light chamber and located at the same site as LP\_15.

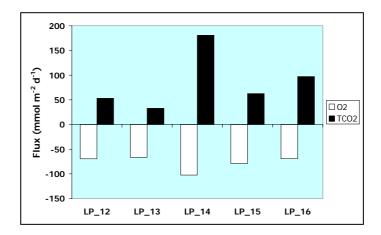


Figure 3-4. O2 and TCO2 fluxes from Lake Powell

All sites had similar  $O_2$  consumption and  $TCO_2$  release rates, except the site with black organic mud (site LP\_14), which had significantly higher  $TCO_2$  than  $O_2$  fluxes (180.8 and -102.3 mmol m<sup>-2</sup> day<sup>-1</sup> respectively).

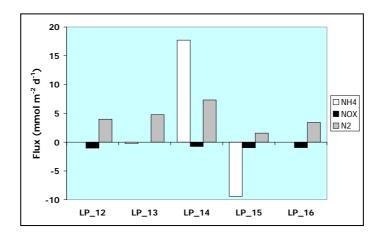


Figure 3-5.  $NH_4^+$ ,  $NO_X$ , and  $N_2$  fluxes from Lake Powell

Site LP\_14 had a large  $NH_4^+$  release (17.7 mmol m<sup>-2</sup> day<sup>-1</sup>) while site LP\_15 had a significant  $NH_4^+$  uptake (-9.4 mmol m<sup>-2</sup> day<sup>-1</sup>). All other sites had negligible  $NH_4$  fluxes.  $NO_X$  fluxes were small and negative at all sites. All sites had positive  $N_2$  fluxes ranging from 1.6 mmol m<sup>-2</sup> day<sup>-1</sup> at site LP\_15 to 7.3 mmol m<sup>-2</sup> day<sup>-1</sup> at site LP\_14

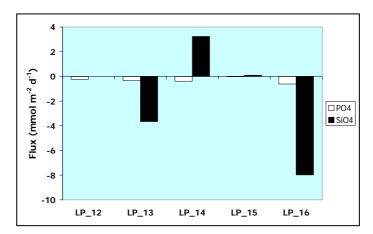


Figure 3-6.  $PO_4^{3-}$  and  $SiO_4^{4-}$  fluxes from Lake Powell

 $PO_4^{3-}$  fluxes were low and mostly negative at all sites. Site LP\_14 has the only significant release of  $SiO_4^{4-}$  (3.2 mmol m<sup>-2</sup> day<sup>-1</sup>), while sites LP\_13 and LP\_16 both had significant  $SiO_4^{4-}$  uptake (-3.7 and -8.0 mmol m<sup>-2</sup> day<sup>-1</sup> respectively)

# 3B3. Marbelup Brook

Figures 3-7 to 3-9 show the benthic nutrient fluxes for Marbelup Brook. The benthic chambers deployed at sites MLB\_1 and MLB\_3 failed to seal adequately, therefore, no data is shown for these sites. Sites MLB\_4 and MLB\_5 were located together with MLB\_5 being a light chambers. However, due to the water clarity, no light would have reached this chamber (see Kd values in Table 3-1 and results in Section 3A3).

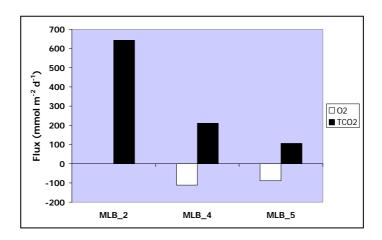


Figure 3-7. O<sub>2</sub> and TCO<sub>2</sub> fluxes from Marbelup Brook

No  $O_2$  flux was recorded at site MLB\_2 due to a failure of the oxygen probe.  $O_2$  uptake rates at sites MLB\_4 and MLB\_5 were very high (-111.4 and -88.9 mmol m<sup>-2</sup> day<sup>-1</sup> respectively). TCO<sub>2</sub> fluxes were also very high, ranging from 106.1 mmol m<sup>-2</sup> day<sup>-1</sup> at site MLB\_5 to 643.3 mmol m<sup>-2</sup> day<sup>-1</sup> at site MLB\_2.

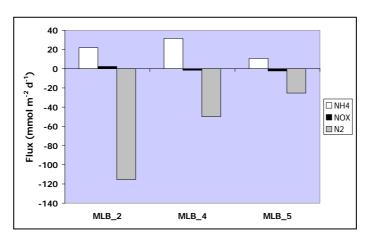


Figure 3-8.  $NH_4^+$ ,  $NO_X$ , and  $N_2$  fluxes from Marbelup Brook

 $NH_4^+$  fluxes were high at all sites, ranging from 10.8 mmol m<sup>-2</sup> day<sup>-1</sup> at site MLB\_5 to 31.6 mmol m<sup>-2</sup> day<sup>-1</sup> at site MLB\_4.  $NO_X$  fluxes are either very small or negative at all sites.  $N_2$  uptake rates were extremely high at all sites and exceeded -100 mmol m<sup>-2</sup> day<sup>-1</sup> at site MLB\_2.

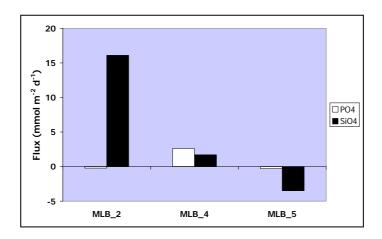


Figure 3-9.  $PO_4^{3-}$  and  $SiO_4^{4-}$  fluxes from Marbelup Brook

The only significant  $PO_4^{3-}$  flux was recorded at site MLB\_4 (2.6 mmol m<sup>-2</sup> day<sup>-1</sup>), the other sites had small negative fluxes.  $SiO_4^{4-}$  fluxes varied widely between sites with 16.1 mmol m<sup>-2</sup> day<sup>-1</sup> at site MLB\_2 and -3.5 mmol m<sup>-2</sup> day<sup>-1</sup> at site MLB\_5.

### 3B4. Lake Manarup

Figures 3-10 to 3-12 show the benthic nutrient fluxes for Lake Manarup. All fluxes were derived from dark benthic chambers except for site MNL\_5, which was a light chamber and located at the same site as MNL 4. Fluxes at all sites were generally similar and relatively small.

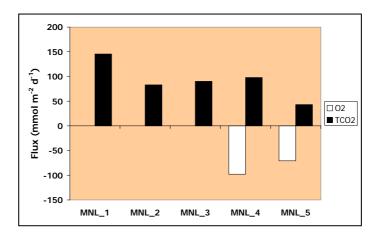


Figure 3-10. O<sub>2</sub> and TCO<sub>2</sub> fluxes from Lake Manarup

No  $O_2$  fluxes were recorded at sites MNL\_1, MNL\_2 and MNL\_3 due to a failure of the oxygen probe.  $O_2$  consumption and  $TCO_2$  release were greater at MNL\_4 than at MNL\_5 possible due to some photosynthetic activity in the light chamber.  $TCO_2$  release rates in the dark chambers ranged from 83.0 to 145.4 mmol m<sup>-2</sup> day<sup>-1</sup>.

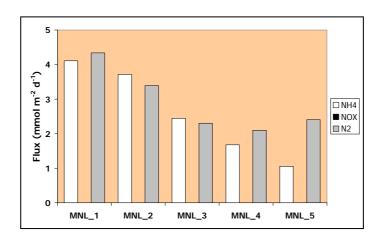


Figure 3-11.  $NH_4^+$ ,  $NO_X$ , and  $N_2$  fluxes from Lake Manarup

 $NH_4^+$  fluxes were low at all sites ranging from 1.1 mmol m<sup>-2</sup> day<sup>-1</sup> at site MNL\_5 to 4.1 mmol m<sup>-2</sup> day<sup>-1</sup> at site MNL\_1.  $NO_X$  was below detection limits at all sites.  $N_2$  fluxes followed a similar trend to the  $NH_4^+$  fluxes with site MNL\_1 having the highest release (4.3 mmol m<sup>-2</sup> day<sup>-1</sup>).

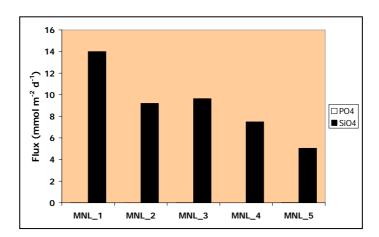


Figure 3-12.  $PO_4^{3-}$  and  $SiO_4^{4-}$  fluxes from Lake Manarup

 $PO_4^{3-}$  was below detection limits at all sites in Lake Manarup.  $SiO_4$  fluxes were reasonably high at all sites. Similar to the  $NH_4^+$  fluxes,  $SiO_4^{4-}$  fluxes were highest at site MNL\_1 (14.0 mmol m<sup>-2</sup> day<sup>-1</sup>) and lowest at site MNL\_5 (5.0 mmol m<sup>-2</sup> day<sup>-1</sup>)

### **3C. POREWATERS**

Vertical porewater concentration profiles of nutrients (Appendix 6) reflect the depth and intensity of organic matter mineralization in sediments. During the process of mineralization carbon, nitrogen, and phosphorus are released from particulate organic matter as  $TCO_2$ ,  $NH_4^+$ , and  $PO_4^{3-}$ .  $SiO_4^{4-}$  builds up in the pore water due to the dissolution of siliceous frustules of diatoms. The sum of nitrate and nitrite  $(NO_X)$  may form in the pore waters by secondary processes, particularly by nitrification  $(NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O)$ .

Concentration gradients with depth indicate the transport of ions by molecular diffusion from the depth of highest concentration to the depth of lowest concentration. A discrete maximum in concentration observed as a peak in the depth profile indicates the depth of maximum production rate. Constant concentrations with depth indicate that the observed solute is neither produced nor consumed. The degree of the build-up of a given porewater solute can be expressed as the porewater pool size (see Section 4D). Transport modes of the exchange of solutes between the porewater pool size and the water column are molecular diffusion and bioirrigation. The solute flux by bioirrigation typically exceeds the molecular diffusion flux several fold. Benthic flux measurements measure the total solute flux across the sediment-water interface.

### 3C1. Torbay Inlet

Two cores from the channel (site TI\_10 and TI\_12) and one core from the central part of Torbay Inlet (site TI\_13) were retrieved and analysed for the porewater composition. Although the two channel sites lie far apart from each other, i.e. site TI\_10 is upstream and site TI\_12 downstream of the central part of Torbay Inlet, the pore water composition is very similar. TCO<sub>2</sub>, NH<sub>4</sub><sup>+</sup>, and PO<sub>4</sub><sup>3-</sup> increase with depth and reach exceptionally high concentrations at the channel sites. As expected, TCO<sub>2</sub> and NH<sub>4</sub><sup>+</sup> depth profiles parallel each other according to concurrent release from organic matter. In contrast, PO<sub>4</sub><sup>3-</sup> shows the steep gradients in the upper 10 cm and levels off below, which may be related to the adsorption equilibrium with Fe-oxides.

The pore water composition in the central part of Torbay Inlet (site TI\_13) differs distinctively from the channel sites. Maximum concentrations of TCO<sub>2</sub>, NH<sub>4</sub><sup>+</sup>, and PO<sub>4</sub><sup>3-</sup> in the central part are less than 10 % of what is found at the channel sites and the concentration gradients in the top 10 cm are less distinct than at the channel sites. The TCO<sub>2</sub> profile at site TI\_13 reveals an intriguing minimum at a depth of 2 cm. This reflects most likely the transition between the formerly brackish bottom water conditions and the most recent more saline bottom water conditions following the opening of the bar. TCO<sub>2</sub> in marine water is more soluble (TCO<sub>2</sub> of 2.1 mM) than under brackish conditions, which leads to a presently ongoing intrusion of TCO<sub>2</sub>-rich saline water into the underlying TCO<sub>2</sub>-depleted brackish water in the sediment. This explanation is supported by all salinity profiles from Torbay Inlet showing higher salinities in the bottom water than at a few centimetres depth.

