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APPLYING GEOSCIENCE TO AUSTRALIA'S MOST IMPORTANT CHALLENGES

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by

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Executive Summary

KEY FINDINGS

Present Day Nutrient Dynamics in Stokes Inlet

The rate of organic matter breakdown in sediments is an indicator for the internal carbon loading within an estuary. Stokes Inlet revealed moderate to high rates of organic matter breakdown, with rates of carbon dioxide (TCO_2) release from sediments ranging from 36 to 108 mmol m^{-2} day^{-1}. Similarly, ammonium (NH_4^+) fluxes were moderate to high compared to other temperate Australian estuaries. Previous GA studies have found that release of nitrogen (N) and phosphorus (P) from the sediments increases exponentially once TCO_2 release exceeds approximately 100 mmol m^{-2} day^{-1}, based on data from over 22 temperate Australian estuaries. In this context, Stokes Inlet is possibly approaching the threshold for developing exceedingly high N and P release from sediments, and becoming eutrophic.

The bathymetry of Stokes Inlet strongly influences nutrient release from sediments. In the deep parts, e.g. at site ST09 at a water depth of 6 m, where frequent stratification leads to anoxic bottom water for periods of months to years, phosphate (PO_4^{3-}) fluxes were found to be very high under both well-mixed, oxygenated conditions, and stratified, anoxic bottom water conditions. This is likely a result of the loss in P-binding capacity during periods of anoxic bottom water conditions, combined with the lack of ability to regain significant P-binding capacity during subsequent periods of oxic bottom water conditions. Water quality could deteriorate particularly during summer, if stratification was to extend into shallower areas, thus increasing the area of anoxic bottom waters and sediments with reduced P-binding capacity.

Differences in the P-binding capacity across Stokes Inlet were also reflected in surface sediment and porewater properties. In the deep basin, the P/Al ratio was low and sulphur highly enriched in surface sediments, whereas in the shallow areas, we would expect a high P/Al ratio and low sulphur enrichment, such as was found at site WE11 in Wellstead Estuary at a water depth of 2.5 m. Comparing porewater profiles from deep and shallow sites in Stokes Inlet, further compliments these findings, with very high porewater PO_4^{3-} concentrations in the surface sediments of the deep basin, and low concentrations in the surface sediments of shallow areas. Resuspension by wave action and subsequent re-oxidation of surface sediments at shallower sites most likely prevents intense sulphurisation and maintains the continued availability of iron oxyhydroxides, a condition favouring high P retention in sediments.

In contrast to P-binding capacity, denitrification appears to re-establish quickly with the return to oxic conditions. Denitrification was evident when bottom waters were well-oxygenated, but this process was inhibited when the Inlet was stratified and bottom waters were anoxic.

Palaeo-Environmental Reconstruction

Sedimentation rates in Stokes Inlet and Wellstead Estuary have increased dramatically since European settlement. In Stokes Inlet, sedimentation rates increased by about 80 times in the late 1950's compared to pre-European rates. These have since reduced; however current sedimentation rates are still more than 10 times higher than pre-European rates. Similarly, sedimentation rates in Wellstead Estuary have increased by about 10 times since the early 1950's. Evidence for sedimentation events has been found at sediment depths of 12 and 40 cm at site ST09 in Stokes Inlet, corresponding ages of 10 and 40 years respectively. These deposits are characterised by high concentrations of organic compounds indicative of terrestrial organic matter.

Records of common and exotic pollen in estuarine sediments give evidence for the establishment of new vegetation communities, including some exotic species, and a significant decline in wetland flora in the catchments of both Stokes Inlet and Wellstead Estuary. This began in the mid 1960s, in the Stokes Inlet catchment, and in the mid 1950s in the Wellstead Estuary catchment. Concurrent with this decline in wetland flora, the relative abundance of the freshwater green alga *Botryococcus* declines significantly in Stokes Inlet in the mid 1960s, providing further evidence for the loss of shallow lake and wetland environments. Biomass found in Stokes Inlet is predominantly derived from the catchment, whereas biomass in Wellstead Estuary is predominantly derived from within the estuary. An increase from 5 to 10 wt% of total organic carbon and a significant increase in micro-algal spores in sediments of Wellstead Estuary over the last 50 years, strongly suggests ongoing eutrophication. Apparently, wild fires have contributed to an increase in nutrient loads to the estuary, but uncontrolled sewage discharge from the township of Bremer Bay may also be a source of nutrients.

MANAGEMENT IMPLICATIONS

Stokes Inlet

In Stokes Inlet, the internal carbon loading, as reflected by the breakdown of organic matter in sediments, was moderate to high in autumn 2007. Also, high P release from sediments was observed in the deeper parts of the basin. The latter observation is particularly important, because primary production appears to be P limited, based on the N to P ratio in the water column at the time of the survey. A drying climate and/or an increase in water abstraction in the catchment would lead to even longer periods of bar closure, a decrease in average water surface area, an increase in salinity, and consequently, an increase in areas exposed to stratification and anoxic bottom water. All these changes, caused by a reduction in freshwater inflow, would lead to deteriorating water quality and ecological integrity. More specifically, larger areas exposed to stratification and anoxic bottom water will lead to higher rates of nutrient release from sediments, fuelling eutrophication and increasing vulnerability to toxic algae blooms. Consequently, the extent of stratification and bottom water anoxia needs to be monitored, and additionally any measures to minimize the development of such conditions will be important.

Also, in addition to already having moderate to high internal carbon loading, present-day sedimentation rates in Stokes Inlet are about ten times higher than during pre-European time, with a large fraction of the sediment biomass being derived from the catchment. Therefore nutrient and sediment loads should be reduced as a precautionary measure by increasing the area of deep-rooted vegetation in the catchment and by improving riparian zone conditions.

The northern part of Stokes Inlet is very shallow due to the prograding bayhead delta near the mouth of the Lort and Young rivers. These shallow environments currently fall dry over periods of months to years when the bar is closed and evaporation exceeds the delivery of river water. Currently, the high sedimentation rate of up to 1 cm per year is leading to infill of the basin even though sea level is rising by 2 to 3 mm per year related to global climate change. Consequently, these shallow margins will expand and will gradually transform into ephemeral wetlands over decades to centuries. This transition of the physical character of Stokes Inlet is immediately associated with an ecological transition and may require additional awareness and appreciation by the community.

Wellstead Estuary

The reconstruction of historical changes of water and sediment quality in Wellstead Estuary has revealed strong indications for progressive eutrophication, i.e. the enrichment of nutrients since European settlement in the 1950's. Two possible nutrient sources are identified: 1. Additional nutrients from catchment soils that are being mobilised through the burning of vegetation, as suggested by the concurrent increase of charcoal in Wellstead sediments. 2. Uncontrolled sewage discharge from the township of Bremer Bay, given the expansion of the town over recent decades, including a mid-size caravan park on the south-western shore of the Estuary. The aquifer around Wellstead Estuary is described by the WA Water Corporation as "extremely vulnerable to contamination from inappropriate land uses because recharge occurs from direct infiltration of rainfall across the whole groundwater system and depth to the aquifer is relatively shallow". It is recommended to reduce the frequency of fires in the catchment and to install a groundwater monitoring well at the south-western shore near the caravan park.

Abbreviations and Units

B.P.	Before Present
Bq kg^{-1}	Becquerel per kilogram
°C	degrees Celsius
C	Carbon
$\delta^{13}C$	Delta ^{13}C
cc	cubic centimetre
Chl-a	Chlorophyll a
CIC	Constant Initial Concentration
cm	centimetre
CO_2	Carbon Dioxide
CRS	Constant Rate of Supply
DIN	Dissolved Inorganic Nitrogen
DIP	Dissolved Inorganic Phosphorus
DO	Dissolved Oxygen
DOW	Department of Water, Western Australian Government
DOE	Department of Environment, Western Australian Government
dpm g^{-1}	disintegration per minute and kilogram
Fe	Iron
GA	Geoscience Australia
gC cm^{-2} y^{-1}	grams of carbon per centimetre squared per year
H_2S	Hydrogen Sulphide
Kd	Light Attenuation Coefficient
km	kilometre
m	meter
m^{-1}	per metre
mAHD	metres above Australian Height Datum
mg/L	milligrams per litre
mm	millimetres
mL	millilitre
mmol m^{-2} day^{-1}	millimoles per metre squared per day
N	Nitrogen
$\delta^{15}N$	Delta ^{15}N
N_2	Dinitrogen Gas
NH_4^+	Ammonium
NO_2^-	Nitrite
NO_3^-	Nitrate
NO_X	Nitrate + Nitrite
O_2	Oxygen
OM	Organic Matter
OSL	Optically Stimulated Luminescence
P	Phosphorus
PAR	Photosynthetically Active Radiation
PO_4^{3-}	Phosphate
Si	Silica
SiO_4^{4-}	Silicate
South Coast NRM	South Coast Natural Resource Management Inc.
TCO_2	Total Carbon Dioxide

TIN	Total Inorganic Nitrogen
TN	Total Nitrogen
TOC	Total Organic Carbon
TP	Total Phosphorus
µg/g	micrograms per gram
µg/L	micrograms per litre
µM	micromolar
WA	Western Australia
Wt%	Weight Percent
XRF	X-Ray Fluorescence

1. Introduction

1A. PURPOSE AND BACKGROUND

This report presents the results of a study by Geoscience Australia (GA) of Stokes Inlet and Wellstead Estuary, based on data collected during surveys undertaken in March 2006 and May 2007 (24th March 2006 and 12th – 23rd May 2007). It compliments and extends the findings of a survey in Wellstead Estuary (14th March – 4th April 2006), reported by Murray *et al*. (2007).

Stokes Inlet and Wellstead Estuary are on the south coast of Western Australia, located approximately 80 km and 300 km west of the town of Esperance, respectively (Figure 1-1 and Figure 1-7). The catchments of both estuaries are extensively modified, with 60% of the Stokes Inlet catchment, and 80% of the Wellstead Estuary catchment cleared of native vegetation and replaced with cropping and pasture. Consequently, there is concern regarding the impact of this land-use change on the environmental condition of these estuaries, with evidence for enhanced nutrient, sediment, and salt input from the catchment, and signs of eutrophication. For more detailed information on the physical attributes and environmental issues affecting Stokes Inlet and Wellstead Estuary, see WA Department of Water, Condition Statement reports: DOW (2007) and WRC (2004), and the publications Hodgkin and Clark (1987), Hodgkin and Clark (1989), and Brearley (2005).

The prime purpose of this study was to investigate the sediment record in Stokes Inlet and Wellstead Estuary to determine historical changes in catchment land-use and relate these to changes in estuarine water quality. Additionally, GA also measured the present-day exchange rate (flux) of nutrients between the sediments and overlying water column. These rates provide information on the processes controlling nutrients within the Inlet, and as such, have a strong influence on water quality, for example, the factors creating oxic or anoxic conditions, whether the nutrient phosphorus is trapped in sediments or released to the overlying water column, or whether the nutrient, nitrogen is released from the sediments as bioavailable ammonium, or lost to the atmosphere as nitrogen gas (denitrification). Benthic fluxes were measured in Wellstead Estuary during the March 2006 survey and are reported by Murray *et al*. (2007). This earlier report also includes a useful explanation of the significance of benthic fluxes and nutrient cycling in estuaries, and the methods used by GA to measure them. Benthic fluxes were measured in Stokes Inlet during the May 2007 survey, which was subsequent to the release of the Murray *et al*. (2007) report, and as such are presented here.

The Western Australian (WA) Department of Water (DOW) commissioned this study in partnership with the regional Natural Resource Management (NRM) group; South Coast Natural Resource Management Inc. (South Coast NRM). DOW and South Coast NRM identified the need to determine present-day and historical sediment accumulation rates and benthic nutrient fluxes in a recent review of information gaps for preparing a management plan for Stokes Inlet. One of the potential threats to the inlet is sedimentation and further information was required to confirm this (DOW 2008). For Wellstead Estuary, the investigation of past and present sedimentation rates was an action in the management plan prepared for the Inlet (DOE 2006). Baseline information and a well-targeted monitoring program are needed to address several existing and emerging environmental issues in both Inlets, such as increased nutrient, sediment and salt loading from the catchment, periods of stratification, anoxia, and the occurrence of harmful algal species.

In a recent study (March 2006) benthic fluxes and down-core nutrient porewater profiles were measured at four sites in Wellstead Estuary (Figure 1-7; Murray *et al*. 2007). The present study follows on from this investigation, by collecting sediment cores for determining sedimentation rates and historic changes in water quality. The earlier survey also collected sediment cores from three sites in Stokes Inlet (ST6, ST7, ST8; Figure 1-1), the results of which are included in this report.

Aim and Objectives

The aim of this study was to determine from sediment records, how changes in catchment land-use have affected sedimentation rates, water quality, and nutrient cycling in Stokes Inlet and Wellstead Estuary.

The main objectives were to:

1. Determine past and present sediment accumulation rates in Stokes Inlet and Wellstead Estuary and attempt to identify the cause of any changes.
2. Investigate other historical changes in the environmental condition of Stokes Inlet and Wellstead Estuary (e.g. source and amount of organic matter) related to changes in catchment land-use (e.g. vegetation clearance and agriculture) and possibly climate change.
3. Determine benthic nutrient fluxes and the present-day nature of organic matter breakdown and nutrient cycling within Stokes Inlet. Note that this has already been done in Wellstead Estuary (see Murray *et al*. 2007).

1B. ENVIRONMENTAL SETTING

1B1. Stokes Inlet

Stokes Inlet is relatively large and deep compared to other estuaries in the region. It has a water area of around 14 km^2 and catchment area of 4 575 km^2. The Inlet is relatively broad and shallow (usually < 1 m water depth) in the northern part, where the Lort and Young Rivers enter (Figure 1-1 and Figure 1-2). The sedimentary environment of this large northern margin is classified as a fluvial bayhead delta (www.ozcoasts.org.au). Towards the ocean, the inlet gradually deepens to over 8 m water depth adjacent to the estuary mouth, where a sand barrier separates the Inlet from the ocean. A depth profile drawn approximately along the centreline of the Inlet, illustrates this distinctive depth gradient (Figure 1-2).

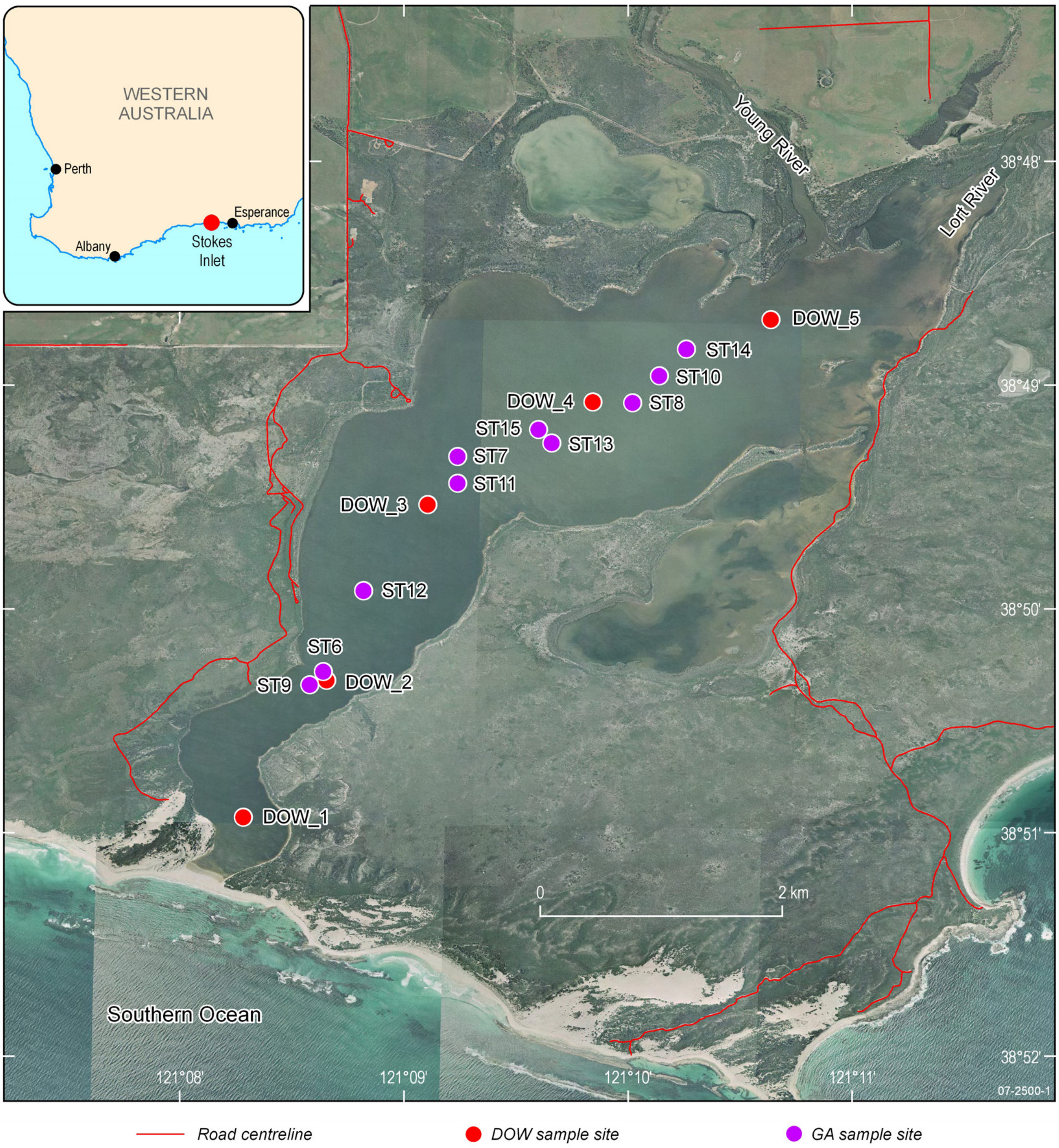


Figure 1-1: *Aerial photo of Stokes Inlet showing Geoscience Australia (GA) sample sites (ST6 – ST15) and WA Department of Water (DOW) monitoring sites (DOW_1 – DOW_5). Base image source: WA Department of Water.*

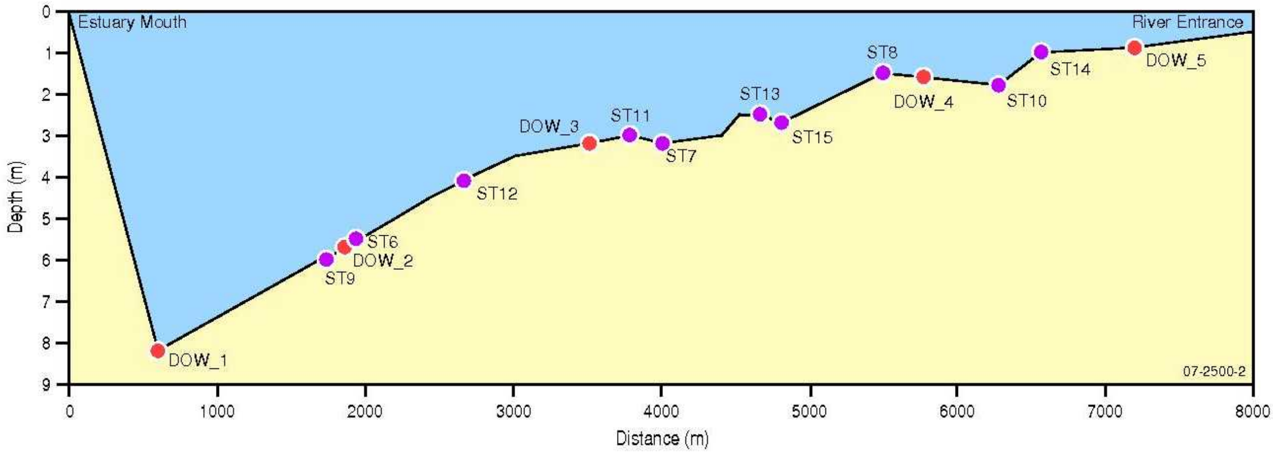


Figure 1-2: *Depth profile of Stokes Inlet along the line of sample sites shown in Figure 1-1.*

Figure 1-1 and Figure 1-2 show the location of Geoscience Australia sampling sites, as well as WA Department of Water (DOW) sampling sites, which the DOW measures for water quality parameters on a quarterly basis as part of an ongoing monitoring program. Note that sites ST6, ST7, and ST8 were sampled (sediment cores only) during the March 2006 survey, whereas sites ST9 - ST15 were sampled during the later May 2007 survey.