The channel sites are not only chemically distinct from the main part of the basin, but also porosity differs significantly. The channel sites are muddy with a rather constant porosity of about 90 % throughout the cores, whereas site TI\_13 in the central part of the basin is sand with porosity varying between 63 and 26 % within the core.

All pore water profiles from Torbay Inlet reveal an increase in salinity below the depth of minimum salinity. This suggests that saline water intrudes from below into the surface sediments and further into the bottom water of Torbay Inlet. The depth-contour map of Torbay Inlet (Figure 2-2) shows

the channel sites and the central basin site to be about -2.2 and -1 mAHD, respectively. This circumstance gives rise to the subsurface hydrologic connectivity between sea and estuarine water.

#### 3C2. Lake Powell

Similar to Torbay Inlet, the pore water composition in the three cores of Lake Powell (site LP\_12, LP\_13, LP\_14) reflects two distinct facies. Site LP\_14 is located in the SW part of the lake and has significantly higher TCO<sub>2</sub>, NH<sub>4</sub><sup>+</sup>, and PO<sub>4</sub><sup>3+</sup> concentrations than site LP\_12 and LP\_13. Steep concentration gradients of TCO<sub>2</sub>, NH<sub>4</sub><sup>+</sup>, and PO<sub>4</sub><sup>3-</sup> are only found in the top 5 cm of site LP\_12 and LP\_13, whereas organic matter break down prevails down to a depth of 20 cm at site LP\_14 based on pore water gradients. Furthermore, site LP\_14 is muddy with porosities consistently above 90 %, whereas sediments at site LP\_12 and LP\_13 consist of silty sands with porosities typically between 45 and 65 %. Despite the large dissimilarities between the silty sand (site LP\_12 and LP\_13) and the muddy facies (site LP\_14), the SiO<sub>4</sub><sup>4-</sup> profiles of sites LP\_12 and LP\_14 are rather similar displaying a constant increase with depth and reaching maximum concentrations of 800 to 1000 μM at about 35 cm depth.

#### 3C3. Marbelup Brook

Marbelup Brook sediments display a high variability in the porewater composition. Site MLB\_3 is located in between site MLB\_1 and MLB\_4 and contains the highest TCO<sub>2</sub>, NH<sub>4</sub><sup>+</sup>, and PO<sub>4</sub><sup>3-</sup> concentrations within Marbelup Brook. Intriguingly, the TCO<sub>2</sub> and NH<sub>4</sub><sup>+</sup> concentrations at site MLB\_3 follow the depth distribution of salinity, which increases below 10 cm with depth and reaches a maximum salinity of 6. If the salinity profile at site MLB\_3 results from brackish water intrusion, then the concentration gradients of TCO<sub>2</sub> and NH<sub>4</sub><sup>+</sup> may rather reflect mixing of waters with different compositions than in situ production of the two solutes from the breakdown of organic matter.

#### 3C4. Lake Manarup

Sediments at Lake Manarup show consistently lowest porewater maximum concentrations and concentration gradients for TCO<sub>2</sub>, NH<sub>4</sub><sup>+</sup>, and PO<sub>4</sub><sup>3-</sup> in all studied waterways. NO<sub>X</sub> concentrations were below detection limit in all cores. As noticed for porewater profiles of Torbay Inlet the depth distribution of NH<sub>4</sub><sup>+</sup> in Lake Manarup parallels TCO<sub>2</sub>, whereas PO<sub>4</sub><sup>3-</sup> shows distinct zones of enrichment and depletion possibly related to the adsorption of PO<sub>4</sub><sup>3-</sup> to Fe-oxides. Similar to Torbay Inlet, salinity increases with depth at all three studied sites of Lake Manarup. This observation suggests that subsurface brackish water intrudes as far north as Lake Manarup.

### 4. Discussion

### **4A. RATES OF ORGANIC MATTER BREAKDOWN**

During organic matter breakdown, microbes convert organic carbon compounds into TCO<sub>2</sub>. This process also releases nutrients in various forms, for example NH<sub>4</sub><sup>+</sup>, N<sub>2</sub>, PO<sub>4</sub><sup>3-</sup>, and SiO<sub>4</sub><sup>4-</sup>, and consumes oxygen, when available (oxic conditions), or other oxidants, such as sulfate, if oxygen is not available (anoxic conditions). Consequently, the release of TCO<sub>2</sub> from the sediment is a direct measure of the amount of organic matter breakdown occurring in the sediment. Figure 4-1 shows the average TCO<sub>2</sub> for Torbay Inlet, Lake Powell, Marbelup Brook, and Lake Manarup.

The channel of Torbay Inlet covers approximately 20 % of the total area of the Inlet and comprises presumably catchment derived, black organic-rich mud. The average TCO<sub>2</sub> flux from the Torbay Inlet channel was extremely high (947 mmol m<sup>-2</sup> day<sup>-1</sup>). This was considerably larger than the average TCO<sub>2</sub> flux from the shallow sandy basin (149 mmol m<sup>-2</sup> day<sup>-1</sup>). The total TCO<sub>2</sub> flux for the entire channel was 110 460 mol/day, whereas for the sandy basin it was 87 186 mol/day. This means the channel contributed disproportionately more to the total daily TCO<sub>2</sub> flux for Torbay Inlet than the sandy basin. The channel sediments accounted for 56 %, whereas the sandy basin accounted for 44 % of the total daily TCO<sub>2</sub> flux for Torbay Inlet. When normalised for areas of sands and muds, the average TCO<sub>2</sub> flux for Torbay Inlet was approximately 282 mmol m<sup>-2</sup> day<sup>-1</sup>.

The surface sediment of Lake Powell comprises silty sands, except for a small area (estimated 5 % of the total area of the lake) of mobile, black, organic-rich mud near the entrance to Marbelup Brook. LP\_14 was the only site located within these muds. The TCO<sub>2</sub> flux at site LP\_14 was over 3 times greater (180.8 mmol m<sup>-2</sup> day<sup>-1</sup>) than the average TCO<sub>2</sub> flux for the sandy sites (49.5 mmol m<sup>-2</sup> day<sup>-1</sup>). The total TCO<sub>2</sub> flux for the area of muds was 10 627 mol/day, whereas for the silty sands it was 55 233 mol/day. Therefore, despite a much larger TCO<sub>2</sub> flux per unit area, the muds only constitute a small area of Lake Powell and as such contributed much less to the total daily TCO<sub>2</sub> flux for the entire Lake than the sands. The sands accounted for 84 % of the total daily TCO<sub>2</sub> flux for Lake Powell.

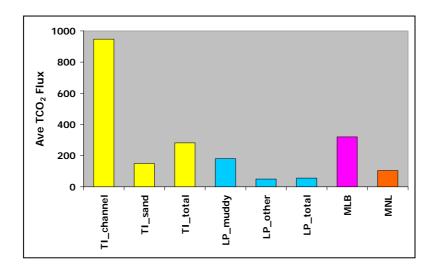


Figure 4-1. Average TCO<sub>2</sub> fluxes for the study sites (mmol m<sup>-2</sup> day<sup>-1</sup>)

TCO<sub>2</sub> fluxes in Marbelup Brook were highly variable, but on average very large (320 mmol m<sup>-2</sup> day<sup>-1</sup>). Fluxes in Lake Manarup were smaller and less variable with an average TCO<sub>2</sub> flux of 104 mmol m<sup>-2</sup> day<sup>-1</sup>.

Figure 4-2 shows the average TCO<sub>2</sub> and NH<sub>4</sub><sup>+</sup> fluxes for Torbay Inlet, Lake Powell, Marbelup Brook and Lake Manarup compared to averages from other temperate Australian estuaries. Generally, the NH<sub>4</sub><sup>+</sup> fluxes mirrored TCO<sub>2</sub> fluxes, reflecting the release of nutrients during organic matter breakdown. Average TCO<sub>2</sub> and NH<sub>4</sub><sup>+</sup> fluxes of the muddy sediments in the channel of Torbay Inlet, Lake Powell (LP\_14), and Marbelup Brook were the highest Geoscience Australia (GA) has ever measured. TCO<sub>2</sub> and NH<sub>4</sub><sup>+</sup> fluxes measured by GA in other temperate Australian estuaries are generally below 70 and 5 mmol m<sup>-2</sup> day<sup>-1</sup> respectively. TCO<sub>2</sub> and NH<sub>4</sub><sup>+</sup> fluxes in the channel of Torbay Inlet were over 13 and 23 times greater than this. Notably, TCO<sub>2</sub> fluxes were higher than 70 mmol m<sup>-2</sup> day<sup>-1</sup> for all sediments in all four waterways, except the sandy sediments in Lake Powell.

Sandy sites within Torbay Inlet and Lake Powell, and all sites in Lake Manarup had average NH<sub>4</sub><sup>+</sup> fluxes similar to or less than the other temperate Australian estuaries. Denitrification probably explains this, where some N was released as N<sub>2</sub> gas instead of NH<sub>4</sub><sup>+</sup> (see Denitrification Section 4E).

The very high fluxes from the muddy sediments in the channel of Torbay Inlet, at the entrance of Marbelup Brook in Lake Powell, and within Marbelup Brook, indicate large amounts of organic matter are being broken down in these sediments, releasing large amounts of nutrients to the overlying water column.

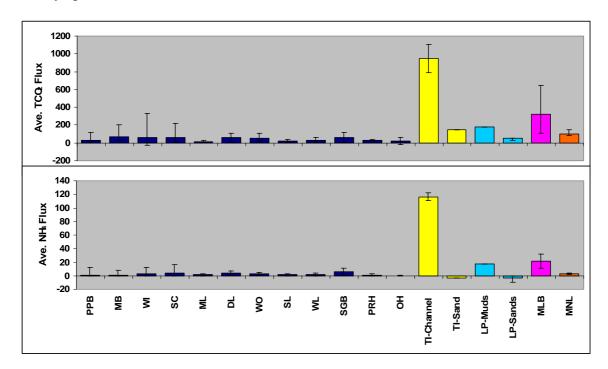


Figure 4-2. Average TCO<sub>2</sub> and NH<sub>4</sub><sup>+</sup> fluxes from temperate Australian estuaries (PPB=Port Phillip Bay, VIC; MB=Morton Bay, QLD; WI=Wilson Inlet, WA; SC=Swan River/Canning River, WA; ML=Myall Lake, NSW; DL=Durras Lake, NSW; WO=Lake Wollumboola, NSW; SL=Smiths Lake, NSW; WL=Wallis Lake, NSW; SGB=St Georges Basin, NSW; PRH=Princess Royal Harbour, WA; OH=Oyster Harbour, WA; Range Bars show maximum and minimum values)

### **4B. TYPE OF ORGANIC MATTER BREAKDOWN**

Carbon dioxide release and oxygen uptake rates in chambers may reflect the type of organic matter breakdown. Decomposition of organic matter in sediments can proceed by a number of biogeochemical pathways but will preferentially occur with oxygen as the main oxidant (aerobic oxidation). Data falling close to the 1:1 line on the TCO<sub>2</sub> versus O<sub>2</sub> flux plot (Figure 4-3) represent organic matter degradation dominated by aerobic oxidation. Data falling to the right of the 1:1 line indicate some other oxidant is degrading the organic matter (mostly sulphate reduction), while data falling to the left of the 1:1 line indicate more oxygen is consumed for the amount of carbon released (possibly due to the oxidation of sulphides).

The  $TCO_2$  fluxes in Torbay Inlet are highly variable whereas the corresponding  $O_2$  fluxes are quite similar, indicating that the same amount of oxygen is being consumed no matter the amount of carbon decomposed. Data for Lake Powell, Marbelup Brook and Lake Manarup all show a similar trend to each other; shallower slope than the 1:1 line and an apparent y-intercept at about -60 mmol  $m^2$  day $^{-1}$   $O_2$ . These results suggest that there is a demand for oxygen even at very low  $TCO_2$  fluxes. Furthermore, it becomes clear that other processes than aerobic carbon oxidation affect the  $O_2$  and  $TCO_2$  fluxes. These processes include anaerobic pathways of organic matter breakdown, e.g. sulphate reduction, nitrogen (and carbon) fixation utilizing  $O_2$  as energy source, and reoxidation of reduced species such as sulphide.

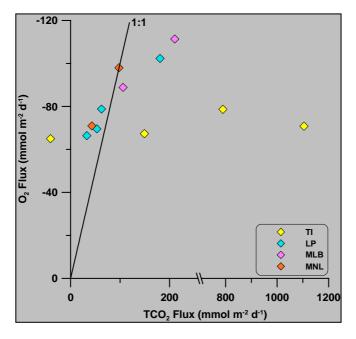


Figure 4-3.  $TCO_2$  flux versus  $O_2$  flux (dark chambers only; note break in x-axis)

### 4C. ORGANIC MATTER SOURCE

Skyring and colleagues (in prep.) have analysed data from over 300 benthic chamber deployments in 10 temperate Australian estuaries and found 87 % of results had a TCO<sub>2</sub>: SiO<sub>4</sub><sup>4-</sup> of 106:16-20. This indicates that diatoms are the major source of organic matter being degraded in the sediments. Diatoms are microscopic algae that have thick outer cell walls made of silicate (SiO<sub>4</sub><sup>4-</sup>). They are very common in estuaries and can live in the water column, on plants such as seagrass or

macroalgae, or at the sediment surface. The plot of  $TCO_2$  flux against  $SiO_4^{4-}$  flux (Figure 4-4) can indicate if diatoms are the major source of organic matter undergoing degradation in the sediments. If diatoms were the major source of organic matter, data would plot close to the 106:17 line (Brzezinski, 1985).

In Torbay Inlet, only the lower channel sites show any sign of a diatomaceous component to their organic matter source (and this is probably less than 40 %). All sites in Lake Powell show a non-diatomaceous source of organic matter.

In Marbelup Brook, only MLB\_2 was found to have a diatomaceous component to its organic matter, but this was only about 15 %. Sites MLB\_4 and MB\_5 showed a non-diatomaceous source of organic matter. Lake Manarup was the only waterway in which diatoms formed a major component of the organic matter source. 50 to 70 % of the organic matter source in Lake Manarup could be attributed to diatoms. Other possible sources of organic matter could be estuarine-derived non-diatomaceous or catchment-derived terrestrial organic matter.

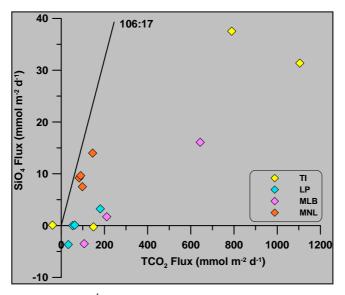
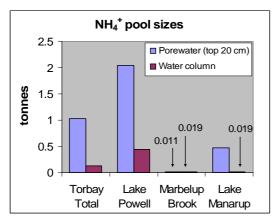


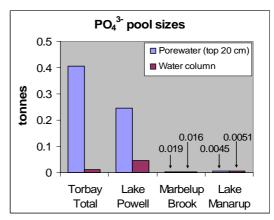
Figure 4-4.  $TCO_2$  flux versus  $SiO_4^{4-}$  flux (dark chambers only)

### **4D. NUTRIENT POOL SIZES**

Nutrient pool size calculations provided a measure of the mass of nutrients in different compartments of the whole system and allowed comparisons between surface sediment porewater and water column pool sizes. Calculations using the water volume and the average measured water column nutrient concentrations gave the mass of NH<sub>4</sub><sup>+</sup>-bound N, PO<sub>4</sub><sup>3-</sup>-bound P, and SiO<sub>4</sub><sup>4-</sup> in the water column of each waterway. The mass of each nutrient in the top 20 cm of sediment (where a depth of 20 cm was estimated as the limit of the most active zone of organic matter degradation) was calculated in each core based on the measured nutrient concentration in each depth layer and the porosity. The average depth-integrated nutrient mass was then multiplied by the respective sediment surface area. The water volume and the sediment surface area were derived from the bathymetry data using GIS analysis. For Torbay Inlet the areas of the muddy channel and the sandy shallow basin facies were calculated separately and nutrient inventories for both facies were calculated separately.

It was found that NH<sub>4</sub><sup>+</sup>, PO<sub>4</sub><sup>3-</sup>, and SiO<sub>4</sub><sup>4-</sup> pool sizes of the porewater in the top 20 cm of sediment by far exceed the nutrient pool sizes in the water column (Figure 4-5). Only Marbelup Brook represents an exception having similar surface sediment and water column nutrient pool sizes. In Marbelup Brook water column nutrient concentrations are by far the highest with average concentrations of 138, 5.3, and 105 μmol/l for NH<sub>4</sub><sup>+</sup>, PO<sub>4</sub><sup>3-</sup>, and SiO<sub>4</sub><sup>4-</sup>, respectively, while porewater nutrient concentrations were relatively low (see Section 3C3). The importance and the impact of the Torbay Inlet channel facies is revealed by its nutrient pool size compared to the pool size of the shallow basin facies. Although the channel area only constitutes about 20 % of the total Torbay Inlet area, the N- and P-pool sizes of the channel are 10- and 20-fold larger than the shallow basin pool size (Appendix 7). Similarly, the depth integrated N- and P-mass of the muddy site of Lake Powell (site LP 14) was more than 10-fold higher than at the sandy sites.





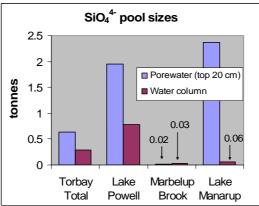


Figure 4-5. Nutrient pool sizes in surface sediments (top 20 cm) and in the water column of Torbay Inlet, Lake Powell, Marbelup Brook and Lake Manarup.

### **4E. DENITRIFICATION AND NITROGEN FIXATION**

Denitrification is a bacterial process of organic matter breakdown that results in the production of  $N_2$  gas. The  $N_2$  gas is subsequently lost to the atmosphere, reducing the pool of nitrogen available for plant growth. Therefore, denitrification is a process by which an estuary can rid itself of some nitrogen and thereby reduce the likelihood of the accumulation of nutrients within the system and eutrophication. Denitrification efficiency is the percentage of the total nitrogen that is released as  $N_2$  gas. Some microorganisms have the ability to convert  $N_2$  gas into forms that can be used for biological growth. This process is called biological nitrogen fixation, and counteracts the benefits of denitrification.

Positive fluxes represent net denitrification, whilst negative fluxes represent overall net nitrogen fixation. As both denitrification and nitrogen fixation may occur simultaneously, these results do not give us actual rates of each process. The channel sites in Torbay Inlet and all sites within Marbelup Brook were found to be net nitrogen fixing (Figure 4-6). The degree of nitrogen fixation appears to be significantly higher in Marbelup Brook compared to the channel sites in Torbay Inlet. The shallow sandy site in Torbay Inlet, Lake Powell and Lake Manarup were all found to be net denitrifying.

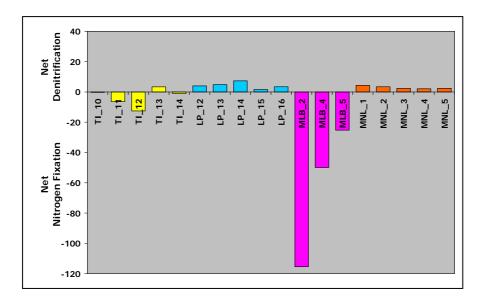


Figure 4-6.  $N_2$  fluxes for the study sites (mmol  $m^{-2}$  day<sup>-1</sup>; positive  $N_2$  flux indicates net denitrification and a negative  $N_2$  flux indicates net N-fixation)

Denitrification efficiencies (Table 4-1) can be calculated using two methods: (1) by direct measurement of N<sub>2</sub> concentrations; or (2) by estimating the N<sub>2</sub> based on a Redfield ratio (refer to Appendix A4B). As we cannot confirm the predominance of organic matter with a Redfield composition (see 4C), we have used the direct method for calculating denitrification efficiencies. The denitrification efficiencies for the shallow sandy margins in Torbay Inlet, and the sands within Lake Powell were found to be close to 100 %. This means that all the nitrogen released from the degradation of organic matter is released as N<sub>2</sub> gas. Denitrification efficiencies at the muddy site within Lake Powell (LP\_14) were low (34 %) as were all sites within Lake Manarup (50 %). As nitrogen fixation dominates in the channel of Torbay Inlet and Marbelup Brook, no denitrification efficiencies are shown, it is likely that they would be close to zero. In the following section (4F) the occurrence of benthic nitrogen fixation is discussed to be related to the availability of PO<sub>4</sub><sup>3-</sup>.

Table 4-1. Dominant processes and denitrification efficiencies for sampling sites.

Location	Sites	<b>Dominant Process</b>	Denitrification
			Efficiency (%)
TI - sands	TI_13	Denitrification	98
TI - channel	TI_11, TI_12	Nitrogen Fixation	-
LP - sands	LP_12, LP_13, LP_15	Denitrification	100
LP - mud	LP_14	Denitrification	34
MLB	MLB_2, MLB_4, MLB_5	Nitrogen Fixation	-
MNL	MNL_1, MNL_2, MNL_3, MNL_4	Denitrification	50

Compared to other temperate Australian estuaries (Figure 4-7), the sandy sediments in Torbay Inlet and Lake Powell had high denitrification efficiencies, whereas Lake Manarup and the muddy sediments in Lake Powell had lower than average denitrification efficiencies. Denitrification efficiencies in the muddy sediments of Torbay Inlet channel and Marbelup Brook are presumably zero, as mentioned above.

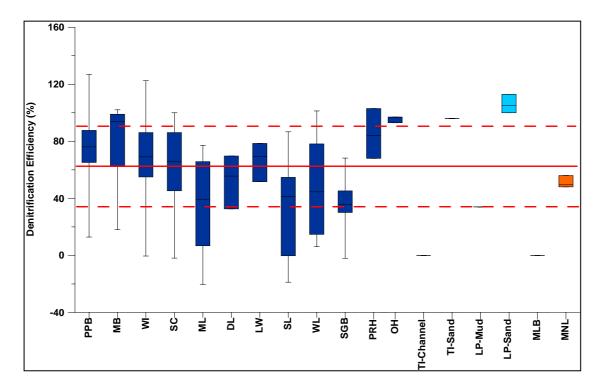


Figure 4-7. Box and whisker diagrams showing denitrification efficiencies for temperate Australian estuaries compared to waterbodies of the Torbay drainage system. The median is the horizontal line within the boxes, the bottom end of each box is the 25<sup>th</sup> percentile and the top end is the 75<sup>th</sup> percentile, and the vertical lines show the range of the outliers. Only the median is shown for TI-Channel, TI-Sand, LP-Mud, and MLB because there are only one or two measurements for these locations. The solid red line represents the average of all denitrification efficiencies and the dashed red lines represent ± one standard deviation. (PPB=Port Phillip Bay, VIC; MB=Morton Bay, QLD; WI=Wilson Inlet, WA; SC=Swan River/Canning River, WA; ML=Myall Lake, NSW; DL=Durras Lake, NSW; WO=Lake Wollumboola, NSW; SL=Smiths Lake, NSW; WL=Wallis Lake, NSW; SGB=St Georges Basin, NSW; PRH=Princess Royal Harbour, WA; OH=Oyster Harbour, WA).