Water Quality and Stratification

Water quality data for Stokes Inlet, collected every three months by the DOW since February 2006, provides a useful context within which to interpret the benthic nutrient fluxes measured during this study. The monitoring data shows that the water column throughout the Inlet is generally well-mixed and well-oxygenated most of the time (Figure 1-3). This is due to persistent wind-driven mixing of the water column, and intermittently, tidal mixing when the estuary mouth is open to the ocean. Notably, the estuary mouth was open during the monitoring period between 5th January 2007 and 4th April 2007. Stratification occurs periodically however, after warm, dry periods, where there is little freshwater inflow and the estuary entrance remains closed. Salinities increase, and highly saline water sinks into the deep basin adjacent to the estuary mouth. This occurred in February 2006, where the deep basin became stratified (Figure 1-3 and Figure 1-4). At this time, the bottom layer (below 5.5 m water depth) was anoxic and hypersaline (> 70 000 mg/L), whereas the top layer remained relatively well-oxygenated and had lower salinities (between 47 000 and 53 000 mg/L). The extent of stratification lessened over the proceeding winter and summer, with only the deepest part of the Inlet (> 7 m water depth) remaining anoxic by December 2006 (Figure 1-4). Notably, in all areas of Stokes Inlet shallower than 5.5 m water depth, the water column remained well-mixed and well-oxygenated (DO between 80 and 110% sat) for the whole monitoring period.

The generally well-mixed water column of Stokes Inlet means there is usually little difference between surface and bottom water concentrations of total nitrogen (TN) and total phosphorus (TP). Over the monitoring period between February 2006 and November 2007, the concentration of TN and TP in surface and bottom waters of both the deep and shallow areas changed in parallel (Figure 1-5). Significantly, the only time TN and TP differed markedly between sites and between surface and bottom waters, was in February 2006, when the deep basin was stratified. At this time, TN and TP concentrations were extremely elevated in the anoxic bottom waters of the deep basin compared to the rest of the Inlet. TP was over 5 times greater in the deep basin compared to the rest of the Inlet, and TN was about 4 times greater. This indicates that organic matter breakdown in the sediments was contributing significantly to water column nutrient concentrations. In addition, under these anoxic conditions, the phosphorus (P) binding capacity of iron oxides in the sediments was lost and any P trapped in the sediment was being released to the overlying water.

In the absence of stratification however, TP levels in both surface and bottom waters were quite low (Figure 1-5). TN was more variable, and dropped significantly when the Inlet opened to the ocean in January 2007, slowly building up again following closure of the estuary mouth in April 2007.

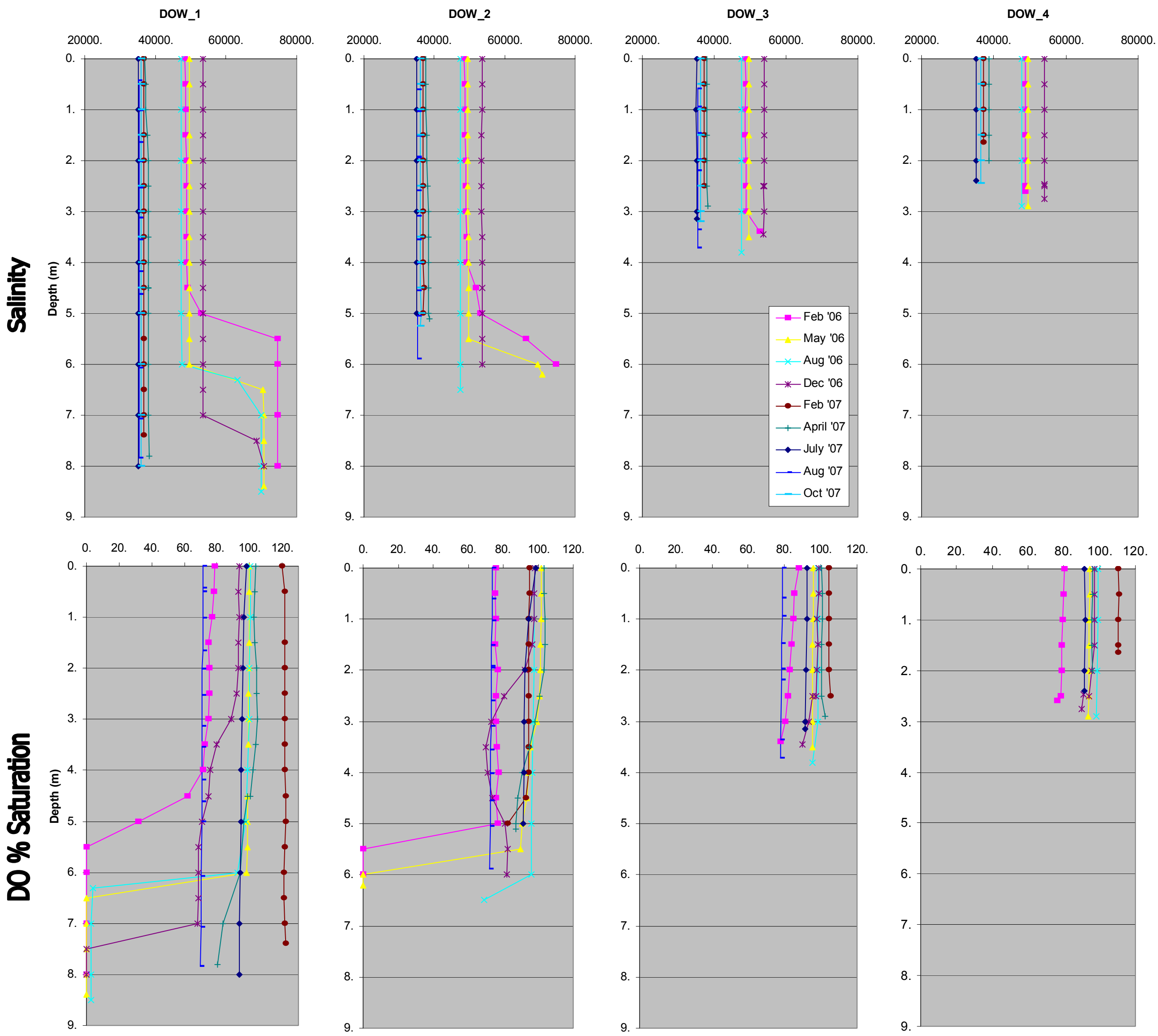


Figure 1-3: *Depth profiles of salinity (top four graphs) in mg/L, and dissolved oxygen (bottom four graphs) in % saturation, for the period February 2006 to October 2007. Graphs are arranged, left to right, from near the estuary mouth (DOW_1), towards the Young and Lort River Entrance (DOW_4). Figure 1-1 and Figure 1-2 show the location of these sites. Graphed using DOW quarterly monitoring data.*

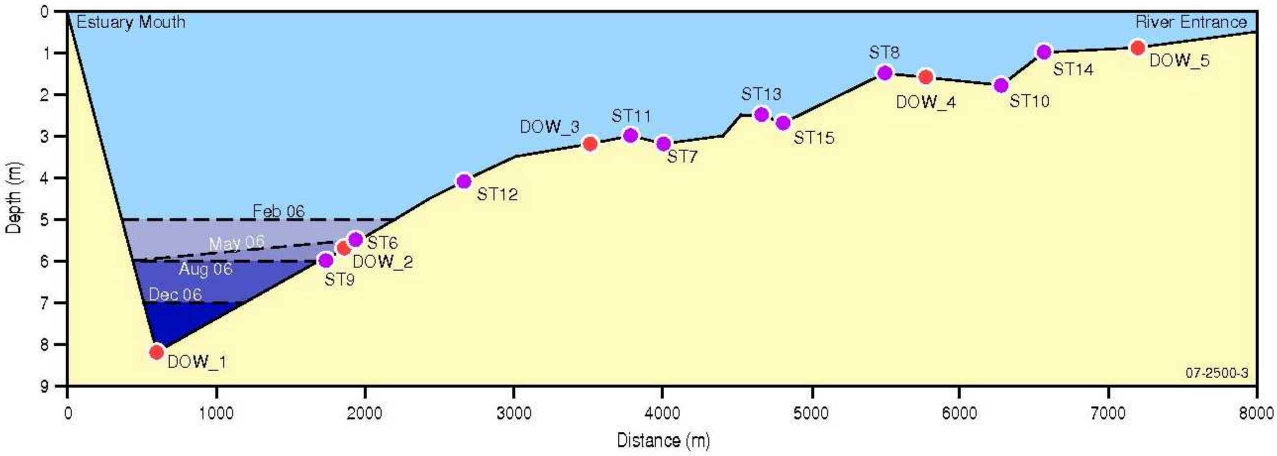


Figure 1-4: *Depth profile of Stokes Inlet showing the stratification boundary, below which, the water column was anoxic and significantly more saline. The depth of this boundary gradually lowered with time and its location is shown for February, May, August, and December 2006.*

Similarly to TN and TP, chlorophyll-a (Chl-a) concentrations were, at any one time, fairly uniform throughout the Inlet and differed little between surface and bottom waters; changing in parallel over the monitoring period (Figure 1-6). Interestingly, there appears to be a seasonal pattern, where the lowest Chl-a concentrations occur around late autumn – early winter (April – June), a time when shorter day length and lowering temperatures, likely result in a decrease in plant productivity. Chl-a concentrations then gradually build up in early spring and over summer, with the highest Chl-a concentrations occurring when the estuary entrance is closed and the water column stratifies over the summer period (e.g. February 2006). Notably, Chl-a concentrations were quite low after the estuary mouth had been open to the ocean for a few months (April 2007).

The dissolved inorganic nitrogen (DIN) concentration, primarily comprising ammonium (NH_4^+), was relatively high (0.25-0.35 mg/L), while the dissolved inorganic phosphorous (DIP) concentration, primarily phosphate (PO_4^{3-}), was very low (0.005 mg/L). Consequently, the calculated (molar) DIN:DIP ratio was very high, namely in the range of 115 to 208, which exceeds the N:P ratio of phytoplankton, which is 16, by about an order of magnitude. This strongly indicates the limitation of primary productivity by P.

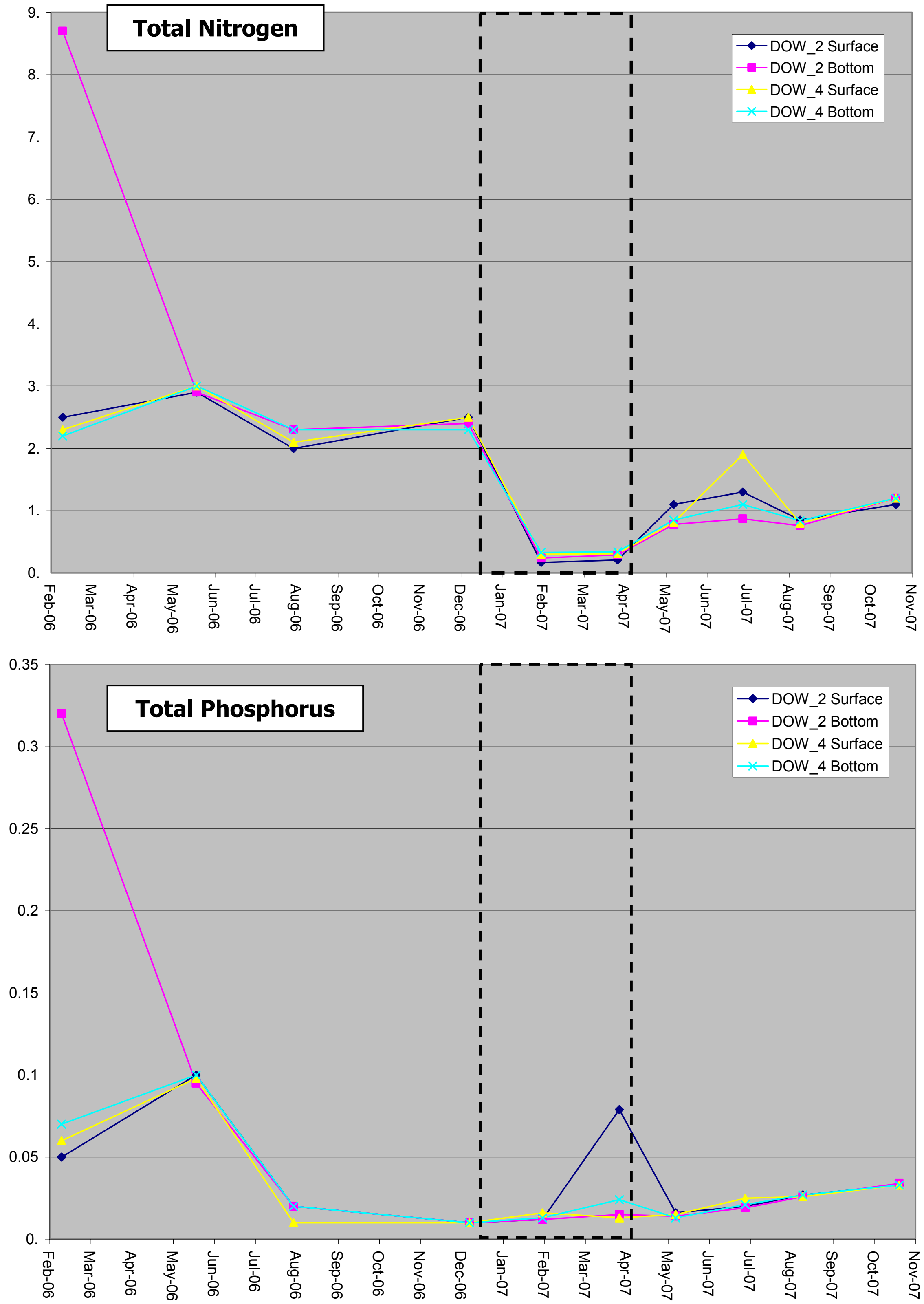


Figure 1-5: *Total nitrogen (TN) and total phosphorus (TP) in mg/L measured from February 2006 to November 2007, in the surface and bottom waters of the deep basin (site DOW_2) near the estuary mouth, and the shallow area (site DOW_4) nearer to the river entrance. The dashed box indicates when the estuary mouth was open to the ocean. Graphed using DOW quarterly monitoring data.*

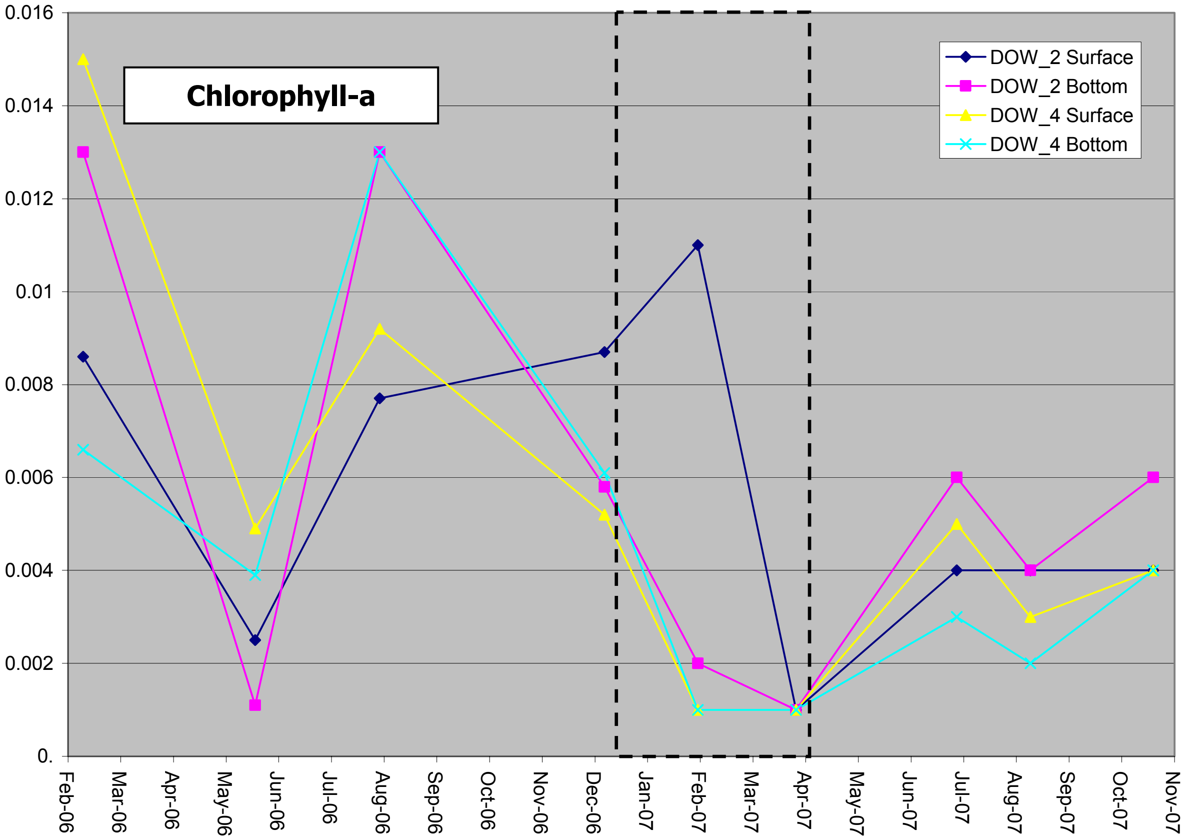


Figure 1-6: *Chlorophyll- a in mg/L measured from February 2006 to November 2007, in the surface and bottom waters of the deep basin (site DOW_2) near the estuary mouth, and the shallow area (site DOW_4) nearer to the river entrance. The box indicates when the estuary mouth was open to the ocean. Graphed using DOW quarterly monitoring data.*

1B2. Wellstead Estuary

The township of Bremer Bay, with a population of 250, is located on the south-western side of Wellstead Estuary and includes a caravan park directly on the Inlet's shoreline. The aquifer is described as "extremely vulnerable to contamination from inappropriate land uses because recharge occurs from direct infiltration of rainfall across the whole groundwater system and depth to the aquifer is relatively shallow" (Water Corporation 2004). Wellstead Estuary has a water area of around 3 km^2 and a catchment area of 720 km^2. It differs to Stokes Inlet, being quite uniformly shallow (generally <1 m water depth) and having a water area over four times smaller (Figure 1-7). The Bremer River enters Wellstead Estuary through a narrow, incised valley. This is the deepest part of the estuary, forming a channel, around 1-2 m deep. The frequency of mouth openings is highly variable, opening every few years for anywhere between a month and a year (Brearley 2005). Figure 1-7 shows the location of sampling sites from both the May 2007 survey (WE10, WE11, WE12) reported here, and the March 2006 survey (WE6, WE7, WE8, WE9), reported by Murray *et al*. (2007).