### 4F. SEDIMENT IMPACT ON OVERALL WATER QUALITY

This section synthesises the findings and relates sediment processes to overall water quality in each of the different waterways. It builds on previous sections of the discussion, which revealed the nature of waterway sediments regarding TCO<sub>2</sub>, O<sub>2</sub>, and nutrient exchange across the sediment-water interface, rates of organic matter breakdown, and key processes such as denitrification and nitrogen fixation.

### 4F1. Torbay Inlet

Torbay Inlet often has water column nutrient concentrations exceeding ANZECC water quality trigger values (ANZECC 2000) and temporarily experiences toxic algae blooms (DoE 2004a). This study found that low salinity surface waters at site TI\_10, upstream of Torbay Inlet, representing recent runoff from the catchment, had the highest nutrient concentrations (Table 3-1). This confirms the findings of previous reports (DoE 2004a; DoE 2005) that identified catchment runoff as a major source of nutrients to the Inlet. Results of the present study also indicated that sediments could serve as an additional source of nutrients.

The most important finding for Torbay Inlet was that channel sediments were the main source of sediment-derived nutrients at the time of the survey. The NH<sub>4</sub><sup>+</sup> porewater pool size of the channel was 10-fold higher than the porewater pool size of the sandy, shallow basin. Furthermore, 100 % of nitrogen released during organic matter breakdown in channel sediments, was released as NH<sub>4</sub><sup>+</sup> rather than N<sub>2</sub> gas, and is therefore available for phytoplankton growth.

Equally important was the release of  $PO_4^{3-}$  from channel sediments. The two channel sites  $TI_1$  and  $TI_1$  recorded very high  $PO_4^{3-}$  fluxes (14 – 20 mmol m<sup>-2</sup> d<sup>-1</sup>), whereas the sandy, shallow sites had  $PO_4^{3-}$  fluxes less than 0.1 mmol m<sup>-2</sup> d<sup>-1</sup>. Also at the channel sites, high  $PO_4^{3-}$  fluxes out of the sediments, coincided with significant benthic nitrogen fixation, indicated by net  $N_2$  fluxes into the sediment (Table 3-2). Cyanobacteria typically carry out nitrogen fixation and their metabolic activity is often limited by  $PO_4^{3-}$  (Howarth *et al.* 1988). The observation of high benthic  $PO_4^{3-}$  fluxes along with nitrogen fixation suggests that  $PO_4^{3-}$  fluxes allow benthic cyanobacteria to occur and be metabolically active. Nitrogen fixation counteracts denitrification, as  $N_2$  is fixed to the sediment instead of being lost to the atmosphere.

Although localised nutrient release in the channel sediments was extremely high, it is important to consider that the channel only comprises 20 % of the total Torbay Inlet area. The shallow, sandy basin constitutes a far larger area (80 % of the total basin), and did not significantly contribute to benthic nutrient release. The shallow basin sediments have a low porosity, comprising fine sand with a low organic carbon content. Furthermore, shallow basin sediments may be largely covered by microbenthic algae as revealed in the benthic chamber results for sites TI\_13 and TI\_14, where fluxes measured using a transparent (light) chamber were distinctly different to the fluxes measured using a blackened (dark) chamber. The results of the transparent chamber incubation (TI\_14), revealed a net production of O<sub>2</sub> and a net TCO<sub>2</sub> and PO<sub>4</sub><sup>3-</sup> flux into the sediment. The NH<sub>4</sub><sup>+</sup> and SiO<sub>4</sub><sup>4-</sup> fluxes of the transparent chamber were much lower compared to the dark chamber (TI\_13). These results argue for the presence of microbenthic algae at the surface of the sediment consuming nutrients and TCO<sub>2</sub>, and producing O<sub>2</sub> during the light phase (photosynthesis).

#### 4F2. Lake Powell

Similar to Torbay Inlet, Lake Powell has two distinct sediment facies; silty sands with presumably low organic carbon content, which compose by far the largest area of the Lake, and organic-rich black muds, which are localised around the entrance to Marbelup Brook in the SW of the Lake. Four of the five chamber sites were located within the silty sand facies, and site LP\_14 was located in the muddy facies. The muddy sediment of Lake Powell had by far the highest benthic TCO<sub>2</sub>, NH<sub>4</sub><sup>+</sup> and SiO<sub>4</sub><sup>4-</sup> fluxes. PO<sub>4</sub><sup>3-</sup> fluxes were insignificant and no net benthic N-fixation was observed throughout Lake Powell (Table 4-1).

At sites LP\_15 and LP\_16 (less than 5 m apart), a dark and a light benthic chamber were deployed respectively, however there was no discernable difference in the results of these incubations (Table 3-2), indicating microbenthic algae were absent. The survival of microbenthic algae depends on environmental variables, including light availability and possibly salinity. Lake Powell was found to have higher light attenuation and significantly lower salinities than Torbay Inlet.

Water column nutrient concentrations were generally very high in Lake Powell but Chl-a concentrations were relatively low (Table 3-1). For example,  $PO_4^{3-}$  was consistently above 4.5 µmol  $I^{-1}$  and Chl-a concentrations were between 2.5 and 7.4 µg  $I^{-1}$ . This indicated that the availability of nutrients was not limiting phytoplankton productivity and that light availability was likely the limiting factor (Cloern 1999). For the growth of floating cyanobacteria,  $PO_4^{3-}$  must be abundantly available, which is the case for Lake Powell and which is likely the critical variable for the presence of planktonic cyanobacteria throughout the year.

### 4F3. Marbelup Brook

Within the suite of waterways studied, Marbelup Brook had the highest water column nutrient concentrations the least amount of light available for photosynthesis due to shading by bordering trees and very high light attenuation (Table 3-1). Similar to Lake Powell, Marbelup Brook experiences floating toxic algae blooms throughout the year.

The results of this study showed that the sediment oxygen consumption was very high, which, combined with long water residence times, has led to oxygen depletion (Table 3-1). Concurrently, benthic  $TCO_2$  and  $NH_4^+$  fluxes were very high, which continuously adds nutrients to the water column and quickly uses up any available oxygen. Most importantly, however, were the large measured fluxes of  $N_2$  into the sediment, indicating significant rates of benthic nitrogen fixation. Most likely, the presence of high  $PO_4^{3-}$  concentrations in the water column allows cyanobacteria to grow at the sediment surface, which adds microbial biomass comprising particulate organic nitrogen and phosphorous to the sediment pool.

In Marbelup Brook, the porewater nutrient pool size was similar to the water column nutrient pool size, which was in contrast to Torbay Inlet, Lake Powell, and Lake Manarup. This was evidenced by very high nutrient concentrations in the water column and only moderately high nutrient concentrations, and concentration gradients, in the porewaters (Section 3C3). These low nutrient porewater concentration gradients, seem anomalous considering the high measured benthic nutrient fluxes. However, this discrepancy may be explained by the high rate of biomass formation through nitrogen fixation at the sediment surface, and concurrent intense organic matter breakdown just below the thin nitrogen fixation layer. The porewater profiles suggest little release of metabolites within subsurface sediments and that organic matter appears relatively refractive. Consequently, the high benthic TCO<sub>2</sub> and NH<sub>4</sub><sup>+</sup> fluxes were likely a result of organic matter breakdown just below the

veneer of nitrogen fixation leading to high fluxes across the sediment-water interface without a significant build-up of metabolites in the porewaters.

### 4F4. Lake Manarup

Water column nutrient concentrations in Lake Manarup were by far the lowest within the suite of waterways studied (Table 3-1). Furthermore, water clarity was the highest as revealed by low light attenuation coefficients and visibility down to the bottom sediments. Rooted aquatic plants are widespread serving as food for birds, particularly swans. Similar to Torbay Inlet, significantly higher nutrient concentrations were found where freshwater enters the basin (site MNL\_7), which confirms catchment runoff as a source of nutrients for the waterway. In addition, similar to the sandy shallow basin of Torbay Inlet, was the occurrence of microbenthic algae at the sediment surface. This was evidenced by comparing dark and light chamber incubations at sites MNL\_4 and MNL\_5 respectively, where net O<sub>2</sub>, TCO<sub>2</sub>, NH<sub>4</sub><sup>+</sup>, and SiO<sub>4</sub><sup>4-</sup> fluxes were lower under light conditions, suggesting photosynthesis and thereby reducing the release of nutrients from sediments.

Lake Manarup had relatively high benthic TCO<sub>2</sub> fluxes, despite low water column nutrient and Chl-a concentrations (Table 3-1; Figure 4-2). Of the four waterways sampled, Manarup was also the only one where the ratio of benthic TCO<sub>2</sub> to SiO<sub>4</sub><sup>4-</sup> fluxes suggested that organic matter degrading in the sediment was primarily diatomaceous in origin. Given the widespread distribution of macroalgae, relatively low Chl-a concentrations reflecting low phytoplankton abundance, and the indication for the presence of microbenthic algae, much of the primary productivity in Lake Manarup may be contributed by diatoms present as epiphytes of macroalgae and as microbenthic algae at the sediment surface. This high primary productivity has likely resulted in the reduced dissolved nutrient concentrations and high biomass production within the waterway; the high input of organic matter to the sediments leads to high benthic TCO<sub>2</sub> fluxes. Concurrent with high TCO<sub>2</sub> fluxes, only low denitrification efficiency is found, i.e. equal quantities of N are released from the sediments as NH<sub>4</sub><sup>+</sup> and N<sub>2</sub>. The latter observation identifies sediments as significant source of nutrients (NH<sub>4</sub><sup>+</sup> and SiO<sub>4</sub><sup>4-</sup>) in Lake Manarup.

## 5. Implications for Management

Several Implications for management arise from the results of this study. The results showed that sediments serve as a source of nutrients in Torbay Inlet, Lake Powell, Marbelup Brook, and Lake Manarup. In particular, the muddy sediments of the Torbay Inlet channel, in Marbelup Brook, and at the entrance to Marbelup Brook in Lake Powell release large amounts of nutrients. Average fluxes in these sediments were the greatest Geoscience Australia has ever measured. However, muddy sediments are restricted to relatively small areas and sandy sediments only insignificantly contribute nutrients to the overlying water column. It is also important to note that the original source of sediment nutrients was the surrounding catchment.

High PO<sub>4</sub><sup>3-</sup> release from sediments of the Torbay Inlet channel, and high PO<sub>4</sub><sup>3-</sup> concentrations in the water column of Marbelup Brook, coincide with apparent nitrogen fixation at the sediment surface. PO<sub>4</sub><sup>3-</sup> availability is critical for cyanobacteria carrying out nitrogen fixation, therefore it is suggested that these sediments support this group of toxic algae. A reduction in the availability of PO<sub>4</sub><sup>3-</sup> could effectively reduce the growth of toxic algae. A decrease in nutrient release from sediments, however, would be most effective if a reduction in nutrient discharge from the catchment was to occur concurrently. In large areas of Lake Powell it was found that nutrient release from sediments was insignificant, yet, nutrient concentrations in the water column were very high, suggesting that nutrient discharge from the catchment is the predominant nutrient source.

Low nutrient and chlorophyll-a concentrations, and high water clarity, reflect good water quality in Lake Manarup. However, high benthic  $TCO_2$  fluxes give evidence for high organic matter input to the sediments. The ratio of benthic  $TCO_2$  and  $SiO_4^{4-}$  fluxes revealed that the labile organic matter in the sediment is predominantly of diatomaceous origin. Concurrent with the high  $TCO_2$  fluxes, denitrification efficiencies were found to be low to moderate indicating that the capacity to transform bioavailable nitrogen into  $N_2$  gas is presently relatively low. Based on this observation, it is recommended to avoid any further nutrient enrichment in Lake Manarup; if possible, present-day nutrient discharge into the lake should be reduced.