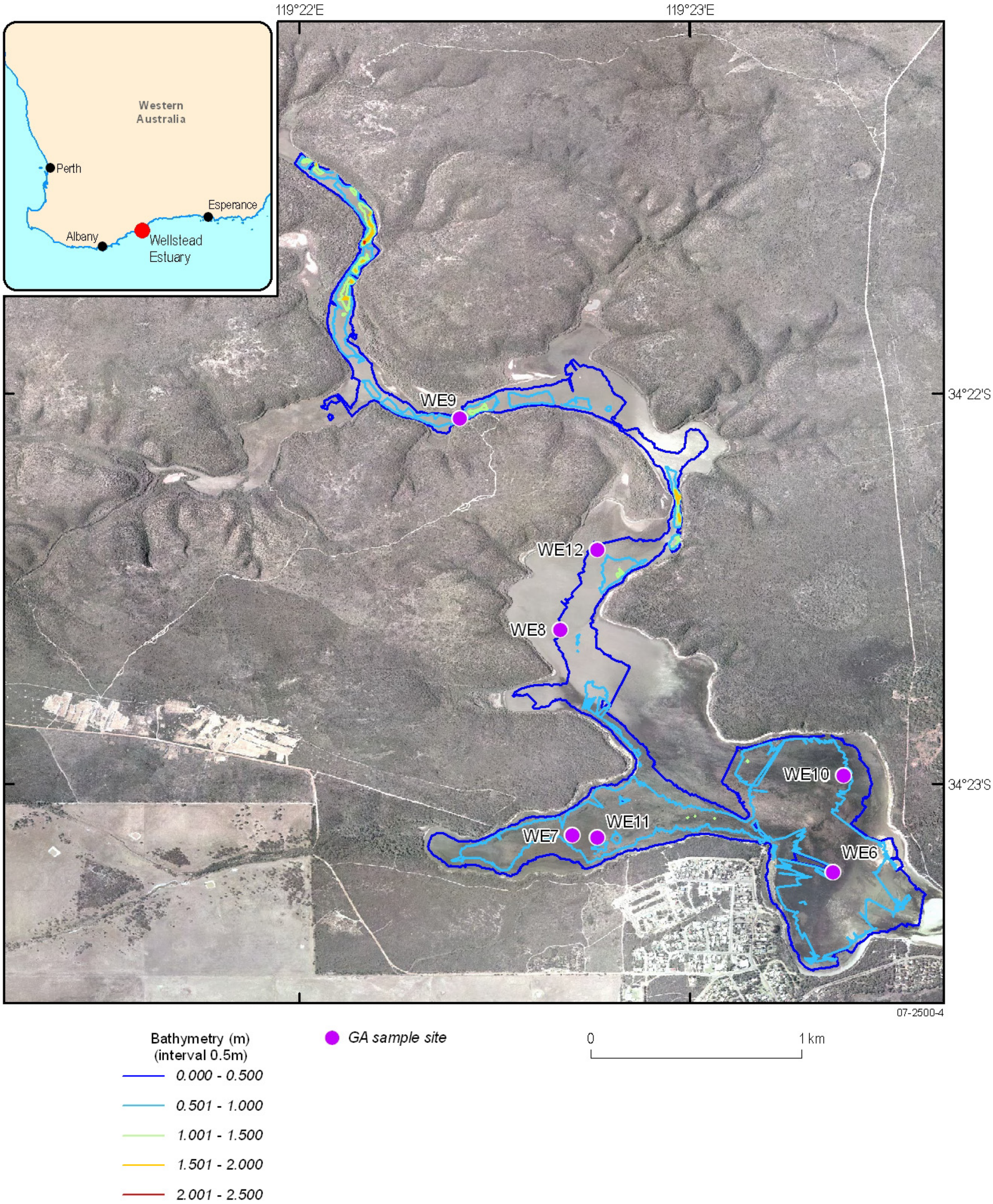


Figure 1-7: *Aerial photo of Wellstead Estuary showing sample sites and bathymetry in mAHD (metres above Australian Height Datum). Note that WE6, WE7, WE8, and WE9 (benthic chamber and sediment core sites) are reported by Murray et al. (2007). Sites WE10, WE11, and WE12 are reported here. Bathymetry and base image source: WA Department of Water.*

2. Methods

Different sampling was undertaken at each site (Table 2-1), where out of a total of 10 sites in Stokes Inlet, benthic chambers were deployed at two sites, sediment grabs taken from 7 sites, and sediment cores collected from 7 sites. In Wellstead Estuary, sediment cores were collected from three sites (WE10, WE11, WE12). These were new sites, additional to the four benthic chamber and sediment core sites (WE6, WE7, WE8, WE9) sampled in March 2006 and reported by Murray *et al.* (2007).

Please refer to Murray *et al.* (2007) for more detailed information on benthic chamber experiments and sample analysis, as well as the methods for sediment coring, porewater chemical analysis, biomarker analysis, and sediment bulk geochemical analysis.

Table 2-1: Site details and sampling undertaken at each site in Stokes Inlet and Wellstead Estuary.

Estuary	Site ID	Long. °E	Lat. °S	Sampling Date	Water Depth (m)[#]	Sediment Core Analysis	Sediment Grab Taken	Benthic Chambers Deployed
Stokes Inlet	ST6	121.144	33.838	24/03/06	6.5	porewater		
	ST7	121.154	33.822	24/03/06	4.2	porewater		
	ST8	121.167	33.818	24/03/06	2.5	porewater		
	ST9	121.143	33.839	15/05/07	6.0	sedimentation rates palaeo environment Chl-a	Yes	3 (night)
	ST10	121.169	33.816	15/05/07	1.8	Chl-a	Yes	3 (night) 3 (day)
	ST11	121.154	33.824	15/05/07	3.0	Chl-a	Yes	
	ST12	121.147	33.832	15/05/07	4.1		Yes	
	ST13	121.161	33.821	19/05/07	2.5	sedimentation rates	Yes	
	ST14	121.171	33.814	19/05/07	1.0		Yes	
	ST15	121.160	33.820	19/05/07	2.7		Yes	
Wellstead Estuary	WE6*	119.385	34.388	16/03/06	0.9	porewater*		1 (night)* 1 (day)
	WE7*	119.372	34.386	16/03/06	0.8	porewater*		2 (night)* 1 (day)
	WE8*	119.371	34.376	18/03/06	0.7	porewater*		2 (night)* 1 (day)
	WE9*	119.366	34.366	18/03/06	0.9	porewater*		1 (night)* 1 (day)
	WE10	119.385	34.383	17/05/07	1.3	sedimentation rates		
	WE11	119.373	34.386	17/05/07	1.0	sedimentation rates palaeo environment		

*Note benthic chamber and sediment core results for WE6, WE7, WE8, and WE9 are reported in Murray *et al.* (2007) and not here. [#]Water depths are absolute depths measured at the time of sampling and are not in reference to the Australian Height Datum.

2A. BENTHIC CHAMBERS

Benthic fluxes were measured at two sites in Stokes Inlet (ST9 and ST10; Figure 1-1; Table 2-1). These sites aimed to represent the two most extensive, but contrasting environments; namely, the relatively deep, southern part, near to the estuary mouth (ST9), where the water depth was 6 m, and the shallower northern part (ST10) nearer to the river entrance, where the water depth was 1.8 m (Figure 1-2).

Nutrient (NH_4^+, NO_X, PO_4^{3-}, SiO_4^{4-}), dissolved oxygen (O_2), nitrogen (N_2), and carbon dioxide (TCO_2) fluxes were measured at the sediment-water interface using benthic chambers. Fluxes were calculated from the change (either positive or negative) in metabolite concentrations over time inside each chamber (see Murray *et al.* 2007 for methods).

Individual deployments involved the placement of three chambers at a site for a duration of over 8 hours. These chambers were made of transparent Perspex, and therefore allowed any available sunlight through. Considering the differing light conditions at each site (outlined in the *Results* section below), two chamber deployments were carried out at site ST10; one during daytime and one during night time, whereas only one deployment was carried out at site ST9. This deployment was during daytime, however, it was assumed that negligible sunlight was able to penetrate the full depth of the water column to the chambers on the sediment surface.

Chamber deployments under *dark* conditions recorded oxygen consumption and nutrient release from respiration processes alone, whereas under *light* conditions, chambers recorded the net fluxes resulting from both respiration and photosynthesis.

2B. SEDIMENT CORES AND GRABS

Sediment grabs were collected from 7 sites in Stokes Inlet for vial incubations, Chl-a, and porosity analysis (Table 2-1). Sediment cores were collected for down core porewater analysis and surface sediment bulk organic matter properties from three sites (ST6, ST7, ST8) in Stokes Inlet (results reported here), and four sites (WE6, WE7, WE8, WE9) in Wellstead Inlet (see Murray *et al*. 2007).

Sites ST9 and ST13 in Stokes Inlet and sites WE10 and WE11 in Wellstead Estuary were selected for the determination of sedimentation rates (Table 2-1). Sites ST13 and WE11 are centrally located (Figure 1-1; Figure 1-7) and these sites are considered to adequately represent the depositional environment of the central basin in each estuary. Site ST9 is of interest because it is located in the deep southern part of Stokes Inlet, which is often stratified with anoxic bottom waters over long periods, for example, such as occurred February to December, 2006 (Figure 1-4). The long term frequency and effects of anoxia and stratification is potentially reflected in the sediment record. Site WE10 is located at the edge of a present-day seagrass area in the south-eastern part of Wellstead Estuary. All cores have a length of approximately 1 m.

In addition to analysis of present-day and pre-European sedimentation rates, several other types of analysis (i.e. pollen, biomarker, bulk organic matter, and bulk geochemical (XRF) analysis) were performed with the aim to reconstruct changes in water quality and palaeo-environmental conditions over time. Because sample preparation and analysis are labour intensive, these additional analyses were only carried out on sediments from one site in each estuary (Table 2-1). Site ST9 in the deep basin, was chosen for Stokes Inlet, because this site is likely to have undisturbed depositional conditions. Site WE11 was chosen for Wellstead Estuary, because the site is likely to be representative for estuary-wide changes in water quality.

2B1. Vial Incubations

The determination of organic matter reactivity in surface sediments using simple vial incubations was trialled for the first time in Stokes Inlet as part of this study. Table 2-1 shows the sites where sediment grab samples were taken for these incubations. The top 1 cm of sediment was incubated under anoxic conditions for 24 hours and the production of dissolved inorganic carbon was determined.

2B2. Porewater Properties

Geoscience Australia collected sediment cores from three sites in Stokes Inlet (ST6, ST7, ST8) for porewater analysis in the earlier survey in March 2006 (Table 2-1; Figure 1-1). The findings from these cores are included in here. Sediment cores for porewater analysis were also collected in March 2006 from four sites in Wellstead Estuary (WE6, WE7, WE8, WE9 in Figure 1-7), the results of which, have already been reported by Murray *et al*. (2007). Down core sediment porewaters were analysed for nutrients (NH_4^+, SiO_4^{4-}, NO_3^-, PO_4^{3-}), and salinity (see Murray *et al.* 2007 for methods).

2B3. Palaeo-Environmental Analysis

Sediment Dating

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

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

The deepest sample in each core with a ^{137}Cs activity exceeding the standard error (0.4 dpm g^{-1}) was taken as a marker for the beginning of nuclear testing in the year 1955. Discrete maxima in ^{137}Cs in the two cores from Stokes Inlet (Figure 3-13) were additionally considered as a marker for the year 1964 when nuclear testing reached its climax, although there is some doubt whether this peak truly represents fallout maximum. Variable rates of topsoil erosion in the Stokes catchment could also be responsible. In addition, the 1964 ^{137}Cs fallout peak in the Southern Hemisphere was not as distinct as it was north of the equator, and the lack of reliability of the 1964 peak as a marker is demonstrated in the two cores from Wellstead Estuary, where no distinct ^{137}Cs maxima are observed (Figure 3-14).

Once the year of deposition was determined for a given sediment depth, e.g. 1955 for sediment at a depth of 64 cm in core ST9, the $^{210}Pb_{exc}$ depth distribution was used to derive a high resolution age model for the upper sediment column. Two models can be applied; one assumes a constant initial concentration (CIC), and the other one, a constant rate of supply (CRS) of ^{210}Pb. The CRS model is generally found to give more reliable results when there are large fluctuations in the measured $^{210}Pb_{exc}$ as a function of depth, i.e. when distinct maxima or minima are observed. This is the case for ST9 and ST13 (Figure 3-13). For these cores, the CIC model gives poor agreement with the observed 1955 ^{137}Cs horizons and it is rejected as a plausible dating alternative. In contrast, ^{210}Pb decreases relatively continuously in cores WE10 and WE11 (Figure 3-14) and the CIC and CRS age models agree reasonably in these cores. In this study, a calibrated CRS model (Applebly 2001) was applied for all cores. The CRS ages were calibrated such that the appearance of ^{137}Cs in the core profile was set at 1955.

Bioturbation may prevail at the sediment surface leading to a homogenisation of sediment and associated radioisotopes. The depth of bioturbation can be constrained from the occurrence of short-living radioisotopes such as ^{228}Th in the subsurface of cores. It was concluded that bioturbation is likely to have been negligible in Stokes Inlet cores, which is expected given the long periods of bottom water anoxia, especially at ST9. If bioturbation is occurring at ST9 it appears to be insignificant compared to the rate of sediment accumulation. For cores taken at sites ST13, WE10, and WE11, the shallow and well oxygenated nature of the water was considered favourable for bioturbation and a bioturbated (mixed) layer of 6 cm was applied. Thus a 2-layer model was applied to ST13, WE10, and WE11, whereby the age models are considered to start at the base of the mixed layer.

The occurrence of the ^{137}Cs maxima in the Stokes cores (noted above) corresponds to CRS dates in the mid-1970's. Given the uncertainty associated with the origin of the ^{137}Cs maxima (discussed above) we have decided not to recalibrate CRS ages in accordance with these maxima. However, it is worth noting that if the ^{137}Cs maxima do represent the 1964 horizon then the trend in elevated sedimentation rates in Stokes Inlet for the period 1955 to ~1965 (see below) would be enhanced even more (~ 2 times).

Bulk Organic Matter Analysis

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

Biomarker Sample Preparation and Analysis

Organic compounds indicative for phytoplankton groups such as diatoms and dinoflagellates, as well as for microorganisms living under anoxic conditions were extracted from cores ST9 and WE11 and analysed in the Geoscience Australia laboratories.

All samples were freeze-dried before analysis. Sample filters were powdered using solvent-clean mortar and pestle. Sediment samples were extracted using a Dionex Accelerator Solvent Extractor

ASE 200 with dichloromethane at 100°C and under 1000 psi. 5% of the total organic extract was derivatized with Bis-trifluroacetimide (BSTFA) before analysis. Aliquots were analysed by GC/MS using a Hewlett Packard MSD 5973 attached to an HP6890 GC. Injections were made on a HP-5 capillary column (50 m, 0.2 mm ID and 0.11 µm film thickness, J&W Scientific) in splitless mode. The oven was programmed from 40°C with 4 min hold to 150°C at 10°C/min, 150°C to 310°C at 4°C/min with 65 min hold at 310°C. Helium was used as a carrier gas at a constant pressure of 25 psi. The mass spectrometer was operated in electron-impact at 70 eV and in full scan mode, scanning a mass range of m/z 50 to 650 at 0.8 $scan.s^{-1}$.

Pollen and Spore Sample Preparation and Analysis

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

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

Bulk Geochemical Analysis (X-Ray Fluorescence (XRF) Spectrometry)

Sediment samples from cores ST9 and WE11 were analysed by X-ray fluorescence at the Geoscience Australia laboratories to determine major, minor, and some trace elements. These were determined using a Philips PW2404 4kW Sequential Spectrometer with a Rh tube and according to a modified version of Norris and Hutton's (1969) methods. The instrument was calibrated using a range of international standards from United States Geological Survey (USGS) and South African Reference Material (SARM). Approximately 1 gm of ground sample was combined with flux material and 0.5 ml of 20% $LiNO_3$. The mixture was heated at 400 ºC for 10 minutes then at 1100 ºC for a further 10 minutes during which time a tablet of Ammonium Iodide was added. The resulting melt was poured into moulds, cooled, and then introduced to the XRF. The reported precision was better than 5%.

3. Results and Discussion

3A. ENVIRONMENTAL CONDITIONS DURING THE SURVEY

Stokes Inlet was open to the ocean for an extended period just prior to the survey; opening following a heavy rainfall event on 5th January 2007, and closing 4th April 2007. Exchange with the ocean during this period had evidently influenced water column properties within the Inlet, creating well-mixed and well-oxygenated conditions, and preventing stratification, which otherwise often develops at this time of year in the deeper areas greater than 5.5 m water depth (Figure 1-3 and Figure 1-4). The opening period was also relatively long, considering that in the past it usually only opens for around 2 weeks every two to seven years (DOW 2007).

Water column profiles of temperature, salinity, dissolved oxygen, and light were measured at a deep site (ST9) and a shallow site (ST10), several times throughout the survey period, and during both overcast and fine weather (Figure 3-1). Light levels (photosynthetically active radiation; PAR) throughout the water column were measured using a quantum sensor LI-COR light meter (LI-250A). These showed there was very little light reaching the bottom sediments at the deep site (ST9), even under clear and sunny conditions (Figure 3-1). Light levels were negligible below 3 m water depth. At the shallow site (ST10), there was distinctly reduced but sufficient light reaching the bottom for photosynthesis to occur at the sediment surface.

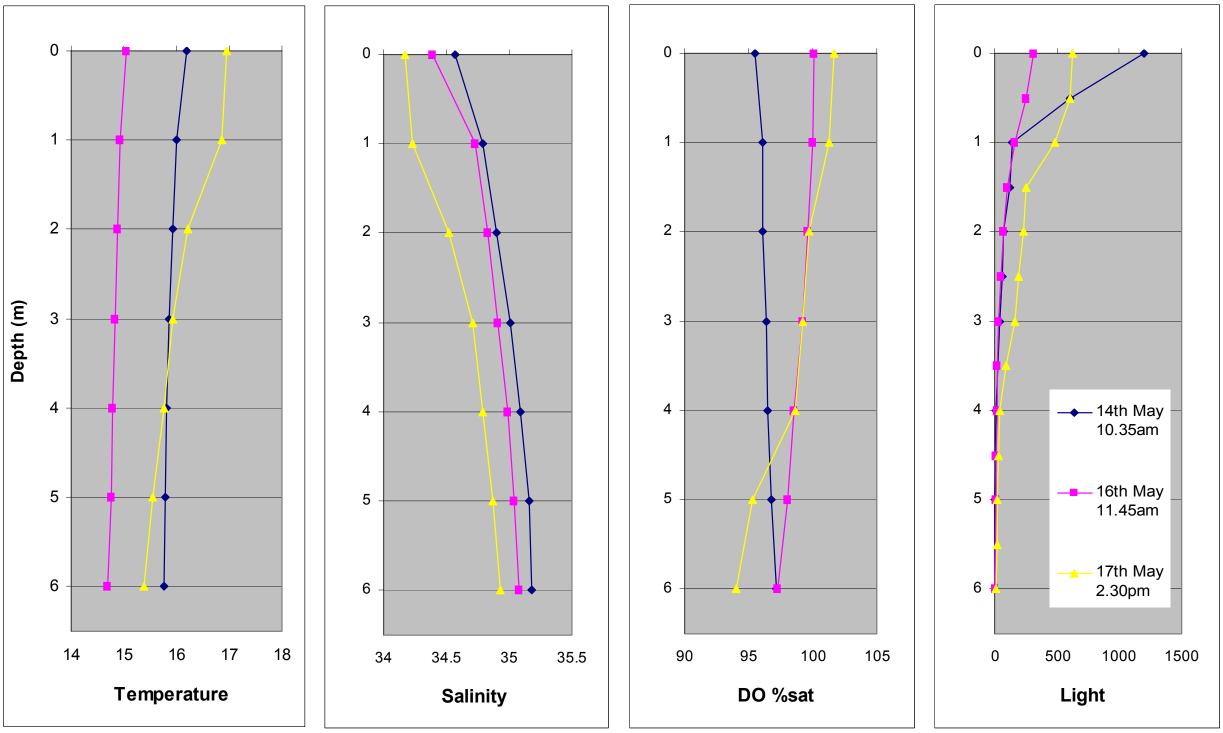
Temperature, salinity, and dissolved oxygen (DO) measured in the water column using a YSI 600XLM sonde did not differ significantly between the two sites (Figure 3-1). These parameters also did not change significantly with water depth at each of the two sites, indicating a well-mixed water column throughout the Inlet. Depth profiles showed that salinity was between 34 and 35, which is close to the salinity of seawater, and temperatures were between 13 and 17ºC. Notably, DO levels were around 100% saturation (between 94 and 113%) throughout the water column and throughout the Inlet. Indications of oxygen uptake (respiration) at the sediment surface was evident at the deep site (ST9) on May 17th with a reduction in DO from 102 to 94% between the surface and bottom.

Phytoplankton was most abundant during the survey period close to the Young and Lort River entrance (Figure 3-2). Phytoplankton diversity was also highest near the river entrance, with 11 categories of phytoplankton present at the site closest to the entrance (DOW_5), and only between 6 to 8 categories at the sites further away from the river entrance. Possibly this is due to the greater abundance of nutrients at this site provided by inflows from the Young and Lort River catchments. Notably, non-nitrogen fixing Cyanophyta species are present at this site, indicating that nitrogen is readily available in the water column here.

Diatoms were by far the most dominant type of phytoplankton and their abundance was fairly similar across the entire Inlet (Figure 3-2).

Water column conditions were not measured in Wellstead Estuary during the May 2007 survey because the immediate water column conditions on the day of sediment core collection were not important for the particular analysis being carried out on the cores (eg. sedimentation rates, palaeo-environmental). Water column parameters were however measured and interpreted in the preceding GA survey involving benthic chamber experiments and porewater analysis (see Murray *et al*. 2007).

ST9 (Deep Site: 6 m)



ST10 (Shallow Site: 1.8 m)

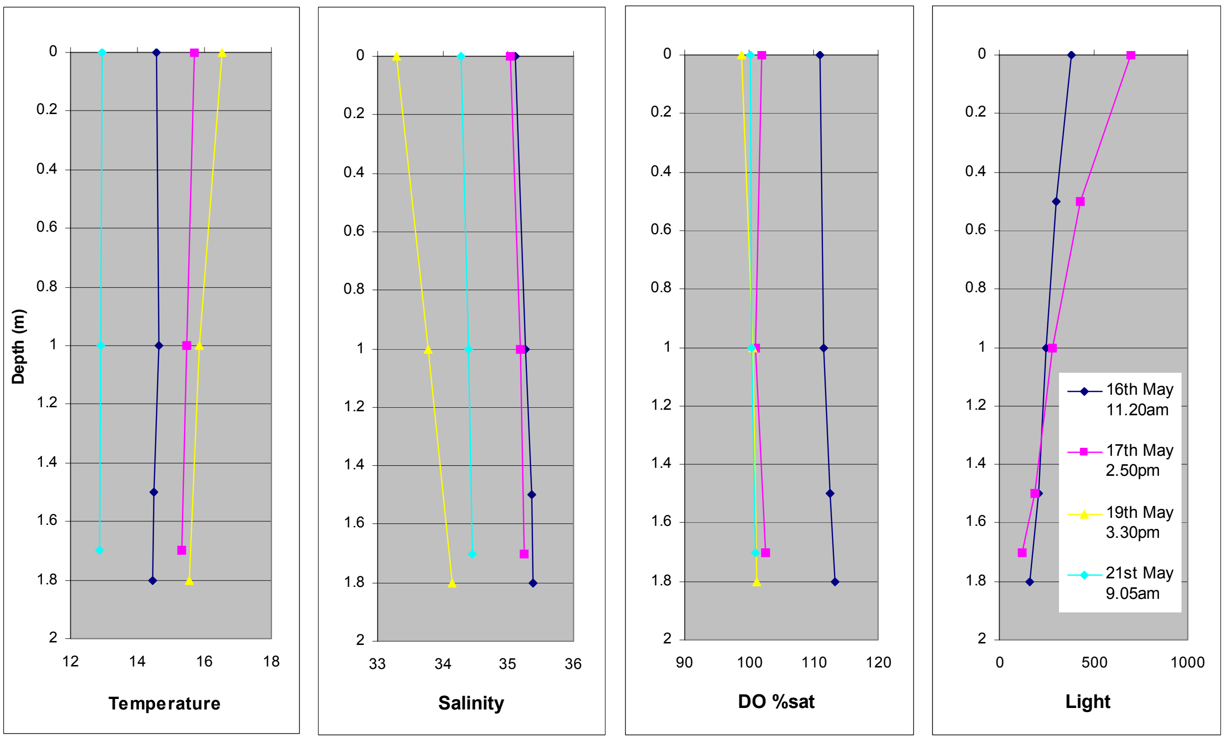


Figure 3-1: *Water column profiles showing changes in temperature, salinity, dissolved oxygen, and light (PAR) with depth at sites ST9 and ST10. Weather conditions were overcast May 14th, 16th, and 21st, and sunny May 17th and 19th.*

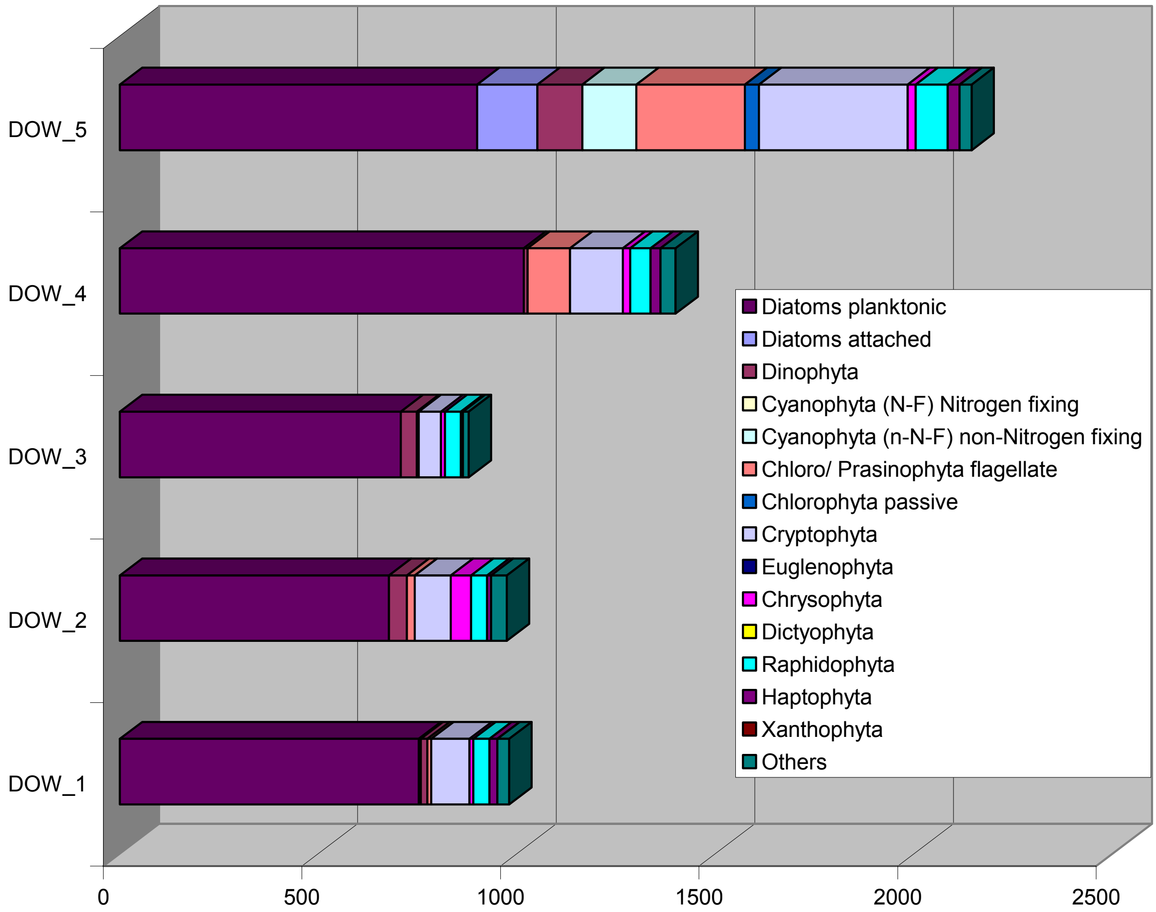


Figure 3-2: *Phytoplankton abundance (cells / mL) at WA Department of Water sampling sites collected on 13th May 2007. The sampling sites are arranged from most upstream near the Young and Lort River entrances (DOW_5) to the most downstream site near the ocean entrance (DOW_1). See Figure 1-1 for site locations.*

3B. PRESENT-DAY NUTRIENT DYNAMICS IN STOKES INLET

Present-day nutrient dynamics in Stokes Inlet is discussed here based on an analysis of the benthic fluxes derived from benthic chamber and vial incubation experiments, and the sediment porewater and surface sediment properties. Note that only Stokes Inlet is discussed. See Murray *et al*. (2007) for an analysis of nutrient dynamics in Wellstead Estuary derived from the results of the earlier GA survey in March 2006.

3B1. Benthic Fluxes

Benthic Chambers

Benthic fluxes derived from benthic chamber experiments showed no significant difference between the deep (ST9) and shallow (ST10) sites in regards to the average benthic fluxes of O_2, TCO_2, and NH_4^+ when considering the overlap in the range of individual flux measurements (Table 3-1; Figure 3-3). In addition, there was also no significant difference between the average O_2, TCO_2, and NH_4^+ fluxes measured under *light* and *dark* conditions at the shallow site (ST10).

Based on these results, it appears that at the time of the survey, in late autumn, the nature of organic matter breakdown throughout Stokes Inlet, both in deep and shallow areas, was fairly uniform, and that respiration dominated over photosynthesis. TCO_2 fluxes were positive in all chambers, including the light chambers at site ST10, indicating that TCO_2 release from organic matter breakdown was greater than TCO_2 uptake from photosynthesis (Figure 3-3). In addition, O_2 fluxes were negative in all chambers, including the light chambers, indicating that O_2 uptake from organic matter breakdown was greater than O_2 release from photosynthesis. This is perhaps typical for this time of year (late autumn), where lowering temperatures and shorter day length (less light availability) reduce plant activity (primary production) and therefore photosynthesis. As such, the breakdown of plant material such as macroalgae that would have grown in the warm spring and summer months, dominates over plant growth and the activity of, for instance, microbenthic algae photosynthesising at the sediment surface. The relatively low Chl-a concentrations throughout the Inlet in late autumn observed in the DOW monitoring data (Figure 1-6) is also indicative of this.

Table 3-1: Benthic fluxes in mmol m^{-2} day^{-1} measured at sites ST9 and ST10 in Stokes Inlet. See Appendix 1 for the raw data used to calculate these benthic fluxes.

Site ID	Light Conditions	Water Depth (m)	Chamber #	O_2	TCO_2	NH_4^+	NO_X	PO_4^{3-}	SiO_4^{4-}
ST9	Dark	6.0	1	-89.2	107.7	7.1	-0.7	0.33	12.3
ST9	Dark	6.0	2	n/a	56.5	6.5	-0.7	0.12	5.3
ST9	Dark	6.0	3	-53.9	36.3	7.8	-0.6	0.06	2.6
ST10	Dark	1.8	1	-71.3	89.3	7.4	-0.3	0.03	4.1
ST10	Dark	1.8	2	-90.9	60.1	6.1	-0.8	0.02	4.1
ST10	Dark	1.8	3	-35.5	43.6	5.0	-0.3	0.01	1.3
ST10	Light	1.8	1	-89.6	66.4	8.1	0.4	0.04	5.9
ST10	Light	1.8	2	-37.2	96.6	6.9	0.3	0.05	4.7
ST10	Light	1.8	3	-26.6	53.7	4.8	0.3	0.02	2.6

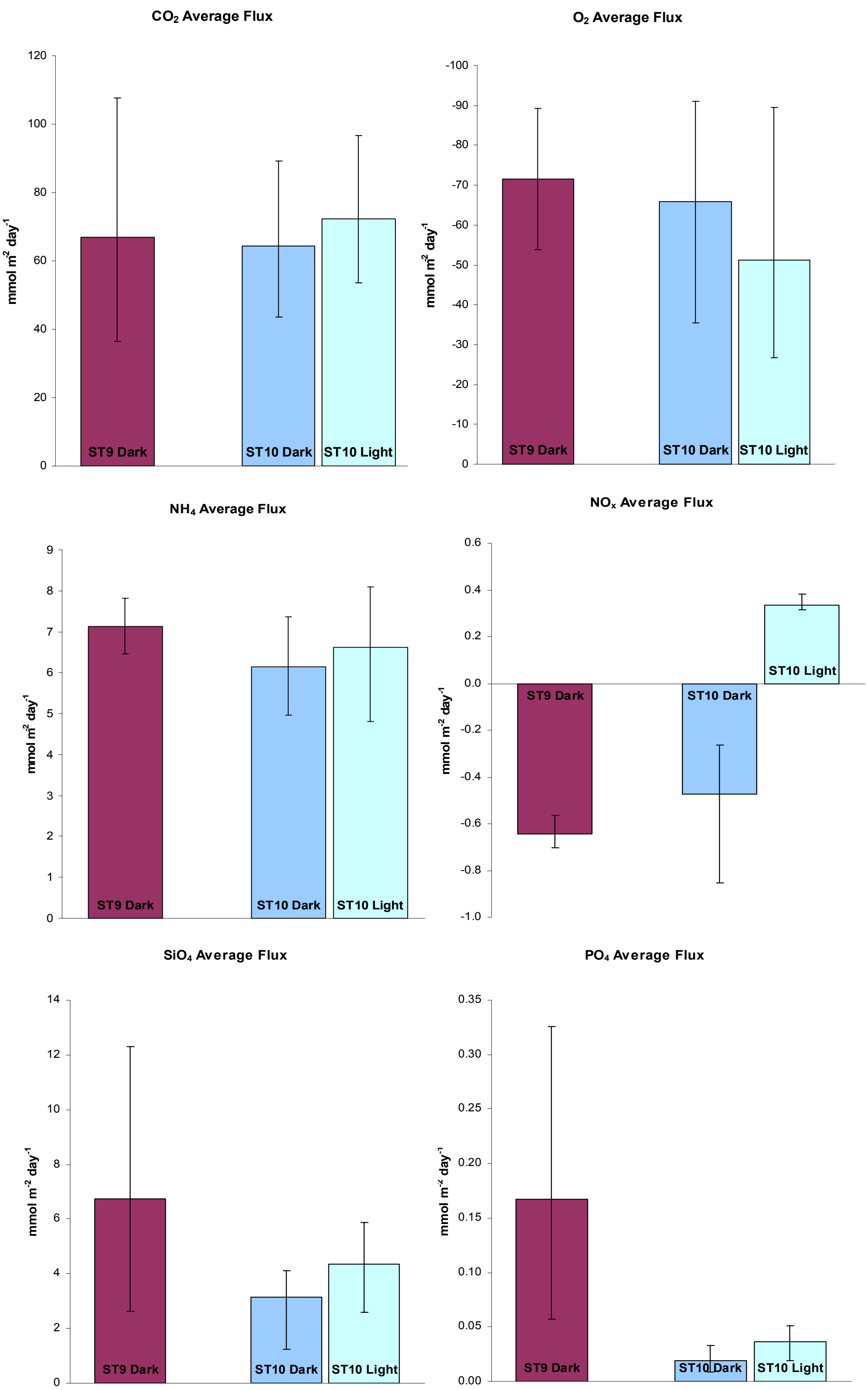


Figure 3-3: *Average CO_2, O_2, NH_4, NO_x, SiO_4, and PO_4 benthic fluxes at sites ST9 and ST10 in Stokes Inlet. Error bars show the maximum and minimum fluxes (i.e. the range). Fluxes were measured under both "Dark" and "Light" conditions at site ST10, but only "Dark" conditions at site ST9.*

One factor leading to the similarity in TCO_2, O_2, and NH_4^+ fluxes across the Inlet was perhaps the opening of the Inlet to ocean exchange for about 3 months (5th January - 4th April 2007), closing only about 5 weeks prior to field sampling. The absence of stratification in the deep part of the Inlet (ST9) was probably due to tidal exchange and mixing with marine water while the estuary mouth was open to the ocean. Water column profiles showed that salinity was marine and fairly homogeneous throughout the estuary (Figure 3-1). Temperatures were also fairly uniform, and dissolved oxygen close to 100% saturation throughout the water column at both shallow and deep sites. Wind-driven mixing may also have contributed to this. Under these conditions, bottom waters in the deep (6 m water depth) parts of the Inlet were almost as well-oxygenated as those in the shallow areas, and organic matter breakdown was mainly aerobic as opposed to anoxic.

Under these aerobic conditions, denitrification was likely occurring. Reasonably high rates of NO_x uptake in all dark chambers at both the deep and shallow sites (Table 3-1; Figure 3-3) certainly indicate that denitrifying bacteria were consuming NO_x during respiration. Further evidence is that NH_4^+ release did not increase with increasing rates organic matter breakdown, indicated by the absence of any increase in NH_4^+ release with increasing TCO_2 release (Figure 3-4). Therefore, assuming the C:N ratio of the organic matter breaking down was similar at both the deep and shallows sites, with increasing rates of organic matter breakdown, an increasing proportion of N was being denitrified and lost to the atmosphere as N_2 gas.

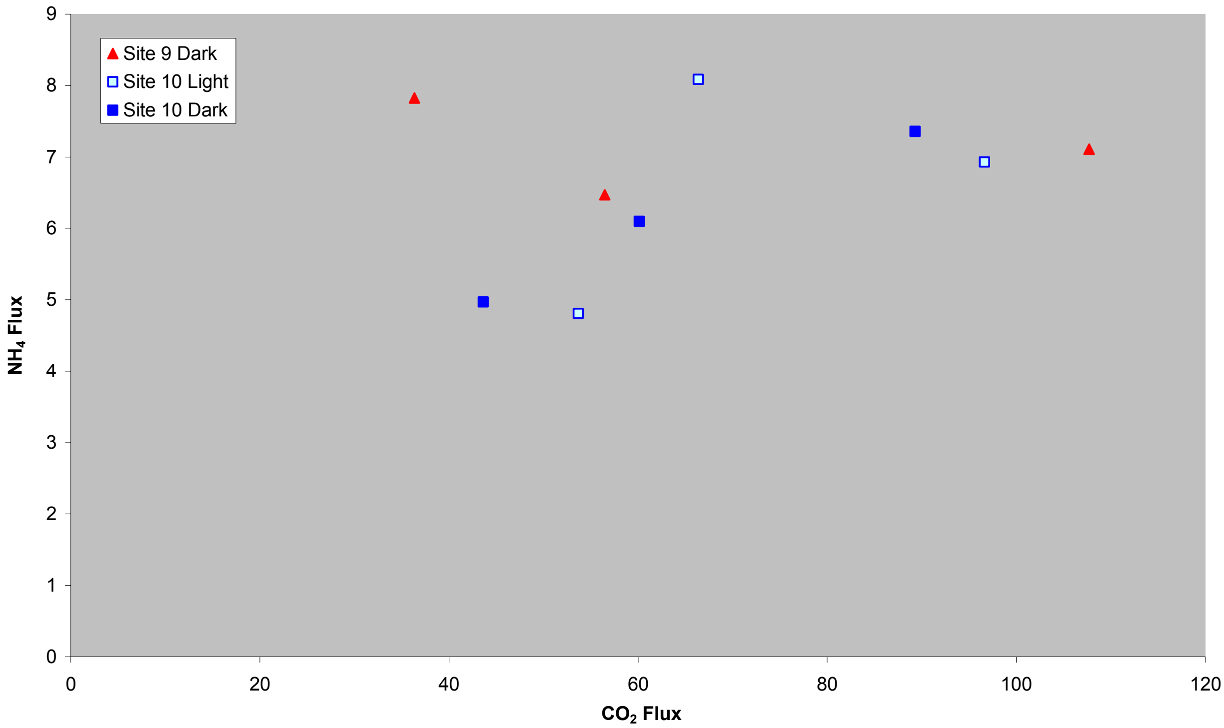


Figure 3-4: *NH_4^+ release plotted against TCO_2 release in mmol m^{-2} day^{-1}.*

In contrast to NH_4^+, rates of PO_4^{3-} release were distinctively higher at the deep site (ST9), compared to the shallow site (ST10), and also increased significantly with increasing TCO_2 release (Figure 3-3 and Figure 3-5). This indicates that at the time of sampling, the sediments at ST9 had little P binding capacity and P was being released to the overlying water column. Notably, this was despite well-oxygenated bottom waters at the deep site at the time of benthic chamber experiments in May 2007 (Figure 3-1). Therefore, extended periods of stratification and bottom water anoxia prior to this, in the deep parts of the Inlet, have likely reduced the P-binding capacity of the sediments, where

P-binding iron oxides were lost and the subsequent period of oxygenated bottom waters had not yet been sufficient to reconvert iron sulphides back into iron oxides. Accordingly, the porewater results, which were obtained during the period of stratification (February to December 2006; Figure 1-4) showed that no P was being retained in the sediment at that time (see section *3B3 Porewater and Surface Sediment Properties*).