The major rain event immediately preceding the survey resulted in the breaching of the Torbay Inlet sand bar, flushing of nutrient- and sediment-loaded water from the catchment into the coastal zone, and subsequent tidal exchange of water between the Inlet and the ocean. The flushing event and the bar opening were highly efficient in exporting catchment-derived sediment and nutrients into the ocean where these compounds were diluted and dispersed within days. If the bar had remained closed, nutrients and sediments would have been trapped in the inlet. Consequently, the hydrodynamic conditions when the bar is open effectively lower nutrient concentrations in the inlet. The intrusion of seawater into the inlet leads to a density stratification. A possible bottom water anoxia associated with stratification is, however, only expected in the deeper parts of the Torbay Inlet channel where oxygen consumption is highest. Because large areas of the basin are very shallow, it is also expected that wind will frequently mix the water column, counteracting stratification and possible bottom water anoxia. Under the given conditions, an open bar has an overall positive impact on water quality in Torbay Inlet.

### 6. References

- Adeney, J.A. (2001). Cyanobacterial Issues in the Lake Powell/Torbay Inlet Drainage System. CSIRO Land and Water, Technical Report, 44/01. Prepared for the Water and Rivers Commission, Western Australia.
- ANZECC (2000). Australian and New Zealand Guidelines for Fresh and Marine Water Quality. Volume 1, The Guidelines. Australian and New Zealand Environment and Conservation Council and the Agriculture and Resource Management Council of Australia and New Zealand, Environment Australia. Commonwealth Government, Canberra.
- Arar E.J. and Collins G.B. (1997). *Method 445.0, In-Vitro Determination of Chlorophyll a and Pheophytin a in marine and freshwater algae by fluorescence*. National Exposure Laboratory, Office of Research and Development, US Environmental Protection Agency, Ohio.
- Berelson, W., Heggie, D., Longmore, A., Kilgore, T., Nicholson, G., and Skyring, G. (1998). Benthic nutrient cycling in Port Phillip Bay, Australia. *Estuarine, Coastal and Shelf Science*, **46**, 917-34.
- Brzezinski, M.M. (1985). The Si:C:N ratio of marine diatoms: Interspecific variability and the effect of some environmental variables. *Journal of Phycology*, **21**(3), 347-357.
- Cloern, J.E. (1999). The relative importance of light and nutrient limitation of phytoplankton growth: a simple index of coastal ecosystem sensitivity to nutrient enrichment. *Aquatic Ecology*, **33**, 3-16.
- Department of Environment (2004a). *Phytoplankton Drivers in Torbay Inlet and Lake Powell, South Western Australia*. Department of Environment, Government of Western Australia.
- Department of Environment (2004b). Water Resources in the South Coast Region, Southern Prospects 2004-2009. South Coast Regional Strategy for Natural Resource Management, Background Paper 4. Prepared for the South Coast Regional Initiatives Planning Team (SCRIPT).
- Department of Environment (2005). *Watershed Torbay Catchment Restoration Plan*. Department of Environment, Government of Western Australia.
- Eyre, B. D., Rysgaard, S., Dalsgaard, T., and Christensen, P. B. (2002). Comparison of Isotope Pairing and  $N_2$ :Ar Methods for Measuring Sediment Denitrification-Assumptions, Modifications, and Implications. *Estuaries*, **25** (6), 1077-1087.
- Forster, S., Glud, R.N., Gundersen, J.K. and Huettel, M. (1999). In situ study of bromide tracer and oxygen flux in coastal sediments. *Estuarine, Coastal and Shelf Sciences*, **49**, 813-827.
- Hall, P.O.J., and Aller, R. (1992). Rapid, small-volume, flow injection analysis for ΣCO<sub>2</sub> and NH<sub>4</sub><sup>+</sup> in marine and freshwaters. *Limnology and Oceanography*, **37**, 1113-1119.

- Harris P.T. and Heap A.D. (2003). Environmental management of clastic coastal depositional environments: inferences from an Australian geomorphic database. *Ocean and Coastal Management*, **46**, 457-478.
- Heggie, D.T., Smith, C.S., Murray, E.J. and Haese, R.R. (2003). *Biogeochemical Processes in the Sediments of Lake Powell and Torbay Inlet, WA: Results from cores taken in March 2002*. Geoscience Australia Report to the Water and Rivers Commission, WA.
- Hodgkin, E.P. and Clark, R. (1990). *Estuaries of the Shire of Albany. Estuarine Studies Series No. 9, November 1990*. Environmental Protection Authority, Perth WA.
- Howarth, R.W., Lane, J. and Cole, J.J. (1988). Nitrogen fixation in freshwater, estuarine and marine ecosystems. 1. Rates and importance. *Limnology and Oceanography*, **33**, 669-687.
- Jørgensen, B.B. (1996). Material flux in sediments. In: *Eutrophication in coastal marine ecosystems*. *Coastal and Estuarine Studies*, 52. Jørgensen, B.B. and Richardson, K. (editors). Pages 115-154.
- Kana, T. M., Darkangelo, C., Hunt, M. D., Oldam, J. B., Bennett, G. E., and Cornwell, J. C. (1994). Membrane inlet mass spectrometer for rapid high-precision determination of N<sub>2</sub>, O<sub>2</sub> and Ar in environmental samples. *Analytical Chemistry*, **66**, 4166-70.
- Mehrbach, C., Culberson, C. H., Hawley, J. E., and Pytkowitcz, R. M. (1973). Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure. *Limnology and Oceanography*, **18(6)**, 897-907.
- NLWRA (2002). Australian Catchment, River and Estuary Assessment 2002. National Land and Water Resources Audit. Commonwealth Government, Canberra. Data and associated reports and information available from the OzEstuaries website: www.ozestuaries.org
- Ryan, D.A., Heap, A.D., Radke, L. and Heggie, D.T. (2003). Conceptual Models of Australia's Estuaries and Coastal Waterways: Applications for Coastal Resource Management. Geoscience Australia Record, 2003/09.
- Seitzinger, S.P. (1990). Denitrification in aquatic sediments. In: *Denitrification in soil and sediment*. Revsbech, N.P. and Sørensen J. (editors). Plenum Press, New York. Pages 301-322.
- Skyring, G.W. and Heggie, D.T. (in preparation). Silicate-Diatoms-Sediment: A nexus for maintaining water quality in temperate estuaries.
- Water and Rivers Commission (2002). Water WA A State of Water Resources report for Western Australia. Prepared by Hydrology and Water Resources Branch, Water and Rivers Commission, Government of Western Australia.

### Appendix 1 – Benthic Chamber Operations

Both the manual and automatic chambers comprised a plexiglass cylinder, which isolated a volume of water (8.4 L) in contact with 0.066 m<sup>2</sup> of bottom sediment. Divers drew samples from manual chambers using 110 mL syringes attached to the end of tubes connected to the inside of each chamber (Figure 2-6). Spring-loaded syringes sampled the automatic chambers controlled by an electronics module that applied a current across burn wires to release each spring-loaded device. Ambient water from immediately outside each chamber replaced water taken for sample draws. This entered each chamber via a narrow 20 cm tube that permitted water entry only during sample draws. Flux calculations involved a correction for the addition of ambient water.

Water inside each chamber must equilibrate with ambient water before lid closure. Chambers were left with the lid open to equilibrate with ambient conditions for at least an hour before shutting the lid and commencing the incubation.

#### Sub-samples for:

- $NH_4^+$ ,  $NO_X$ ,  $SiO_4^{4-}$ ,  $PO_4^{3-}$  were filtered immediately after collection through 0.45  $\mu M$  filters and then taken to a nearby field laboratory for analysis.
- pH were left unfiltered and analysed immediately at the nearby field laboratory.
- alkalinity were filtered immediately after collection through  $0.45~\mu M$  filters and analysed by Gran titration within 24 hours of collection at the nearby field laboratory.
- N<sub>2</sub> gas analysis were left unfiltered and carefully transferred (avoiding the introduction of bubbles) into 10 ml gas tight Quickfit glass vials containing 50 μL of concentrated HgCl<sub>2</sub> solution to preserve the sample. The glass vials were stored in a water bath at in-situ temperature (~20 °C) until analysed 3 weeks later at the Southern Cross University laboratories in Lismore.

# Appendix 2 – Core Sample Procedures

Using a pole corer (Figure 2-7), we collected cores using core barrels comprising a PVC tube, 73 mm in diameter. Once in the sediment, the core barrel was sealed by closing a ball valve at the top. This prevented disturbance of the sediment inside the core barrels during retrieval. In each core barrel, we obtained a sediment depth of around 400 mm and left a 100 mm cap of water to prevent exposure of the sediment to air.

Cores were processed at a nearby field laboratory immediately after collection. We extruded and sliced each core into 1cm intervals. Sediment slices were loaded into centrifuge tubes, which were centrifuged at 11 000 rpm for 5 min to separate the solid phase from the porewaters. The porewaters were removed using a syringe and filtered through 0.45 µm filters. TCO<sub>2</sub> was analysed by means of conductivity (Appendix 3). The remaining sample was analysed for PO<sub>4</sub><sup>3-</sup>, NH<sub>4</sub><sup>+</sup>, NO<sub>X</sub>, and SiO<sub>4</sub><sup>4-</sup> within 48 hours of sample collection at the NMI laboratories in Perth (Appendix 3).

Porosity was measured by pre-weighing 10 cc of wet sediment and then oven drying. The samples were re-weighted once dried. The porosity of the sample was calculated by subtracting the dry weight from the wet weight, and then dividing it by the volume. Volumes were corrected for seawater density if from a marine environment.

# Appendix 3 - Chemical Analysis

### A3A. ALKALINITY AND CARBON DIOXIDE

The alkalinity was determined by Gran titration, whilst the carbonate alkalinity (CA) was estimated by subtracting the alkalinity contribution of B(OH)<sub>4</sub>. Carbon dioxide (TCO<sub>2</sub>) was estimated from pH and carbonate alkalinity according to Mehrbach *et al.* (1973) using:

$$TCO_2 = CA \frac{1 + K_2 / a_H + a_H / K_1}{1 + 2K_2 / a_H}$$

Where:

 $a_h$  is the activity of the hydrogen ion

K<sub>1</sub> and K<sub>2</sub> are the first and second ionisation constants of carbonic acid (H<sub>2</sub>CO<sub>3</sub>).

### A3B. CARBON DIOXIDE BY MEANS OF CONDUCTIVITY

For porewater samples, we determined TCO<sub>2</sub> by means of conductivity according to the method described by Hall and Aller (1992). The continuous flow system comprised a peristaltic pump supporting three flow channels (sample, acid, and base), a cell mixing the sample and acid channels, a gas permeable membrane separating TCO<sub>2</sub> from the acidified sample flow, and a conductivity cell analysing TCO<sub>2</sub> in the receiving base flow by means of a change of conductivity. The conductivity cell was kept in a water bath with a constant temperature of 30 °C. The pump speed was set to '5', and we chose Skalar silicon tubing colours as follows:

Sample: yellow-white; acid (HCl): orange –white; and base (NaOH): blue-white. A conductivity cell with k=0.117 was used, but the instrument was set to k=0.351. Standard solutions (1, 2, 5 mM) were prepared from a 100 mM stock solution, of Na<sub>2</sub>CO<sub>3</sub> and purged demineralized water. They were kept gas-tight in small bottles with septa. We used a 30 mM HCl acid solution and 5-10 mM NaOH base solution. The conductivity meter was linked to a computer for continuous recording. The conductivity of the carbonate-free base flow gave a signal of ~ 1000 mV and standard sea water (2.1 mM TCO<sub>2</sub>) mixed with the acid resulted in a drop of ~200 mV. The signal was stable with  $\pm$  2 mV resulting in an analytical precision of  $\pm$ 20  $\mu$ M. Calibration was highly reproducible over several days (Figure 3A).