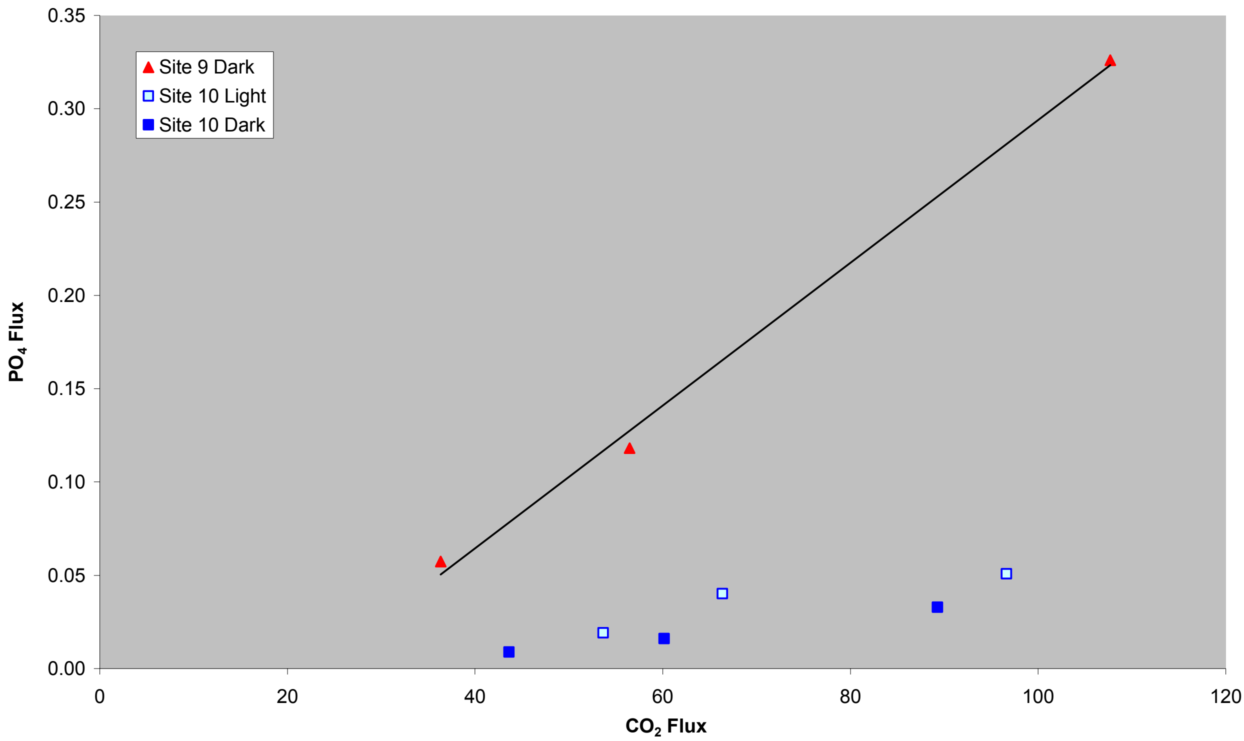


Figure 3-5: *PO_4^{3-} release plotted against TCO_2 release in mmol m^{-2} day^{-1}.*

The benthic fluxes can also give clues on the composition of organic matter breaking down in the sediment. Firstly, looking at the phytoplankton analysis undertaken on samples collected during the survey, it appears that the phytoplankton community in the Inlet was 80-90% diatom dominated (Figure 3-2). However, the benthic fluxes indicate that some other plant material, most likely macroalgae, which is known to grow in the Inlet, was also contributing to the organic matter breaking down in the sediments. This notion is based on the plot of SiO_4^{4-} against TCO_2 fluxes (Figure 3-6), which plot below the ratio expected for the breakdown of 100% diatom material. Given this however, comparing the deep and shallow sites, it could be said that a greater proportion of the organic matter breaking down at the deep site (ST9) was diatomaceous, since SiO_4^{4-} release was higher at the deep site.

More broadly, compared to other temperate Australian estuaries, rates of organic matter breakdown in Stokes Inlet were moderate to high, having TCO_2 fluxes ranging from 36 to 108 mmol m^{-2} day^{-1} (Figure 3-7). Similarly, NH_4^+ fluxes are moderate to high compared to other temperate Australian estuaries (not shown). Previous GA studies have found that release of N and P from the sediments increases exponentially once TCO_2 fluxes exceed 100 mmol m^{-2} day^{-1}. This was based on plots of the average TCO_2, NH_4^+, and PO_4^{3-} fluxes from over 22 temperate Australian estuaries, where GA has measured benthic fluxes. In this context, Stokes Inlet is possibly on the threshold of developing exceedingly high N and P release, and becoming eutrophic, if organic matter loading to the sediments were to increase.

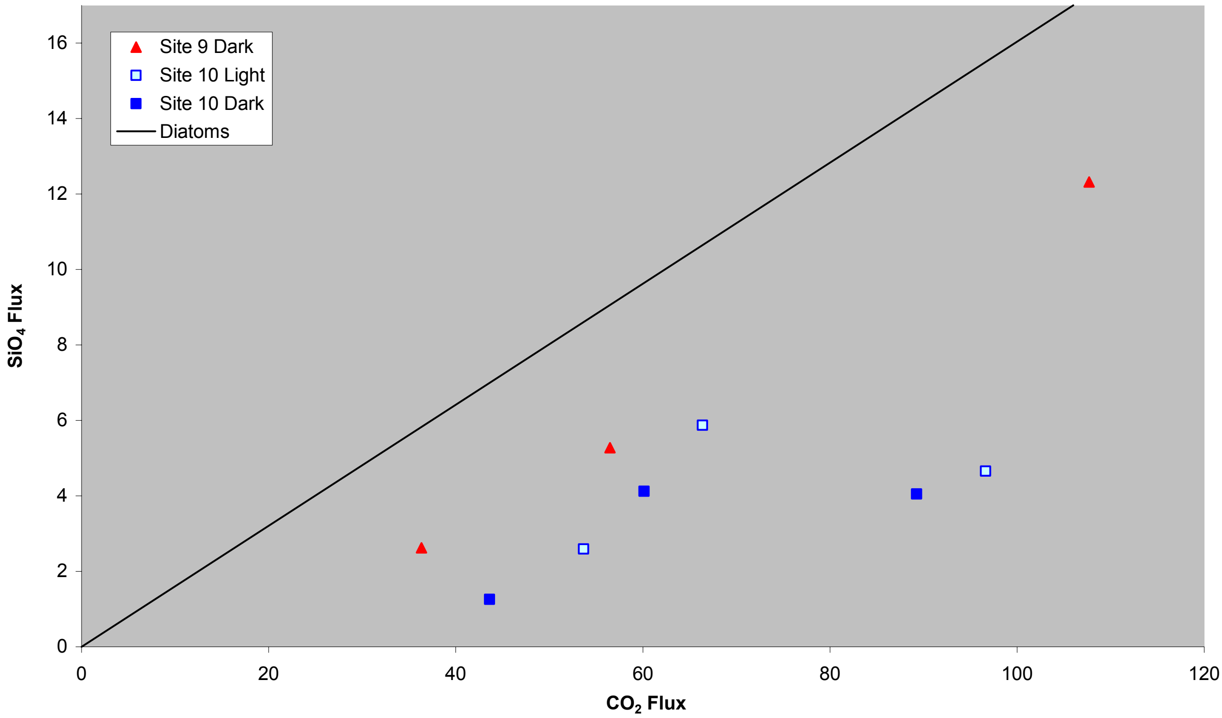


Figure 3-6: *SiO_4 release plotted against TCO_2 release in mmol m^{-2} day^{-1}.*

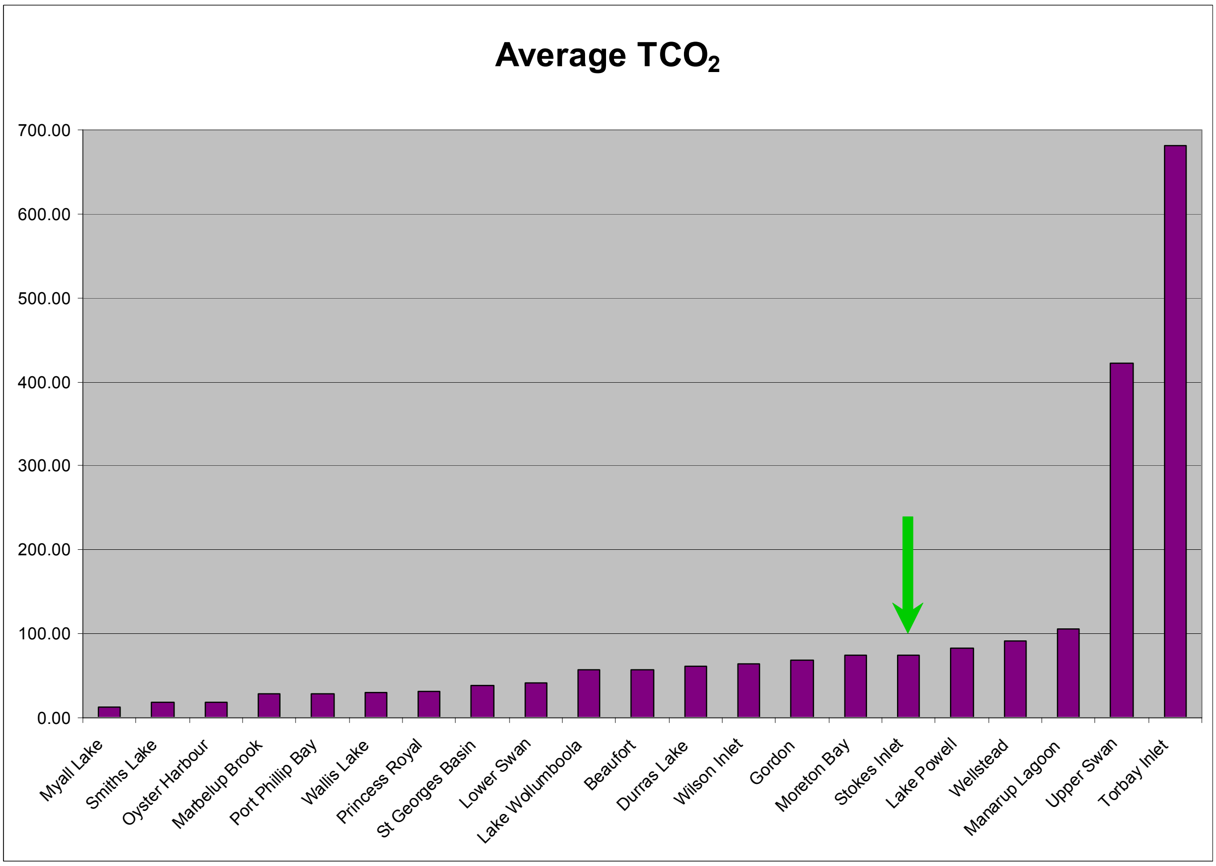


Figure 3-7: *Average TCO_2 fluxes of Stokes Inlet compared to other temperate Australian estuaries surveyed by Geoscience Australia.*

Vial Incubations

The vial incubations showed that at the time of the survey, the highest organic matter reactivity was in the shallow northern part of Stokes Inlet (ST14), gradually decreasing with increasing water depth, to a water depth of 3 m (ST11; Figure 3-8). Along this depth transect, porosity and Chl-a concentration in surface sediments were also decreasing with increasing water depth, suggesting that the distribution of reactive organic matter and Chl-a are predominantly controlled by the distribution of fine sediments.

Only the deep site ST9 at a water depth of 6 m is an exception, as fine sediments and high Chl-a concentrations occur, but the reactivity of organic matter in the top 1 cm of sediment is low. Interestingly, this contrasts to the benthic chamber results, where the magnitude of inorganic carbon fluxes measured at sites ST9 (6 m water depth) and ST10 (1.8 m water depth) were very similar. This discrepancy may be related to the fact that the thickness of the reactive organic matter layer is extending deeper at site ST9 than at site ST10, which enhances the *total* resulting production of inorganic carbon from the sediment to the overlying water column.

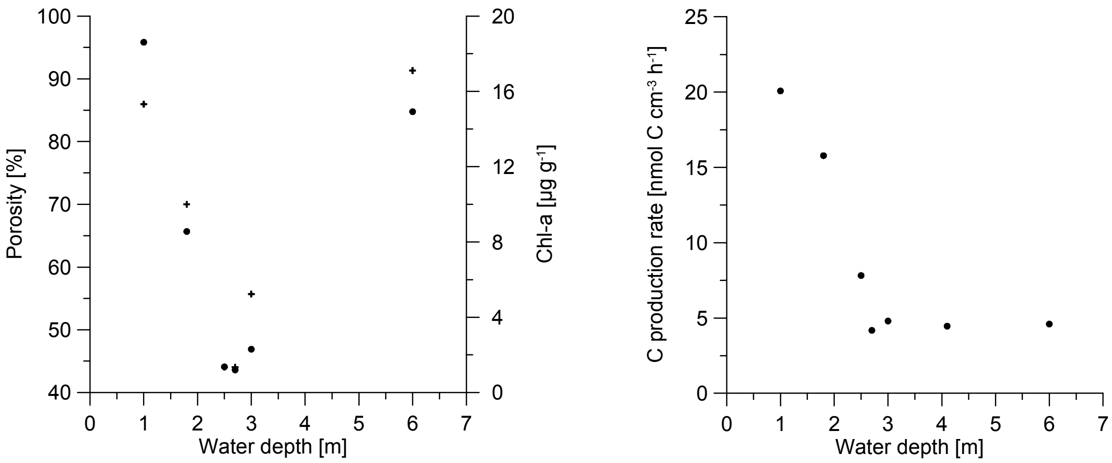


Figure 3-8: *The change in porosity (shown as crosses) and Chl-a (shown as dots) with water depth (left graph) and the change in carbon production with water depth (right graph).*

3B2. Porewater and Surface Sediment Properties

Sediment cores were collected from three sites in Stokes Inlet (ST6, ST7, ST8) for porewater and sediment analysis in March 2006 (Table 2-1; Figure 1-1). Unfortunately these could only be collected from sites with water depths greater than 2 m, as sites shallower than this had sediments that were too coarse and compacted to allow for coring. This is likely due to the exposure and drying of these sediments when the bar is open and the water level drops to sea level.

The retrieved sediment cores had a length of 50 to 60 cm. Sediments were generally very fine ('muddy'), dark grey to black in colour, and shell fragments were found particularly in lower parts of the cores. A deep green, fluffy layer was found on top of cores from sites ST7 and ST8, which suggests recent deposition of organic rich material possibly from a summer phytoplankton bloom period.

Surface sediment organic matter concentrations ranged between 5.1 and 8.4 wt% carbon (Table 3-2), which is in the range of typical estuarine sediments. The stable isotopic composition of organic carbon and nitrogen also suggests that the organic matter in surface sediments was largely formed within the estuary (Figure 3-9). However, the surface sediment at the shallow site (ST8), which is also the closest site to the river mouth, appears to contain the largest fraction of catchment-derived organic matter as it has the most negative $\delta^{13}C$ value (Table 3-2).

Table 3-2: Surface sediment properties for the three sites where sediment cores were collected in Stokes Inlet.

Site ID	Water Depth (m)	TOC (wt%)	TN (wt%)	$\delta^{13}C$-TOC [‰]	$\delta^{15}N$-TN [‰]
ST6	6.5	5.1	0.6	-22.8	6.3
ST7	4.2	5.0	0.6	-23.0	5.2
ST8	2.5	8.4	1.0	-24.6	6.8

Porewater profiles did not show steep gradients in salinity with depth in the sediment (Figure 3-10, Figure 3-11, and Figure 3-12) suggesting that salinities in surface sediments were the same as those in the bottom water. Following that conclusion, the bottom water at a water depth of 6.5 m (site ST6) had a salinity of 75, whereas the bottom water at sites with water depths between 2.5 and 4.2 m (sites ST7 and ST8) had a salinity of 50, indicating the presence of a density stratification boundary between 4.2 and 6.5 m water depth. This is in agreement with the DOW monitoring record, where the boundary separating higher salinity, anoxic bottom waters from relatively less saline and well-oxygenated surface waters was between 5 and 6 m water depth, during the period February to May 2006 (Figure 1-3 and Figure 1-4). Furthermore, the generally high salinities in Stokes Inlet at this time indicate there had been very little recent freshwater catchment run-off into the Inlet prior to sampling (March 2006), along with extensive evaporation, leading to the high salt content. Alternatively, run off from the catchment is highly saline.

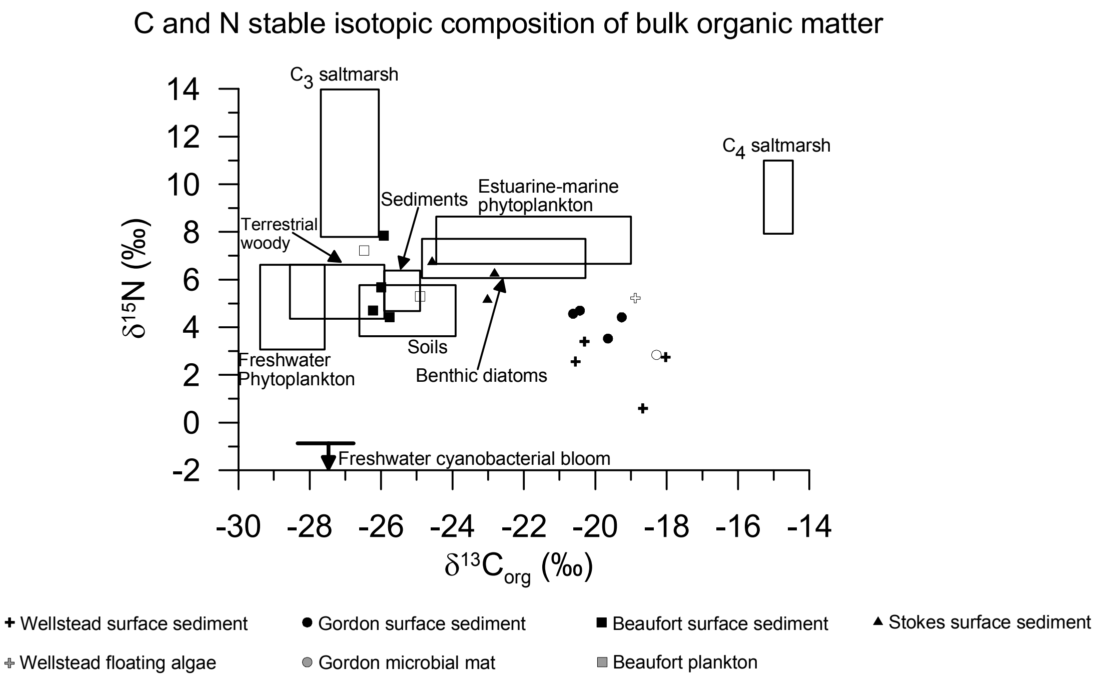


Figure 3-9: *Cross plot of organic carbon and nitrogen stable isotopic composition in surface sediments. Rectangles indicate end members of organic matter sources according to Cloern et al. (2002).*

Nutrient porewater profiles from sites with shallow (ST8) and intermediate (ST7) water depths were very similar (Figure 3-11 and Figure 3-12), however the porewater profiles from the deep site (ST6; Figure 3-10) differed distinctively from those of the shallower sites. Surface sediment concentrations of NH_4^+, Si, and PO_4^{3-} at the shallower sites were very low, suggesting low rates of nutrient release from the sediments and consequently, likely low nutrient concentrations in bottom waters. In contrast, surface sediment porewater nutrient concentrations at the deep site (ST6) were very high, suggesting very high nutrient fluxes out of the sediments in the deep basin. This is in agreement with the DOW monitoring data record (Figure 1-5) for early 2006, which shows elevated TN and TP concentrations in the bottom water of the deep basin compared to shallow sites and also surface waters across the entire Inlet.