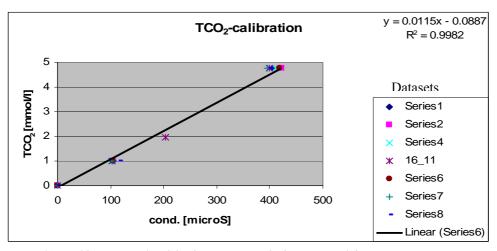


Figure 3A. Calibration results of the direct TCO<sub>2</sub> method over several days.

### A3C. DISSOLVED INORGANIC NUTRIENTS

Ammonia ( $NH_4^+$ ), nitrate + nitrite ( $NO_X$ ), phosphate ( $PO_4^{3-}$ ), and silicate ( $SiO_4^{4-}$ ) were determined within 48 hours of sample collection at the 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 3A).

### NH<sub>3</sub>-N/NH<sub>4</sub>-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<sup>-1</sup>.

### NO<sub>x</sub>-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 anaphthylethylenediamine 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  $L^{-1}$ .

### Silica as SiO<sub>2</sub>-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 ( $\beta$ )-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<sup>-1</sup>.

### PO<sub>4</sub>-P (sol react): Automated Ascorbic Acid Reduction method

Soluble reactive phosphorus (SRP) or PO<sub>4</sub>-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<sup>-1</sup>.

Table 3A. 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 NH3-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 NH3-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 NO2-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 NO2-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 NO3- 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 NO3- 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 SiO2	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 PO4-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 PO4-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%

### A3D. NITROGEN

Southern Cross University Environmental Analysis Laboratory analysed the benthic chamber samples for  $N_2$ . The laboratory used the method and instrumentation of Kana *et al.* (1994) with the following modifications. Gases were detected with a Balzers QMS422 quadrupole mass spectrometer and a water bath ( $\pm 0.01$  °C) was used to stabilize sample temperature in the water line upstream of the membrane. The effect of  $O_2$  in the sample on the  $N_2$  signal measured by the membrane inlet mass spectrometer was corrected by making a standard curve of  $O_2$  concentration against  $N_2$ :Ar ratios using water standards made from the incubation water equilibrated with the atmosphere at constant temperature (Eyre *et al.* 2002).

### A3E. CHLOROPHYLL A

Chl-a in the water column was measured in discrete water samples and by continuous recording using the field fluorometer. The frozen filter papers from the discrete water samples were placed in plastic vials and 20 mL of 90 % acetone added. The vials were shaken vigorously by hand and then in an ultrasonic bath. The samples were centrifuged and a 0.5 mL sample taken for analysis. Each sample was diluted with 5 mL of 90 % acetone in the fluorometer cuvettes. The samples were analysed by fluorometry according to the standard procedure adapted from Arar and Collins (1997).

### A3F. TOTAL SUSPENDED MATTER

Total suspended matter (TSM) was measured gravimetrically. After filtering a known volume of water from the surface water samples, the pre-weighed filters were oven dried at 60 °C and re-weighed. The difference in weight before and after filtering was used to determine TSM (mg/L).

# Appendix 4 – Benthic Flux and Denitrification Efficiency Calculations

# A4A. BENTHIC FLUXES ACROSS THE SEDIMENT-WATER INTERFACE

Fluxes were calculated by first performing a linear regression through the solute (nutrient and gas) concentrations measured during each chamber incubation, corrected for the addition of ambient water to replace that drawn for samples. Figure 4A shows, as an example, a linear regression through  $O_2$  and  $TCO_2$  concentrations measured in a chamber. For all solutes measured, only data points within the period of linear decrease in  $O_2$  were included, as a linear decrease in  $O_2$  over time indicated that conditions in the chamber were unperturbed, or not effected by the presence of the chamber itself.

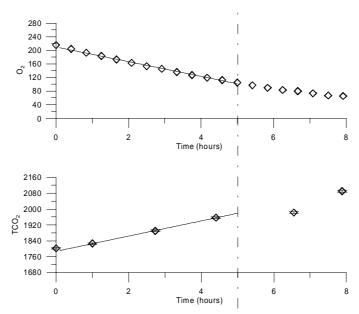


Figure 4A.  $O_2$  and  $TCO_2$  in  $\mu M$ . Fluxes were determined only from data points that fell within the time that  $O_2$  uptake was linear. In this example,  $O_2$  uptake was linear for the first 5 hours; indicating that, during this time, the chamber was not significantly perturbing the nutrient dynamics of the system. Therefore, solute fluxes ( $TCO_2$  in this particular example) were determined using only data points from the first 5 hours of the incubation.

### A4B. DENITRIFICATION EFFICIENCY

Denitrification efficiency is the percentage of total N (the sum of  $NH_4^+$ ,  $NO_X$ , and  $N_2$ ) released from the sediment as  $N_2$  gas. We calculated  $N_2$  fluxes using two methods: (1) by directly measuring the change in  $N_2$  concentrations inside each chamber, and (2) by assuming a Redfield ratio organic matter source (106C:16N:1P) and calculating the total N flux expected based on  $TCO_2$  fluxes, and subtracting the  $NH_4^+$  and  $NO_X$  flux components.

The equations used for calculating denitrification efficiencies for each of the two methods were:

(1) 
$$Denitr.eff.[\%] = \frac{6.6J(N_2)}{J(TCO_2\_org)} \times 100$$

(2) 
$$Denitr.eff.[\%] = \frac{\left(\frac{J(TCO_2\_org)}{6.6} - J(NH_4^+ + NO_X)\right)6.6}{J(TCO_2\_org)} \times 100$$

Where:

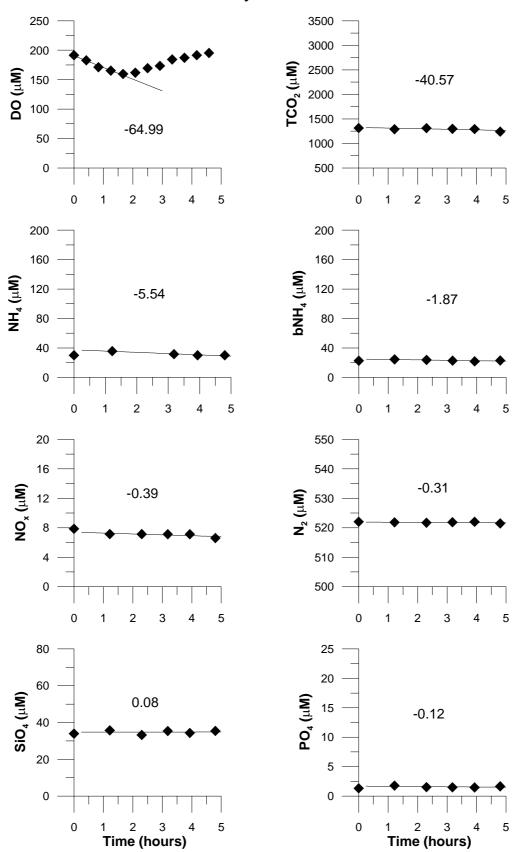
 $J(N_2)$  is the  $N_2$  flux measured in each chamber

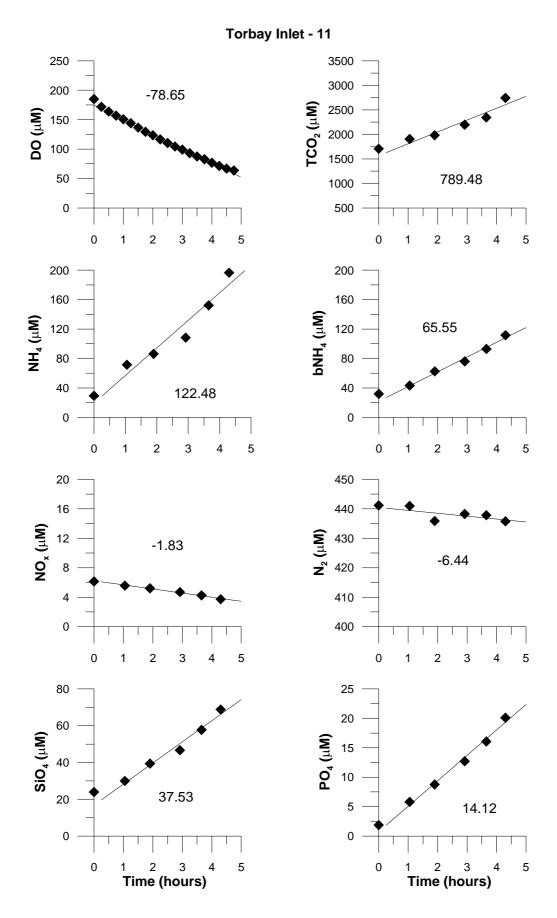
 $J(TCO_2\_org)$  is the  $TCO_2$  flux related to organic matter decomposition in the sediment  $J(NH_4^+ + NO_X)$  is the sum of  $NH_4^+$  and  $NO_X$  fluxes measured in each chamber

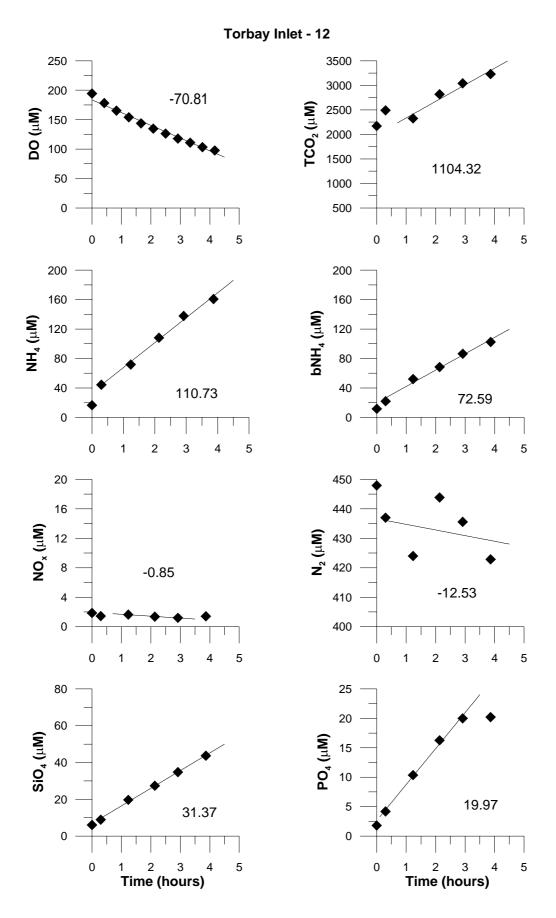
# Appendix 5 – Solute vs Time Plots

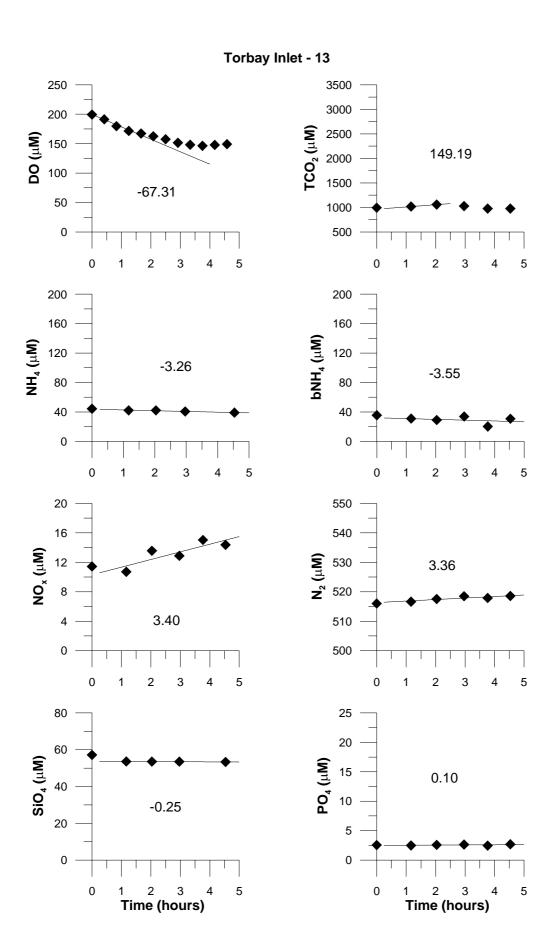
(Note:  $bNH_4$  refers to ammonia measured by an alternative method. This data was not used for reporting purposes)