Stratification of the water column is the likely cause for the elevated release of nutrients from the deep basin sediments. Anoxic bottom waters in the deep basin, as indicated in the DOW monitoring data would be inhibiting both (1) the retention of PO_4^{3-} by adsorption to iron oxides, and (2) the transformation of NH_4^+ into N_2 by denitrification. Consequently, these nutrients are released from sediments at a higher rate in the deeper part of the basin compared to the shallower part. In addition, photosynthetic activity by microbenthic algae at shallow and intermediate water depths may also additionally reduce the release of nutrients from sediments by assimilating nutrients into biomass. In summary, from salinity and nutrient concentration profiles in sediments, it is concluded that the deeper part of Stokes Inlet (> 5m water depth) receives a significant input of nutrients from sediments, whereas shallower sediments (< 5 m water depth) retain and transform bioavailable nutrients efficiently.

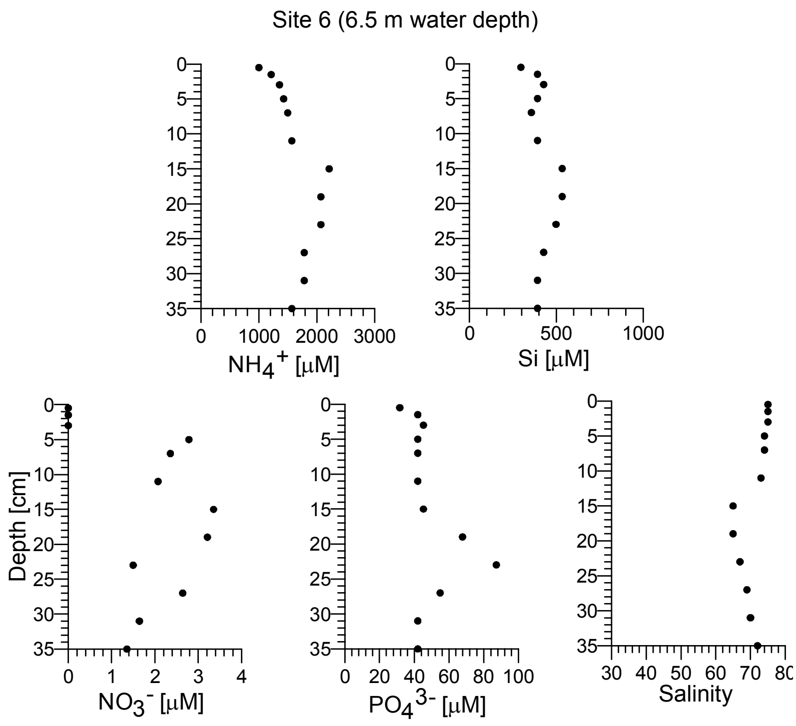


Figure 3-10: *Sediment porewater profiles of NH_4^+, Si, NO_3^-, and PO_4^{3-}, concentrations, and Salinity at site ST6 in Stokes Inlet.*

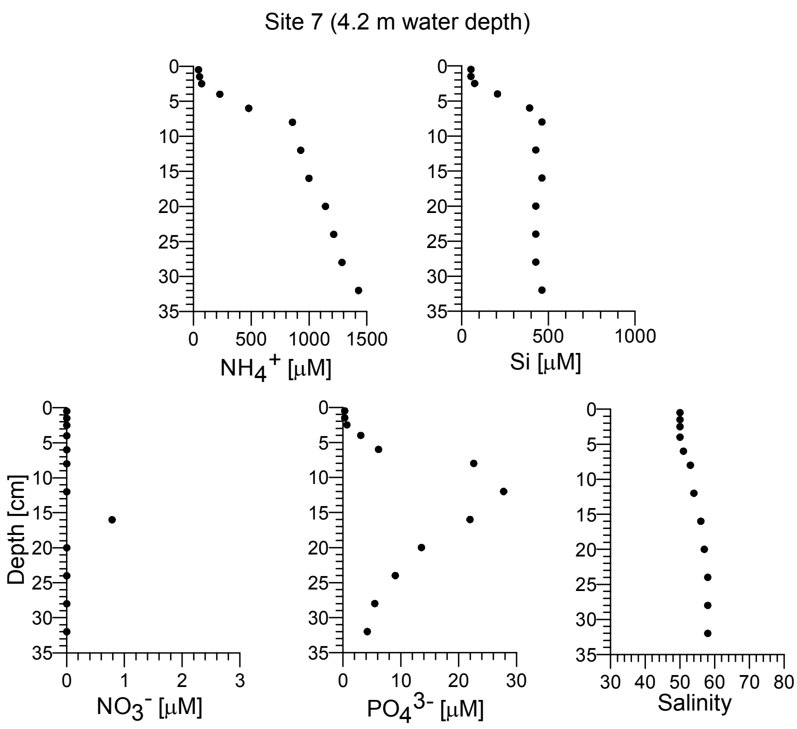


Figure 3-11: *Sediment porewater profiles of NH_4^+, Si, NO_3^-, and PO_4^{3-}, concentrations, and Salinity at site ST7 in Stokes Inlet.*

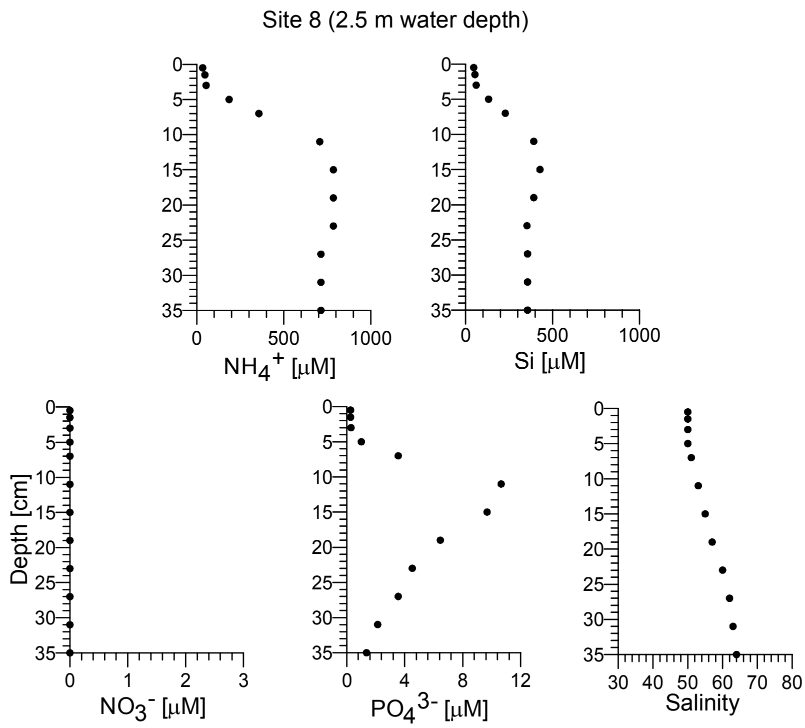


Figure 3-12: *Sediment porewater profiles of NH_4^+, Si, NO_3^-, and PO_4^{3-}, concentrations, and Salinity at site ST8 in Stokes Inlet.*

Comparing the porewater results, which were obtained in March 2006, a time when the Inlet was stratified, to the benthic chamber results, which were obtained in May 2007, when the Inlet was well mixed, reveals some significant findings. Firstly, as mentioned in the benthic chamber section previously, PO_4^{3-} fluxes in May 2007 in the deep basin were very high, despite well-oxygenated bottom waters. This is likely a result of the loss in P-binding capacity during periods of stratification and bottom water anoxia. Of concern however, is that the sediment had not regained any P-binding iron oxides, despite over 4-5 months of well-oxygenated bottom waters. An important question is how long is required for the sediments to regain a sufficient pool of iron oxides? Evidently, based on these results, it is longer than 5 months.

The second important finding, in contrast to P-binding capacity, is that denitrification appears to re-establish with the reintroduction of aerobic conditions following periods of anoxia, where denitrification was evident in the benthic chamber results.

3C. PALAEOENVIRONMENTAL RECONSTRUCTION

Changes in environmental condition over time in Stokes Inlet and Wellstead Estuary are discussed here based on an analysis of the sediment dating, pollen, organic biomarker, and bulk geochemical properties results.

3C1. Sediment Dating

The ^{137}Cs marker for the year 1955 (= 52 years B.P.) was found at a depth of 64 and 42 cm in cores ST9 and ST13, respectively (Figure 3-13). In cores from Wellstead Estuary, this marker depth is found at shallower depths, i.e. at 26 and 30 cm for cores WE10 and WE11, respectively (Figure 3-14). For the bottom of each core, an absolute age was determined using the optically stimulated luminescence (OSL) dating method (Table 3-3).

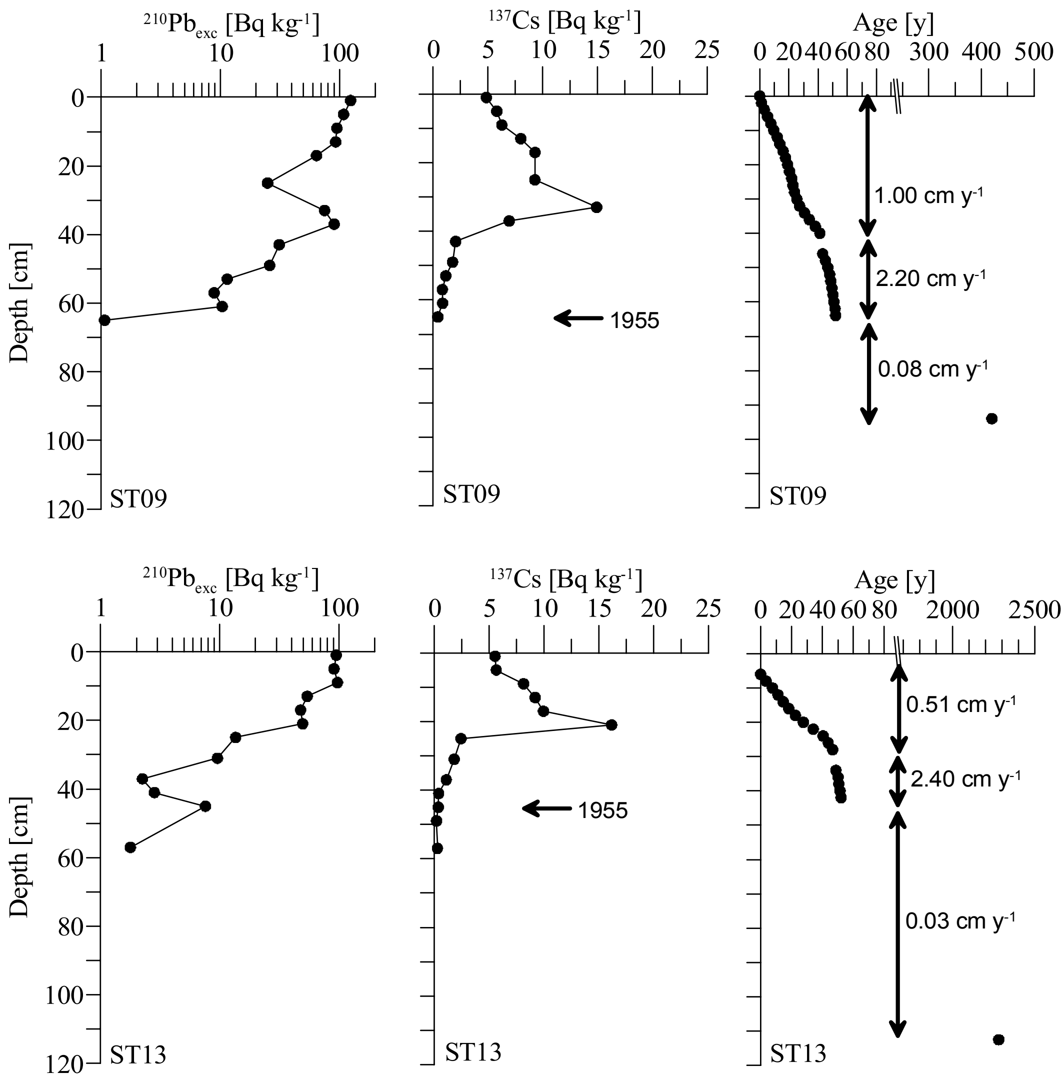


Figure 3-13: *Depth profiles of $^{210}Pb_{exc}$, ^{137}Cs, and sediment ages in cores ST9 (top) and ST13 (bottom). An initial ^{137}Cs activity exceeding a background value is taken as a marker for the beginning of nuclear bomb testing in 1955. Note the broken x-axis for the sedimentation rate. Sedimentation rates in [cm y^{-1}] are displayed next to vertical arrows.*

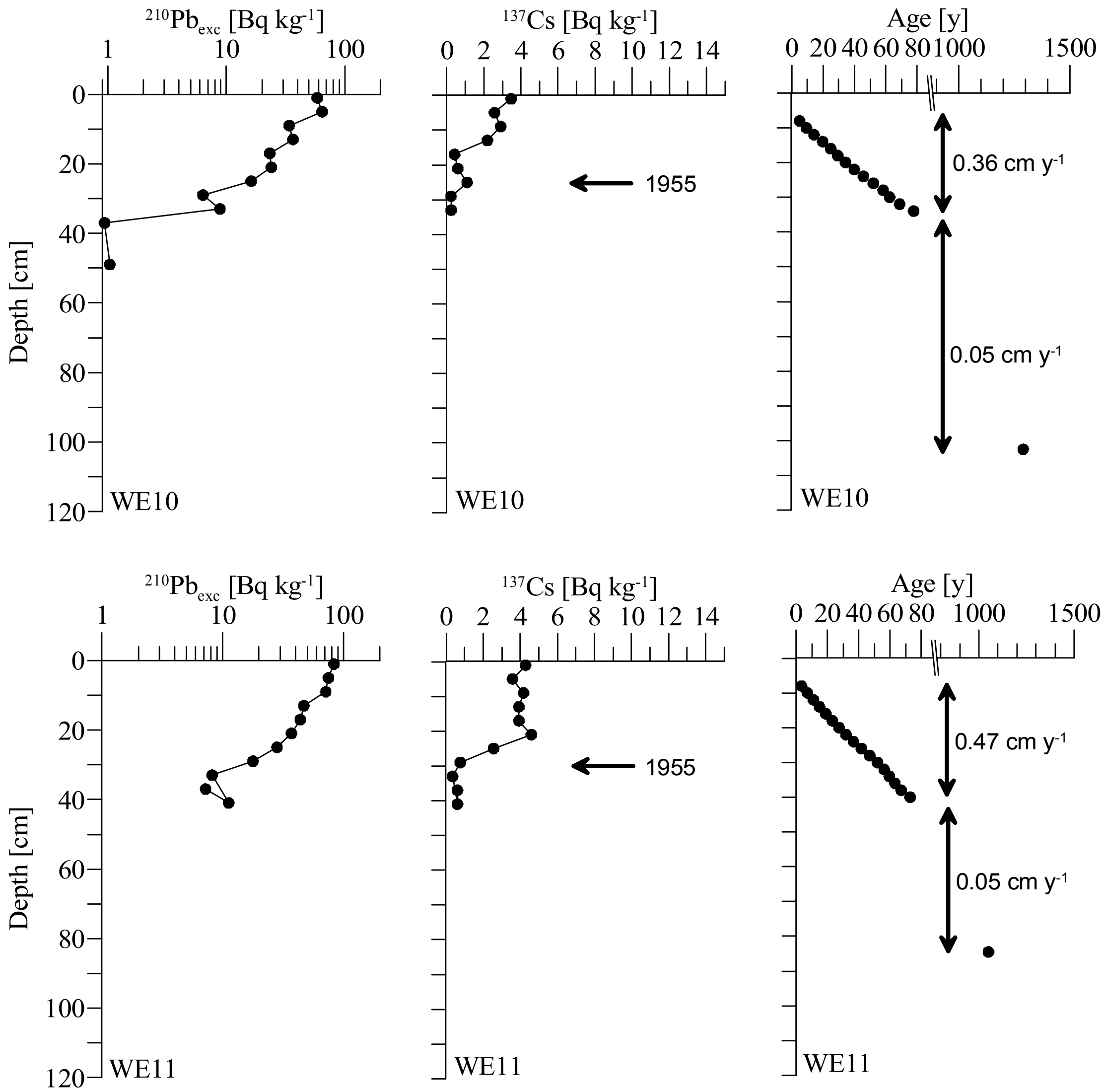


Figure 3-14: *Depth profiles of $^{210}Pb_{exc}$, ^{137}Cs, and sediment ages in cores WE10 (top) and WE11 (bottom). An initial ^{137}Cs activity exceeding a background value is taken as a marker for the beginning of nuclear bomb testing in 1955. Note the broken x-axis for the sedimentation rate. Sedimentation rates in [cm y^{-1}] are displayed next to vertical arrows.*

Table 3-3: Sediment ages determined by optically stimulated luminescence (OSL) at the bottom of cores.

Sample	Age B.P. [y]
ST9, 91-93 cm	350 ± 50
ST9, 93 – 95.5 cm	420 ± 60
ST13, 111 – 114 cm	2280 ± 300
WE10, 100 – 103 cm	1290 ± 180
WE11, 83 – 86 cm	1050 ± 150

In Stokes Inlet, the derived age models (see *Methods* section) suggest a distinct change in sedimentation rate in the early to mid 1960's for both cores from Stokes Inlet (Figure 3-13). For core ST9, a sedimentation rate of 2.2 cm y^{-1} is calculated for the period from 1955 to 1966, followed by a lower sedimentation rate of 1 cm y^{-1} for the period from 1966 to present. Similarly in core ST13, a sedimentation rate of 2.4 cm y^{-1} is calculated for the period between 1955 and 1960, followed by a lower sedimentation rate of 0.5 cm y^{-1} for sediments younger than 1960.

For the lower section of each core, only a single average sedimentation rate could be calculated between the 1955 marker depth and the depth dated by OSL. It turns out that the average sedimentation rate is 0.08 cm y^{-1} in core ST9 for the period between 420 and 52 years B.P. and 0.03 cm y^{-1} in core ST13 for the period between 2280 and 52 years B.P. (Figure 3-13). This means that the current sedimentation rate is more than 10-times higher than the pre-1950's sedimentation rate, a result consistent with recent work undertaken in the Gippsland Lakes (Hancock and Pietsch 2007). Significantly in core ST13, sedimentation rates in the late 1950's to early 1960's appear to be up to 80 times higher than pre-1950's sedimentation rates.

The significant increase in sedimentation 50 to 60 years ago in Stokes Inlet is most likely coupled to changes in catchment land use. Land in the catchments of the Young and Lort Rivers was released for farming activities in the 1950's (DOW 2007), which coincides with a dramatic increase in sedimentation for an estimated period of 5 to 10 years. This short period of very high sedimentation was followed by more moderate sedimentation likely controlled by a more stabilised topsoil layer as a result of the establishment of pasture and implementation of stable cropping practices.

In contrast to Stokes Inlet, relatively constant sedimentation rates are found for the period between 1955 and present in both cores from Wellstead Estuary (Figure 3-14). For cores WE10 and WE11, sedimentation rates for the last 50 year period were 0.36 and 0.47 cm y^{-1} respectively. These are about 10 times higher than the average pre-1950's sedimentation rate of 0.05 cm y^{-1}.

Interestingly, a short period of high sedimentation, which can be related to the early period of farming as in Stokes Inlet, is not observed in the results from Wellstead Estuary. However, the catchment of the Bremer River experienced land clearance and farming starting earlier than in the Stokes Inlet catchment, which is prior to the period for which a high resolution age model is derived. Consequently, a section of very high sedimentation rates may be included in the lower core interval, which is not detected due to a lack of high resolution chronometers for the pre-1955 period. This also implies that the long-term sedimentation rate (last 1000 years) may be even lower than we have calculated, and the post-settlement enhancement of sediment fluxes to the estuary may even be greater than 10 times.

3C2. Bulk Organic Matter Concentration and Composition

The organic matter composition of core ST09 is studied at two levels. Firstly, the down-core record of the concentration and stable isotopic composition of bulk organic matter, δ^{13}C-OM and δ^{15}N-OM, is analysed to derive changes in the accumulation rate of organic matter and to make preliminary inferences on the source of organic matter. Secondly, records of pollen, spores, and organic compounds indicative for specific sources of organic matter such as terrestrial plants or algal groups are used to derive more detailed information on the source of organic matter. For core WE11, only information on bulk organic matter, pollen and spores are available.

In core ST09, total organic carbon concentration (TOC), varies little between ~3 and ~4 wt% throughout the core (Figure 3-15). When accounting for the sedimentation rate to calculate the organic carbon accumulation rate, however, it turns out that the carbon accumulation rate in recent sediments (0.02 gC cm^{-2} y^{-1}) is more than 10 times higher than before land clearance commenced (with a rate of 0.0017 gC cm^{-2} y^{-1}). TOC concentrations in core WE11 are consistently higher than in core ST09 (Figure 3-15), with TOC doubling from 5 to 10 wt % between a sediment depth of 30 cm and the sediment surface, i.e. over the last 50 years. This equates to a 20-fold higher TOC accumulation rate at present of 0.0265 gC cm^{-2} y^{-1}, compared to a pre-European rate of 0.0013 gC cm^{-2} y^{-1}. Results of the pollen and spores study (*Section 3C4*) will demonstrate that micro-algal biomass production in Wellstead Estuary has increased following European settlement, i.e. that eutrophication in the estuary has led to increasing TOC accumulation rates.

The δ^{13}C-OM profile of core ST09 (Figure 3-15) shows a shift of -2 ‰, and the δ^{15}N-OM starts to gradually become depleted above a depth of 40 cm. The molar C:N ratio starts to decrease within the depth interval inferred to reflect European settlement. In core WE11, a positive shift in δ^{13}C-OM by approximately +1 ‰ is observed concurrent with the increase in TOC at a depth of 30 cm. Similar to core ST09, a gradual decrease in δ^{15}N-OM is found above a depth of 30 cm and the molar C:N ratio decreases over the length of the core.

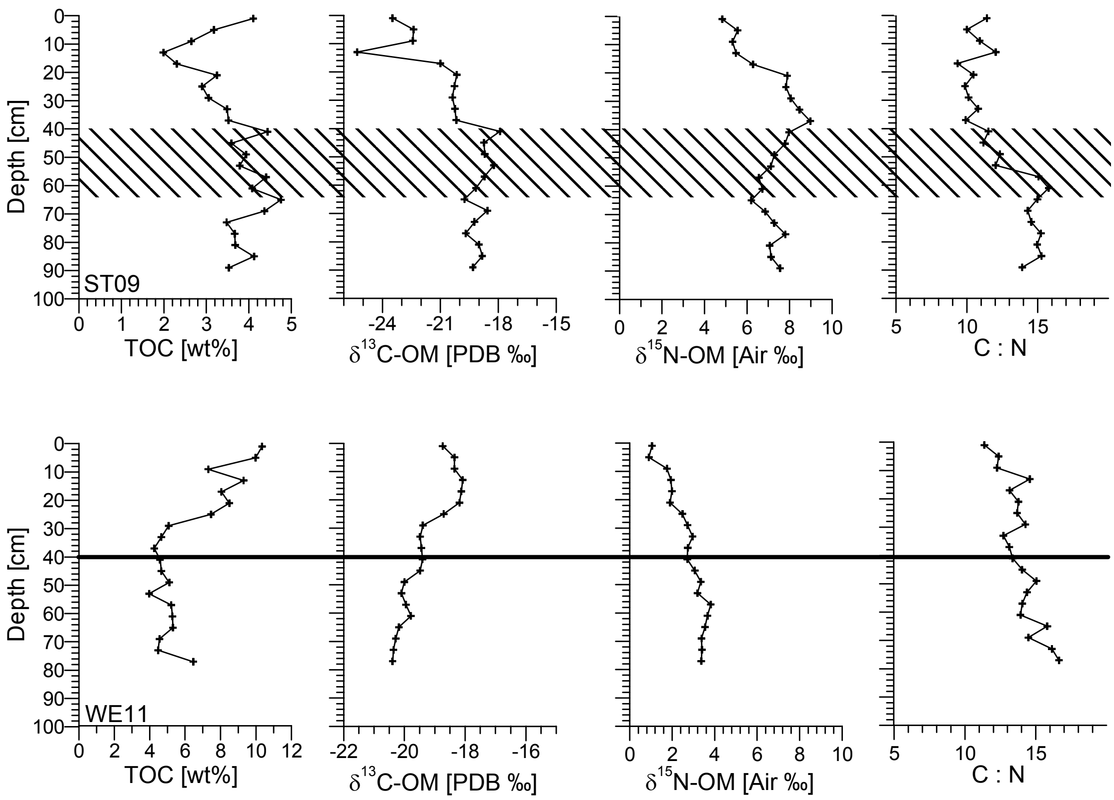


Figure 3-15: *Total organic carbon (TOC), the stable isotopic composition of organic matter (δ^{13}C-OM and δ^{15}N-OM), and the molar C:N ratio of organic matter in cores ST09 and WE11. Hatched interval shows depth interval representing the period of land clearance in the Lort-Young (Stokes Inlet) catchment. Horizontal line marks European settlement in the Bremer River (Wellstead Estuary) catchment.*

The organic carbon stable isotopic record is useful to identify trends in the mixture of terrestrial and marine derived organic matter (Rullkötter 2006). Almost all trees, most shrubs, and phytoplankton incorporate carbon into their biomass via the C3-photosynthetic pathway, leading to a typical terrestrial δ^{13}C-OM value of -27 ‰ and a marine (phytoplankton) δ^{13}C-OM value of -20 to -22 ‰. Terrestrial plants using the C4-photosynthetic pathway such as subtropical savanna grasses and sedges, however, have a δ^{13}C-OM value of -14 ‰. Since δ^{13}C-OM in the lower section of the core ST09 (~ -19 ‰) is more positive than the isotopic composition of terrestrial C3 (-27 ‰), and marine organic carbon (~ -21 ‰), terrestrial C4 plant biomass is likely contributing to the biomass deposited in pre-European times. The depletion in δ^{13}C above the high sedimentation interval could therefore be a result of a decline in terrestrial C4- and a rise in C3-plants or a gradual shift from marine to terrestrial C3-dominated biomass under the current land-use. Results of the pollen analysis provide important information on this question (see *Section 3C4*). The distinct negative spike in δ^{13}C-OM in core ST09 at a depth of 12 cm indicates a flood event followed by the deposition of sediment low in organic carbon concentration. Given the low δ^{13}C-OM value, the flood related biomass is clearly of terrestrial origin, which is further substantiated by biomarker records (see *Section 3C3*).

Concurrent with the decrease of δ^{13}C-OM in the upper section of the core STO9, a decrease in δ^{15}N-OM is also observed (Figure 3-15). A combination of two changes in land-use may lead to this observation: after the (partial) clearance of the catchment in the mid 1960's new plants have established, likely C3 plants, and in the case of legumes, C3 plants that incorporate nitrogen through N-fixation. Secondly, fertilizer application likely became common practice, which introduced strongly depleted δ^{15}N, i.e. nitrogen with a δ^{15}N value of 0 (Udy and Dennison 1997). Both N-fixation by crops, as well as the application of fertilizer would lead to more negative δ^{15}N-OM values.

A shift in the C:N ratio can be caused by a range of introduced changes, including a change in the primary organic matter composition due to the plantation of new plants and selective removal of biomass fractions (e.g. eucalyptus heartwood with a C:N ratio of 402-733 as opposed to leaf litter with a C:N ratio of 27-146; Gifford 2000). The addition of nitrogen through fertilizer application, or a change in the degree in C:N ratio preservation (i.e. N-rich compounds such as amino acids tend be better preserved under high burial conditions resulting in a decrease in the C:N ratio found in sediments; e.g. Rullkötter 2006) can also shift the C:N ratio. In core ST09, between a depth of 60 and 40 cm (hatched area in Figure 3-15), the C:N ratio is decreasing from 15 to 10 concurrent with higher burial rates, but also concurrent with the onset of European land use including the plantation of new plants and harvesting of timber. In contrast, C:N ratios gradually decrease from ~15 to 11 throughout core WE11.

3C3. Organic Biomarkers

Specific organic compounds indicative for different plant and microbial groups, 'biomarkers', are selected to reveal the deposition of organic matter derived from different sources. The above discussion on the character of bulk organic matter in core ST09 demonstrated that the establishment of new plants after land clearance resulted in a likely shift towards C3 land plants, which are likely depleted in cellulose relative to native vegetation and incorporate nitrogen through N-fixation and/or the uptake of fertiliser. This shift is also evident from the gradual increase in sitosterol (Figure 3-16), a biomarker for vascular plants (Volkman 1986). Concurrent with the negative spike in δ^{13}C-OM (Figure 3-15), sitosterol shows positive spikes at 12 and 40 cm depth giving further evidence for instantaneous deposition of catchment-derived organic matter, likely following flood events. Records of biomarkers for terrestrial higher plant waxes such as C24, C26, and C28 alkanol (Pancost *et al*. 2004) support observations suggesting instantaneous deposition of terrestrial organic matter at depths of 12 and 40 cm, as well as higher proportions of these fractions following the establishment of new plants in the catchment (Figure 3-16). Other biomarkers for terrestrial plant waxes such as C24, C26, and C28 fatty acids follow the same trend (data not shown).

Interestingly, biomarkers for algal groups such as dinosterol and C25:1 HBI indicative for dinoflagellates and diatoms, respectively (Volkman *et al*. 1998, Sinninghe Damsté *et al*. 2004), are most enriched at depths of 12 and 40 cm (Figure 3-16), where flood event deposits have been suggested. Additionally, diatom-biomakers are generally enriched in the interval deposited during initial land clearance. It remains unclear whether the flood events and intense run-off during land clearance caused increased productivity of dinoflagellates and diatoms in Stokes Inlet or whether these algae were formed in streams and pools in the catchment and washed into the Inlet. It is, however, noteworthy, that diatoms currently dominate the phytoplankton community all year round, but the respective biomarkers are very low in concentration in surface sediments.

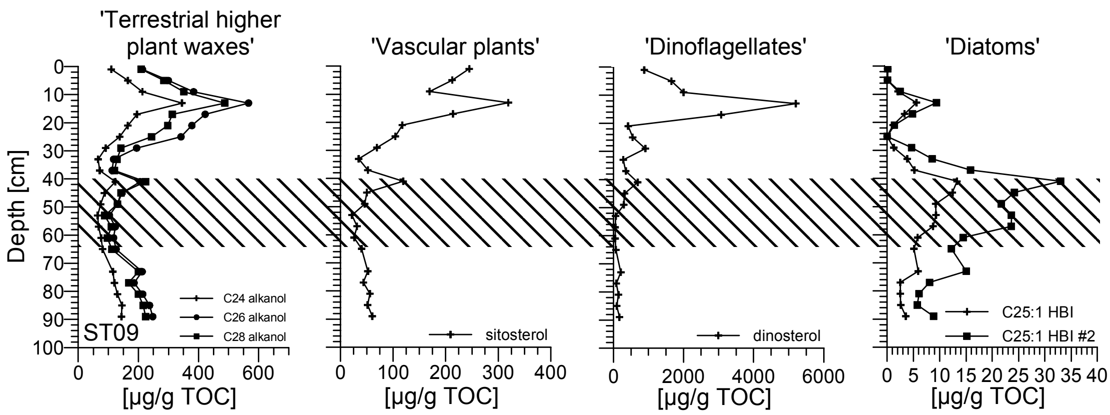


Figure 3-16: *Records of biomarkers in core ST09 indicative for different sources of organic matter. Hatched interval shows depth interval with a sedimentation rate of 2.2 cm y^{-1} (see Section 3C1).*

3C4. Pollen, Spores, and Cysts

Dryland fossil pollen assemblages recovered from cores ST09 and WE11 are dominated throughout by pollen of shrubs and small trees (*Allocasuarina*, *Eucalyptus*, Myrtaceae cf *Melaleuca*) that are common in mallee scrub and heath communities on the Esperance Plain (Beard 1990). Proteaceae scrub-heath is less well-represented due to the relatively low pollen production/dispersal characteristics of commonly occurring shrub species such as *Banksia speciosa* and *Lambertia inermis*. *Pinus* is the one definitely introduced (‘exotic’) tree species recorded in the study and its pollen is found in the top 34 cm in core ST09, and in the top 6 cm of core WE11 (Figure 3-17). The stratigraphic distribution of unconfirmed ('probable') exotic pollen types such as Asteraceae (*Liguliflorae* and micro-echinate types) and Brassicaceae shows a pre-dominance in the upper 30 to 40 cm in both cores but also occur sporadically below the depth of European settlement. This may be due to bioturbation but a more likely explanation is that the specimens represent relatives in the native flora. It is noteworthy that cereal pollen have not been observed in the sediment records despite cereal crops being planted upstream in the catchments. This is likely related to selective storage of such arable pollen in river pool sediments as has been observed elsewhere (Brown *et al*. 2007).

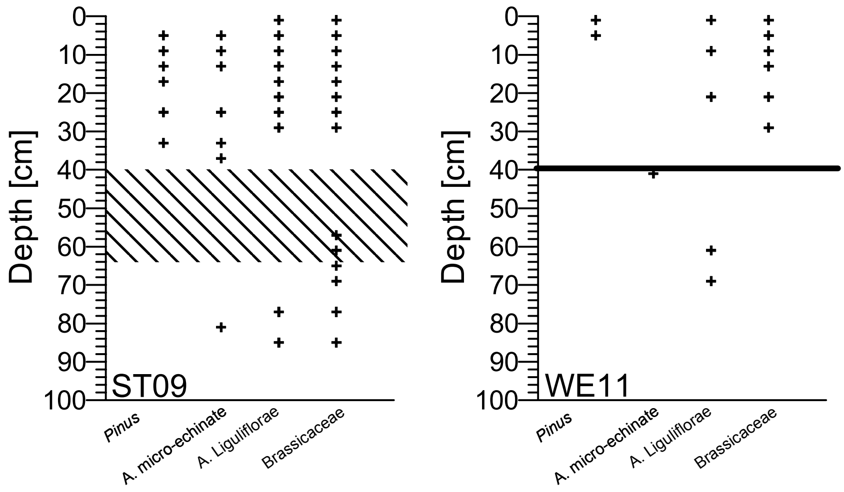


Figure 3-17: *The presence (+) of definite (Pinus) and probable (Asteraceae Liguliflorae, Asteraceae micro-echinate, Brassicaceae) exotic pollen in cores ST09 and WE11. Hatched interval shows depth interval with a sedimentation rate of 2.2 cm* y^{-1} *in core ST09 and horizontal line marks European settlement at site WE 11.*

Eucalyptus has tended to expand gradually at the expense of *Allocasuarina* throughout the time covered by the sedimentary record in cores ST09 and WE11 (Figure 3-18). In core WE11, *Melaleuca* pollen abundances have increased considerably as well. Importantly, the relative abundances of Cyperaceae and Restionaceae decrease markedly following land clearance, suggesting sedges and other wetland herbs may have been replaced by grasses (Poaceae) and (core ST09) samphires (Chenopodiaceae-Amaranthaceae) as the dominant riparian plants.

Botryococcus is a green micro-algae found in shallow, slow-moving fresh- to brackish water environments and high concentrations have been associated with eutrophic conditions (van Geel 2001) though this has been contested recently (Chmura *et al*. 2006). Mirroring the decline in wetland herbs, numbers of *Botryococcus,* colonies drop sharply at the marker depth of 40 cm in core ST09 (Figure 3-18) although the alga remains a minor component up to the present. Equally important, *Botryococcus* is consistently highly abundant within the high-sedimentation interval between 64 and 40 cm depth. In contrast, cysts and spores of unidentified micro-algae are relatively low throughout core ST09. Aquatic algae records of core WE11 display a very different pattern: *Botryococcus* abundances are consistently low, but unidentified micro-algae cysts/spores are highly variable and increase significantly from an average of ~150 to ~250% of total dryland pollen and spores from pre- to post-European time. The latter trend agrees well with the increase in TOC from 5 to 10 wt% following European settlement (*Section 3C2*) and gives further evidence for eutrophication in Wellstead Estuary.

Interestingly, the apparent eutrophication in Wellstead Estuary is not reflected in the abundances of *Ruppia* pollen, which varies between 1 and 6 % of total dryland spore and pollen count throughout the core WE11 (data not shown). In contrast, *Ruppia* pollen are only found occasionally and in very low numbers (≤ 1 % of total dryland spores and pollen) in core ST09. The reason for this is unclear although it is possible that seagrass populations are limited by factors other than nutrient influx into the estuary.

The abundance of carbonized particles drops distinctively at the marker-depth of 40 cm in core ST09 (Figure 3-18) and abundances remain consistently very low up to surface sediments. In contrast, in sediments below 40 cm of core ST09 abundances of carbonized particles vary significantly suggesting a decrease in wildfire frequency and/or intensity starting in the mid 1950s. In contrast, abundances of carbonized particles are consistently higher in core WE11 than in core ST09 and high variability is found throughout the whole record. Interestingly, maxima in unidentified micro-algae can be correlated with maxima in carbonised particle abundances in Wellstead sediments. More precisely, maxima in carbonised particles immediately precede maxima in unidentified micro-algae spores suggesting nutrients are leached out of burnt soils by rain (e.g. Orians and Milewski 2007) leading to higher micro-algae productivity in aquatic environments. Apart from temporary spikes in micro-algae productivity following wild fires, micro-algal abundances have tended to gradually increase overall since European settlement. Micro-algal productivity as recorded by the relative abundances of unidentified micro-algal spores is most likely occurring within Wellstead Estuary, because abundances of the freshwater algae *Botryococcus* remain low throughout the core WE11.