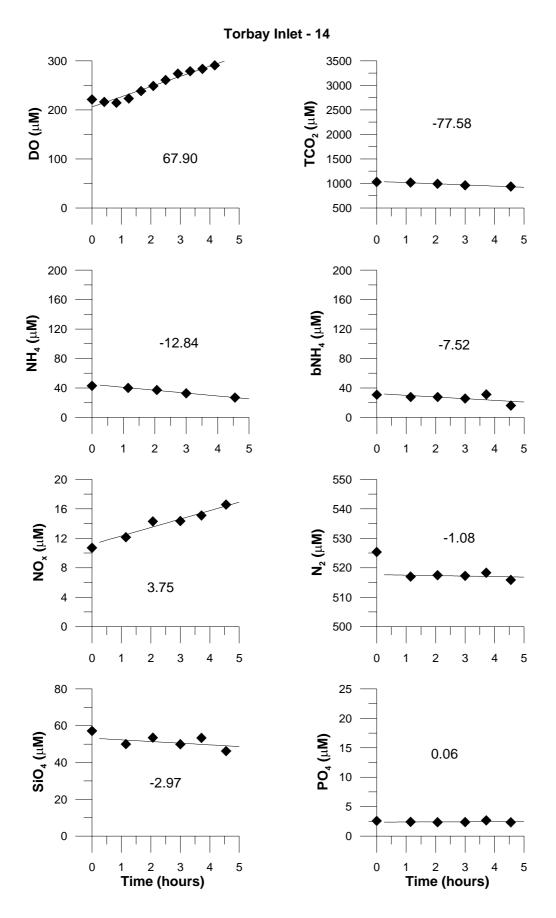
### Torbay Inlet - 10



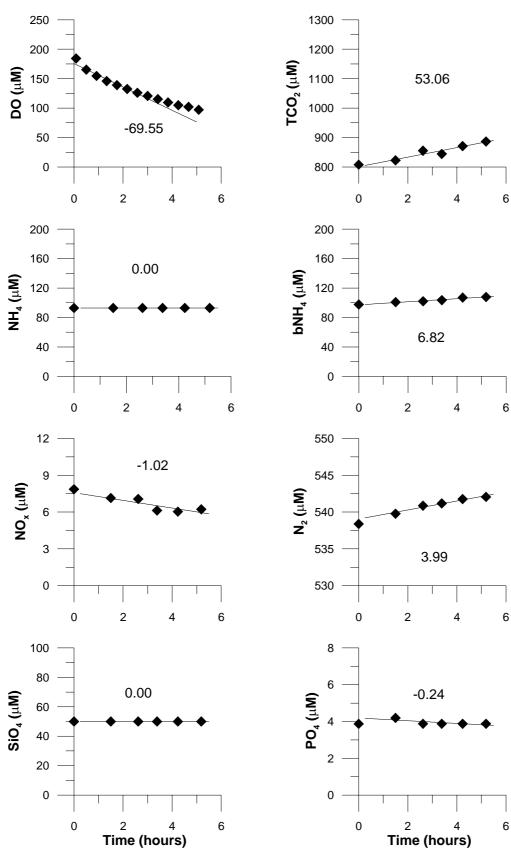


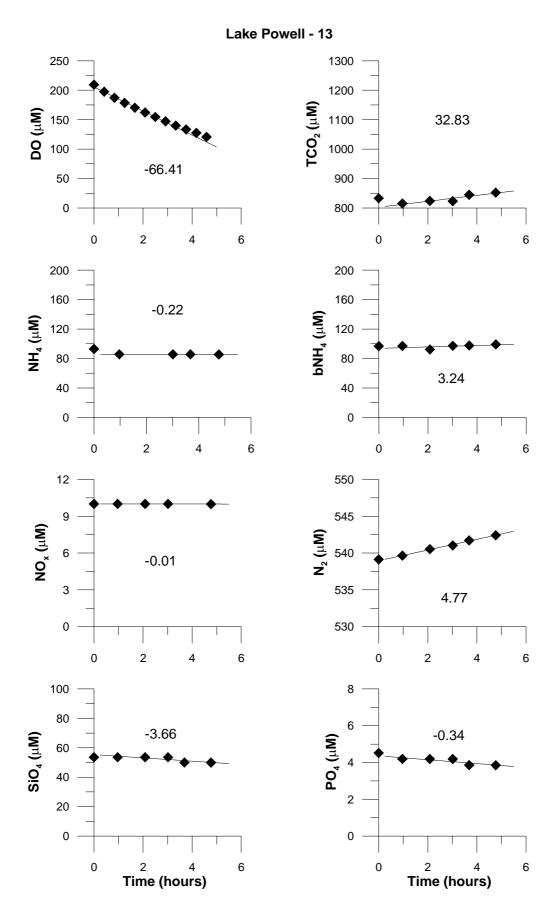


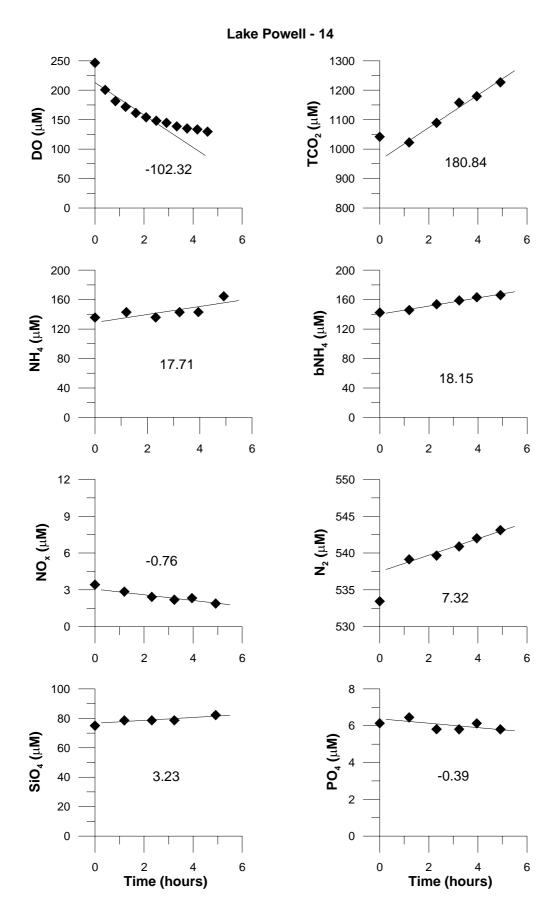




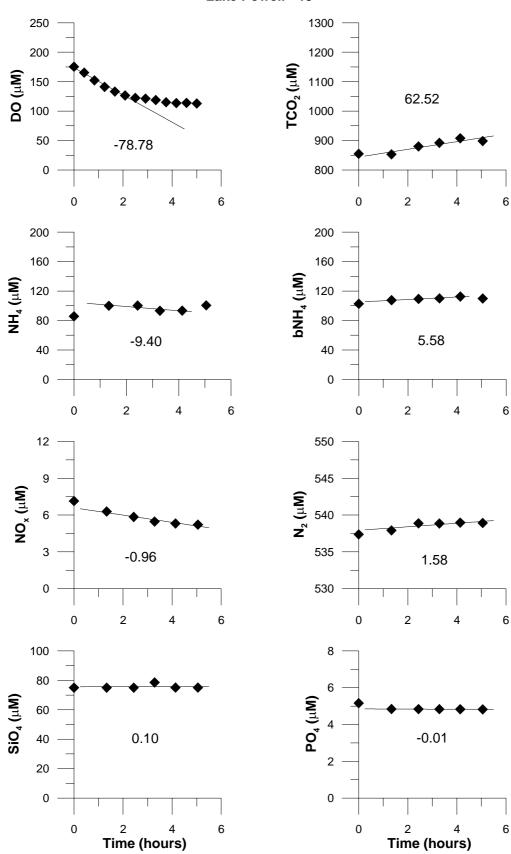
### Lake Powell - 12



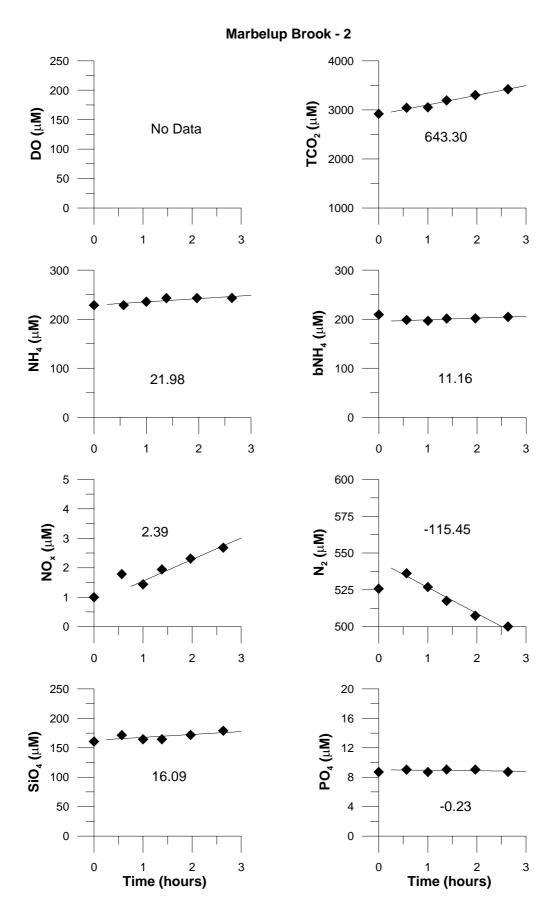




### Lake Powell - 15

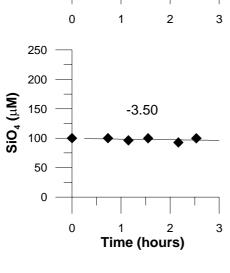


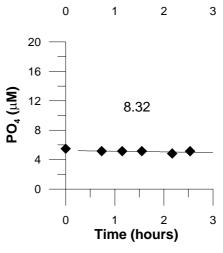
#### Lake Powell - 16 $TCO_2$ ( $\mu$ M) DO (μΜ) 97.19 -69.27 bNH₄ (μM) NH4 (µM) 1.39 0.00 NO<sub>x</sub> (μΜ) (M<sub>I</sub>) 540 -0.95 3.42 SiO<sub>4</sub> (μΜ) PO<sub>4</sub> (μM) -0.62 -7.98 2 4 Time (hours) 2 4 Time (hours)

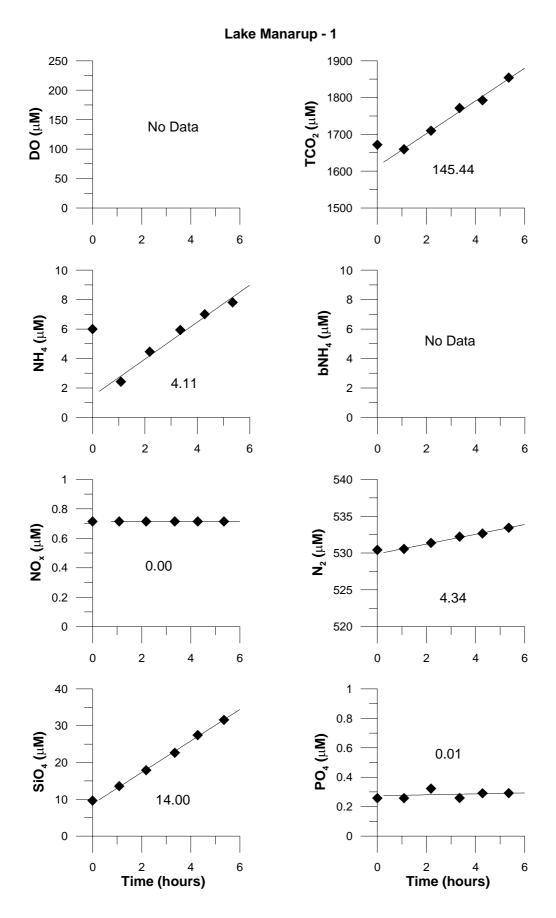


#### Marbelup Brook - 4 -111.36 $TCO_2$ ( $\mu$ M) DO (μM) 210.67 **(M3) 100** bNH₄ (μM) 18.51 31.64 (M<sup>21</sup>) 550 -1.59 -49.91 SiO₄ (μM) PO<sub>4</sub> (μΜ) 1.70 2.61 1 2 Time (hours) 1 2 Time (hours)

#### Marbelup Brook - 5 -88.85 $TCO_2$ ( $\mu$ M) DO (μΜ) 106.13 NH₄ (μM) bNH₄ (μM) 10.84 8.32 -2.30 -25.30

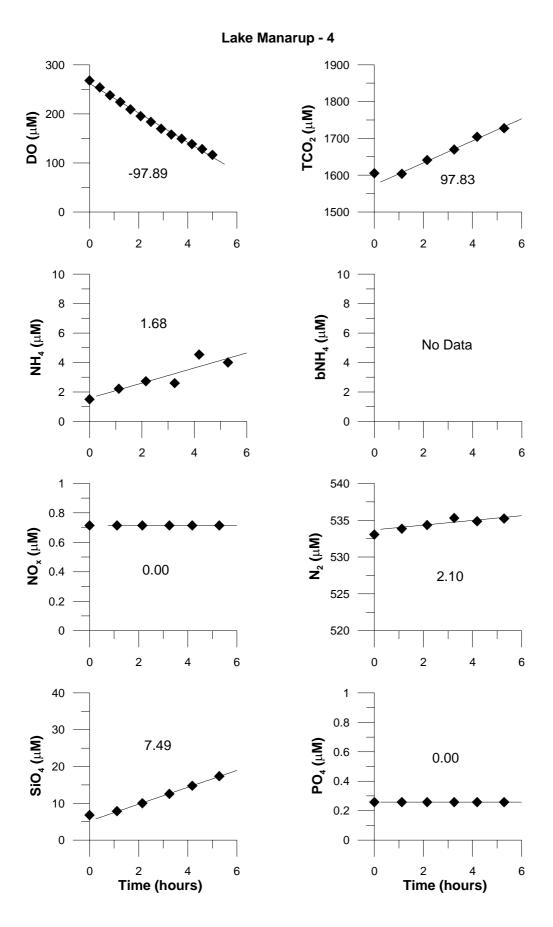


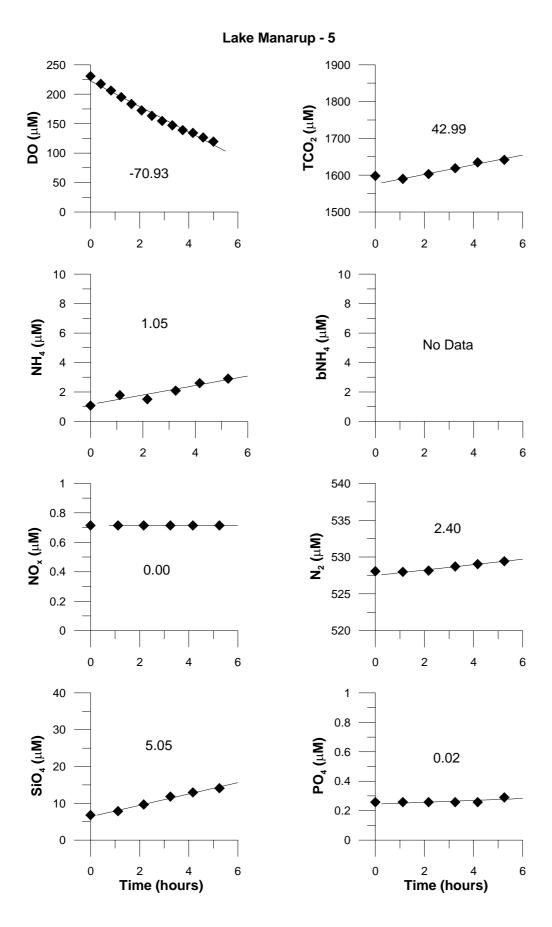




#### Lake Manarup - 2 $TCO_2$ ( $\mu$ M) DO (μM) No Data 83.01 3.72 bNH₄ (μM) No Data 0.8 0.6 ON 0.4 0.00 3.39 0.2 0.8 $SiO_4$ ( $\mu$ M) $PO_4$ ( $\mu M$ ) 9.20 0.6 0.01 0.4 0.2 2 4 Time (hours) 2 4 Time (hours)

#### Lake Manarup - 3 $TCO_{2}$ ( $\mu$ M) DO (μM) No Data 90.10 bNH₄ (μM) NH₄ (μM) 2.45 No Data 0.8 0.6 ON 0.4 0.00 2.30 0.2 0.8 $SiO_4$ ( $\mu$ M) $PO_4$ ( $\mu M$ ) 9.64 0.6 0.01 0.4 0.2 2 4 Time (hours) 2 4 Time (hours)





# Appendix 6 – Down Core Porewater Plots

(Note: the same axis scale was used within each waterway unless down core concentrations varied markedly, then the axis scale was modified and coloured red)

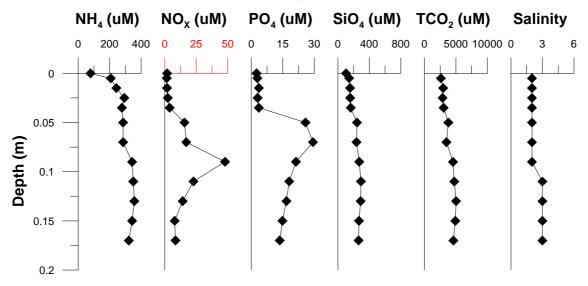
# **Torbay Inlet - Site 10** PO<sub>4</sub> (uM) SiO<sub>4</sub> (uM) TCO<sub>2</sub> (uM) NO<sub>x</sub> (uM) NH<sub>4</sub> (uM) Salinity 0 3000 6000 0 12 0 600 1200 0 400 800 0 2500050000 0 6 15 0.1 **Depth (m**) 0.2 0.3 0.4 0.5 **Torbay Inlet - Site 12** 600 1200 0 400 800 0 2500050000 0 125 250 0 3000 6000 <mark>0</mark> 0.1 **Depth (m)** 0.2 0.3 0.4 0.5 **Torbay Inlet - Site 13** 12 0 10 20 0 120 240 0 100 200 0 2000 4000 0 6 **Depth (m)** 0.1 0.2

0.3

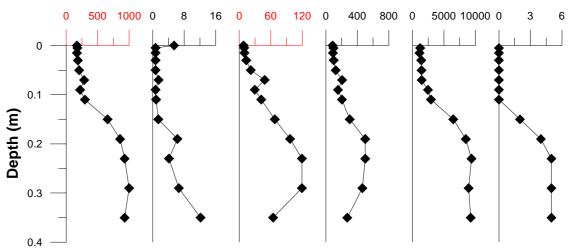
## Lake Powell - Site 12 PO<sub>4</sub> (uM) SiO<sub>4</sub> (uM) TCO<sub>2</sub> (uM) NH<sub>4</sub> (uM) $NO_{x}$ (uM) **Salinity** 15 30 0 600 1200 0 1000 2000 0 150 300 0 0.1 Depth (m) 0.3 0.4 **Lake Powell - Site 13** 30 0 600 1200 0 150 300 0 15 1000 2000 0 0.05 Depth (m) 0.1 0.15 0.2 Lake Powell - Site 14 10 0 100 200 0 600 1200 0 8000 16000 0 2000 4000 0 0.1 Depth (m) 0.2 0.3

0.4 -

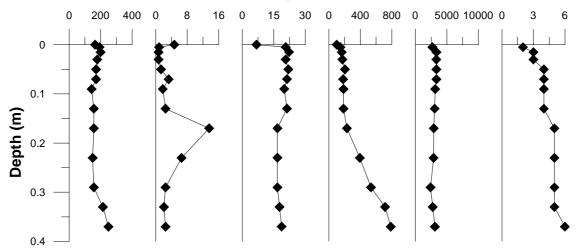
## Marbelup Brook - Site 1



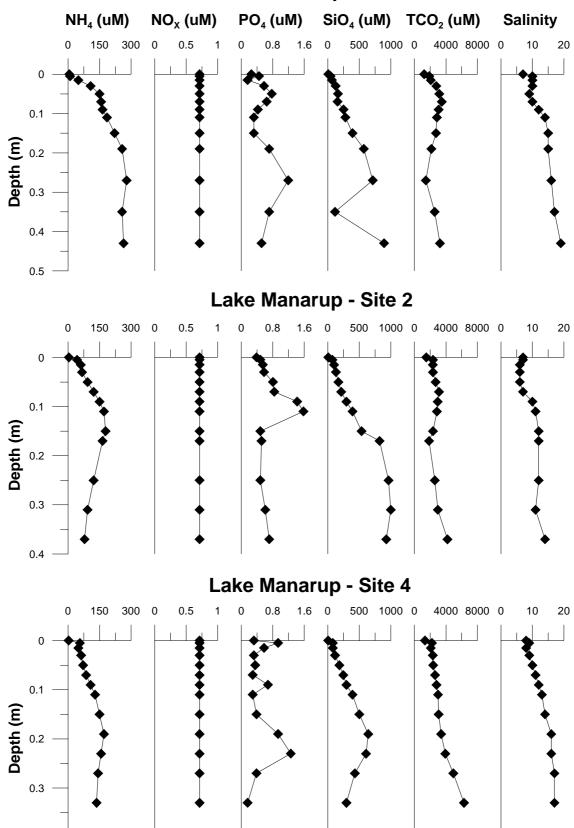
## Marbelup Brook - Site 3



## Marbelup Brook - Site 4



## Lake Manarup - Site 1



0.4

# Appendix 7 – Surface Sediment and Water Column Nutrient Pool Sizes

Table. Surface areas and volumes of waterways, nutrient pool sizes in surface sediments (top 20 cm) and in the water column.

			Surface sediment pool size			Water column pool size		
Waterway	Area	Volume	NH <sub>4</sub> <sup>+</sup>	PO <sub>4</sub> <sup>3-</sup>	SiO <sub>4</sub> <sup>4</sup> -	NH <sub>4</sub> <sup>+</sup>	PO <sub>4</sub> <sup>3-</sup>	SiO <sub>4</sub> <sup>4</sup> -
	m <sup>2</sup>	$m^3$	tonnes	tonnes	tonnes	tonnes	tonnes	tonnes
Torbay Inlet (shallow)	584374	158412	0.0923	0.0216	0.2290	0.1220	0.0103	0.2609
Torbay Channel	116654	17188	0.9419	0.3841	0.4045	0.0132	0.0011	0.0283
Torbay total	701028	175600	1.0342	0.4057	0.6335	0.1352	0.0114	0.2892
Lake Powell	1175254	322280	2.0364	0.2450	1.9517	0.4458	0.0467	0.7842
Marbelup Brook	18202	9918	0.0110	0.0019	0.0205	0.0192	0.0016	0.0293
Lake Manarup	1377060	428803	0.4781	0.0045	2.3678	0.0192	0.0051	0.0635