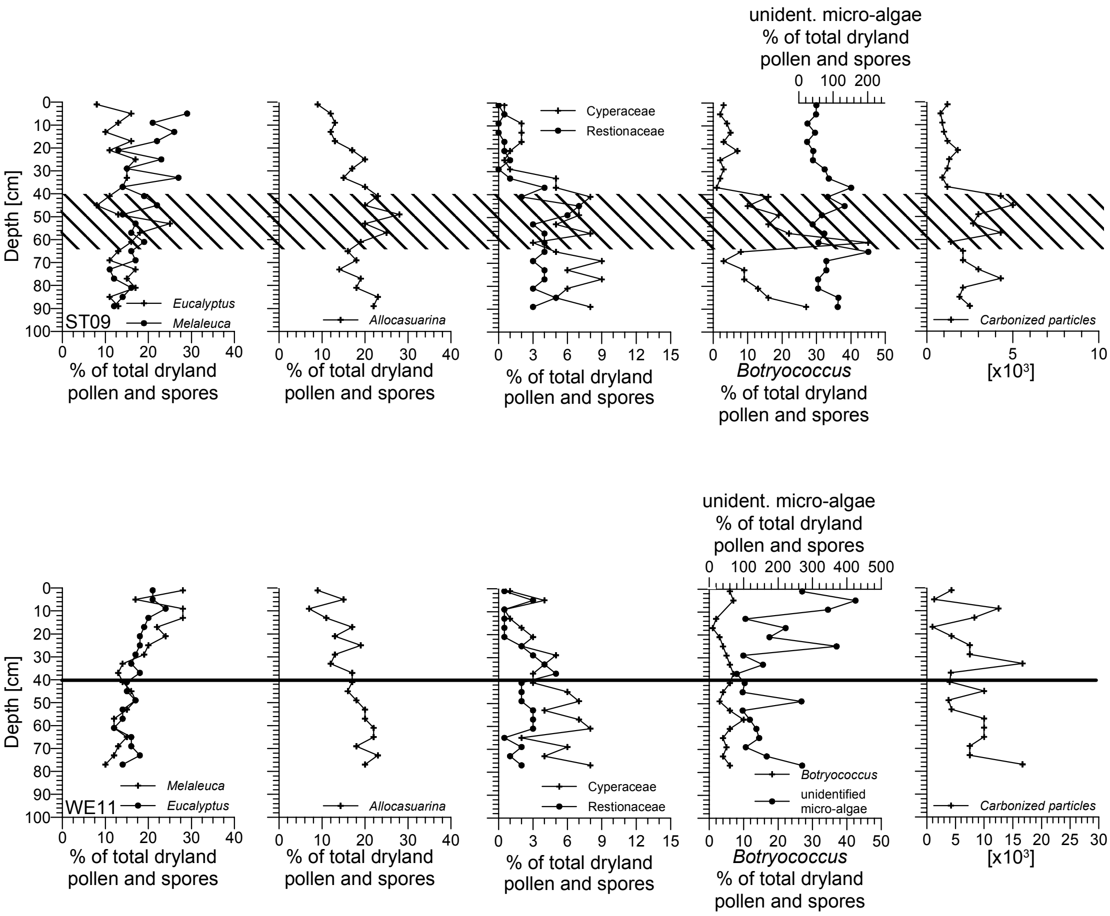


Figure 3-18: *Records of relative abundances of pollen and spores of cores ST09 and WE11. Eucalyptus, Allocasuarina, and Melaleuca are dryland trees and shrubs. Cyperaceae (Type 2) and Restionaceae (other than Lyginia) represent wetland sedges and wire-rushes, respectively. Botryococcus is a green alga found in fresh- to brackish water. Unidentified micro-algal cysts have likely been produced by free-floating or attached species living in the estuary. Hatched interval shows depth interval representing land clearance in the Lort-Young (Stokes Inlet) catchment and the horizontal line marks European settlement in the Bremer River (Wellstead Estuary) catchment.*

3C5. Bulk Geochemical Properties

The down-core records of major, minor, and trace element concentrations are used to identify changes in the composition and source of the mineralic fraction which may be related to changes such as the intensity of rock weathering or erosion of sub-soil as opposed to top-soil only. The ratio of Fe:Al is shown to reveal whether the delivery of reactive iron, in particular Fe-oxyhydroxides to the estuary has changed. The availability of Fe-oxyhydroxides largely controls the P-binding capacity in estuarine and marine sediments (Slomp *et al*. 1996). The latter is represented by the P:Al-ratio. Fe-oxyhydroxides may, however, also be reduced and turned into Fe-sulphides, which then no longer adsorb and permanently bind phosphate. As a consequence, sediments rich in Fe-sulphides have higher benthic phosphate fluxes. The degree of sediment sulphurisation is reflected in the sediment sulphur concentration.

In core ST09, the Al, Ti, and Rb concentrations significantly increase following European settlement at a depth of 40 cm (Figure 3-19) suggesting a higher proportion of mafic sheet silicates such as biotite and muscovite. In contrast, carbonate minerals represented by Ca, Mg, and Sr (data not shown) concentrations and Fe-oxides, represented by the Fe:Al ratio, decrease concurrently. Given the δ^{15}N-OM record, which suggested the application of fertiliser under European land management (*Section 3C2*), the decrease in the delivery of carbonate minerals is possibly related to increased nitrification ($NH_4^+ + O_2 + H_2O \rightarrow NO_3^- + 2H^+$) leading to soil acidification and dissolution of Ca and Mg carbonates (e.g. Faurie and Fardeau 1990). Fe-oxides may also have been dissolved by lower pH conditions in soils resulting in a lower Fe:Al ratio in sediments of Stokes Inlet under European land management practice as opposed to pre-European times. Alternatively, the higher rate of sediment erosion in the catchment may no longer allow the development of a top-soil horizon with diagenetically enriched Ca, Mg, and Fe.

The geochemical records of core WE11 do not show distinctive changes in Al, Ti, Rb, or Ca concentrations at a depth of 40 cm (Figure 3-19), which marks the depth of European settlement. However, the Si concentration decreases distinctively and the Mg concentration increases slightly above a depth of 40 cm. It remains unclear what caused these changes.

Importantly, at the sediment surface of site WE11, the reactive P concentration is relatively high, i.e. (P_2O_5*1000):Al_2O_3 is 17, and the sulphur concentration is low, i.e. SO_3 is 0.8 wt%. In contrast, at site ST09 the reactive P concentration is low, i.e. (P_2O_5*1000):Al_2O_3 value is 7.5, and the sulphur concentration is high, SO_3 is 4.7 wt%. This contrast between site WE11 and ST09 is particularly surprising, because the reactive Fe concentration is similar at both sites (Figure 3-19), and based on the much higher TOC concentration at the surface of site WE11 (10 wt%) as opposed to site ST09 (4 wt%) a higher sulphur concentration was expected for site WE11. However, site WE11 is located in a more central part of the estuary, and at a water depth of 2.5 m, whereas ST09 is located in a more sheltered area and at a water depth of 6 m, where bottom water becomes occasionally anoxic. As a consequence, wave-action most likely leads to frequent resuspension and reoxidation of surface sediments at site WE11, inhibiting the intense sulphurisation as found at site ST09.

The distinct difference in P-binding capacity between sites WE11 and ST09 is well mirrored in the benthic P fluxes. While there was no P release measurable at three sites in the central basin of Wellstead Estuary (Murray *et al.* 2007), the average benthic P flux at site ST09 in Stokes Inlet was 0.17 mmol m^{-2} d^{-1}. Such high P flux has only been found in exceptional settings, e.g. in Beaufort Inlet, where the high P release was leading to a very low DIN:DIP ratio in the water column (Murray *et al.* 2007).

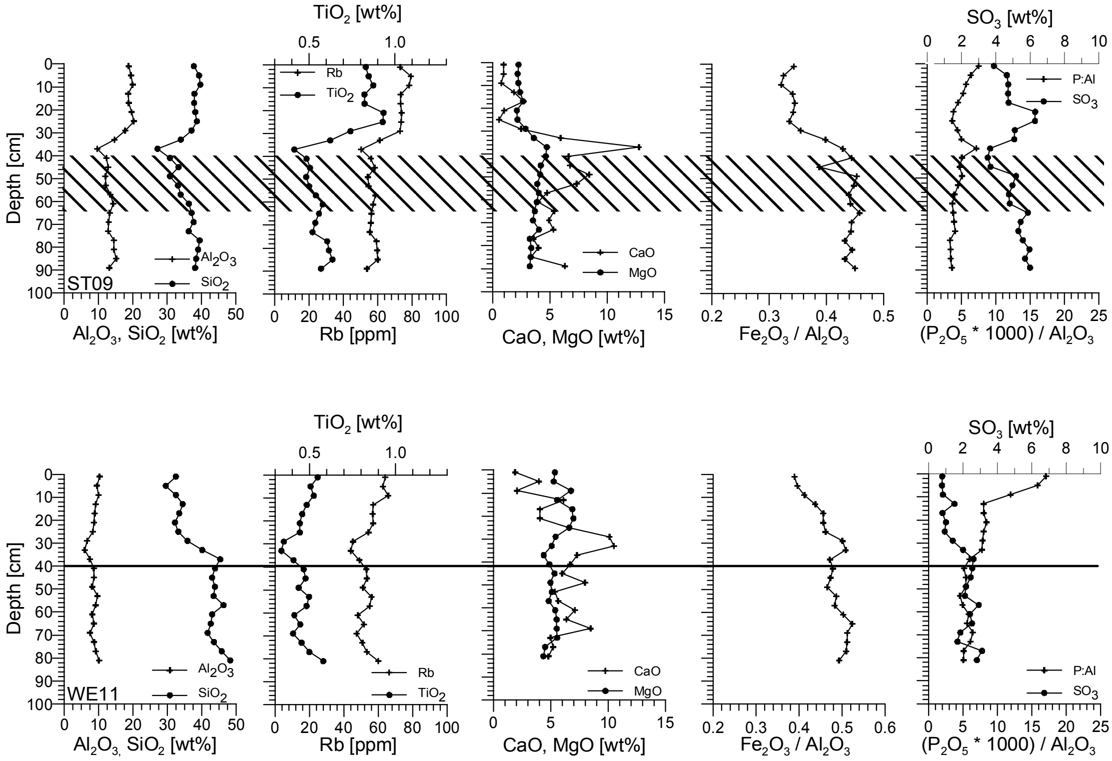


Figure 3-19: *Records of major, minor, and trace elements of cores ST09 and WE11. Hatched interval shows depth interval representing land clearance in the Lort-Young (Stokes Inlet) catchment and the horizontal line marks European settlement in the Bremer River (Wellstead Estuary) catchment.*

4. Key Conclusions

PRESENT DAY NUTRIENT DYNAMICS IN STOKES INLET

Stokes Inlet showed TCO_2 and NH_4^+ fluxes in the ranges of 36 to 108 mmol m^{-2} day^{-1}, and 4.8 to 8.1 mmol m^{-2} day^{-1} respectively, which is considered moderate to high compared to benthic fluxes in other estuaries of southern WA.

The size of PO_4^{3-} fluxes depended on water depth, i.e. at the shallow site (1.8 m) in the central part of the basin, the average benthic PO_4^{3-} flux was 0.03, but at the deep site (6 m), the average PO_4^{3-} flux was 0.5 mmol m^{-2} d^{-1}. The large difference in PO_4^{3-} fluxes can be explained by the fact that the deeper site is frequently exposed to anoxic bottom water conditions which is leading to a loss of the P-binding capacity of sediments. Iron oxyhydroxides become diagenetically enriched in surface sediments under oxic bottom water conditions and have the capacity to adsorb free PO_4^{3-}. Whereas, under suboxic/anoxic bottom water conditions, however, iron oxyhydroxides turn into iron sulfides leading to a loss of P-binding capacity. These processes were also reflected in surface sediment and porewater properties. In the deep basin, the P/Al ratio was low and sulphur highly enriched in surface sediments, whereas in the shallow areas, we would expect a high P/Al ratio and low sulphur enrichment, such as was found at site WE11 in Wellstead Estuary at a water depth of 2.5 m. Also comparing porewater profiles from deep and shallow sites in Stokes Inlet further compliments these findings, with very high porewater PO_4^{3-} concentrations in the surface sediments of the deep basin, and low concentrations in the surface sediments of shallow areas. Resuspension by wave action and subsequent re-oxidation of surface sediments at shallower sites most likely prevents intense sulfurisation and continued availability of iron oxyhydroxides, a condition favouring high phosphorous retention in sediments. This observation highlights the importance of bathymetry for nutrient release from sediments and suggests that the P/Al ratio and the S concentration in sediments can be used as an indicator for P-binding capacity.

In contrast to P-binding capacity, denitrification appears to re-establish quickly with the return to oxic conditions. Denitrification was evident when bottom waters were well-oxygenated, but this process was inhibited when the Inlet was stratified and bottom waters were anoxic.

PALAEO-ENVIRONMENTAL RECONSTRUCTION

Sedimentation rates in Stokes Inlet and Wellstead Estuary have increased dramatically since European settlement. In Stokes Inlet, in the late 1950's, sedimentation rates increased to about 80 times pre-European rates. This has since reduced, however current sedimentation rates are still more than 10 times higher than during pre-European time. Similarly, sedimentation rates have increased by about 10 times since the early 1950's in Wellstead Estuary. Evidence for sedimentation events has been found at sediment depths of 12 and 40 cm at site ST09 in Stokes Inlet; corresponding to an age of approximately 10 and 40 years respectively. These deposits are characterised by high concentrations of organic compounds indicative of terrestrial organic matter.

Records of common and exotic pollen in estuarine sediments give evidence for the establishment of new vegetation communities, including some exotic species, and a significant decline in wetland flora in the catchments of both Stokes Inlet and Wellstead Estuary. This began in the mid 1960s, in the Stokes Inlet catchment, and in the mid 1950s in the Wellstead Estuary catchment. Concurrent with this decline in wetland flora, the relative abundance of the freshwater green alga *Botryococcus* declines significantly in Stokes Inlet in the mid 1960s, providing further evidence for the loss of shallow lake and wetland environments. Biomass found in Stokes Inlet is predominantly derived from the catchment, whereas biomass in Wellstead Estuary is predominantly derived from within the estuary. An increase from 5 to 10 wt% of total organic carbon and a significant increase in micro-algal spores in sediments of Wellstead Estuary over the last 50 years, strongly suggests ongoing eutrophication. Apparently, wild fires have contributed to an increase in nutrient loads to the estuary, but uncontrolled sewage discharge from the township of Bremer Bay may also be a source of nutrients.

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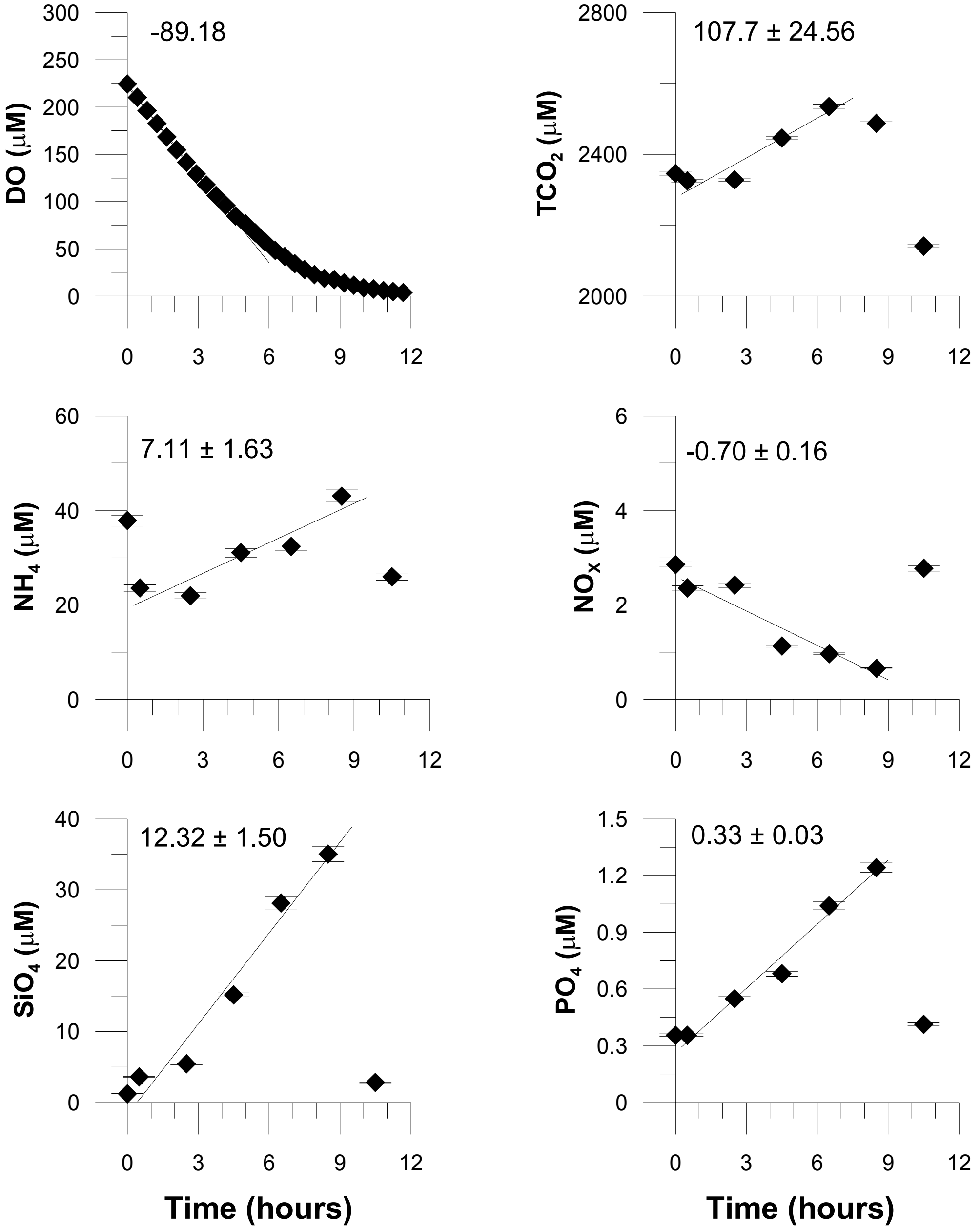
Appendix 1.

Raw benthic chamber results used to calculate benthic fluxes.

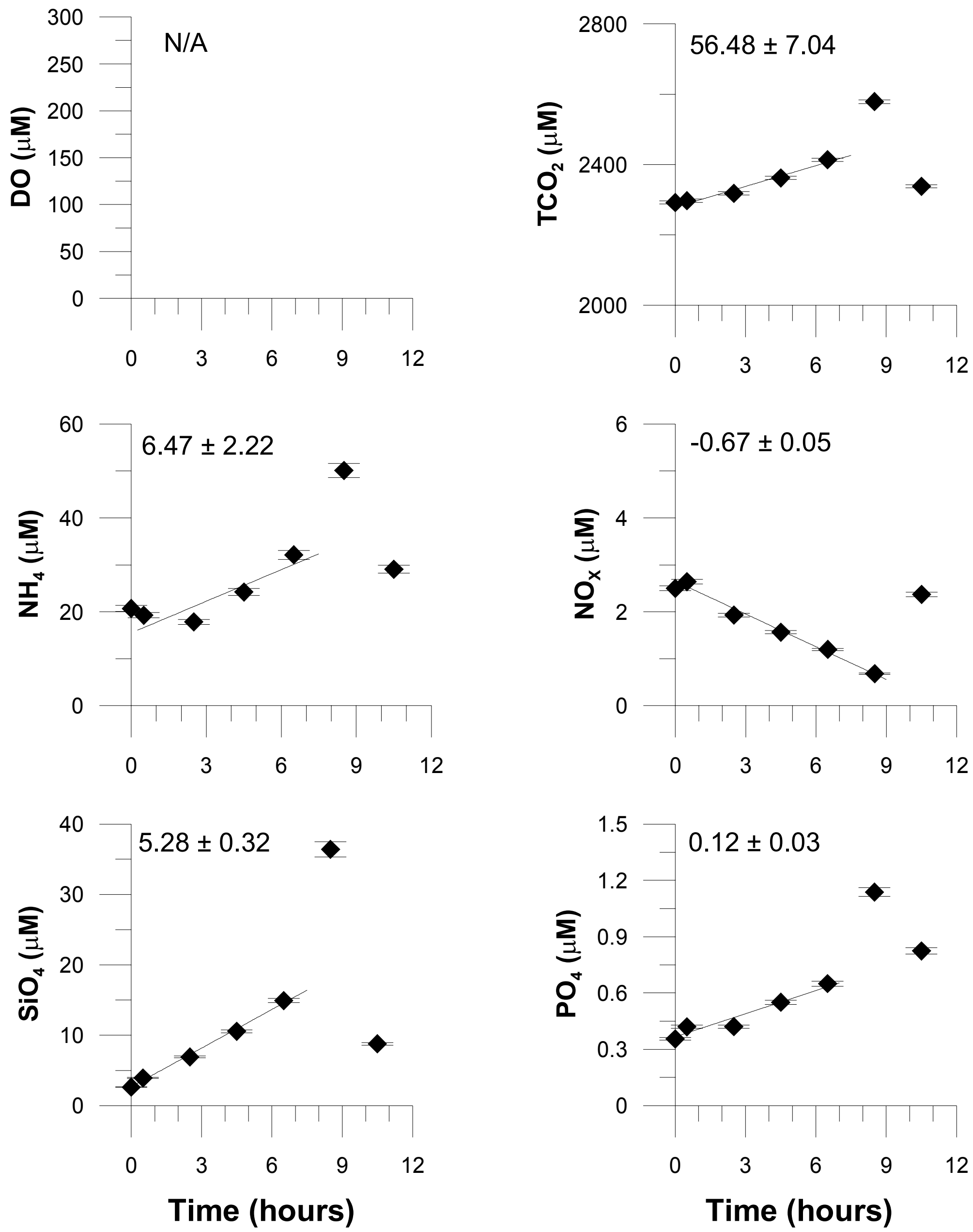
Dark

ST9A_1



Dark

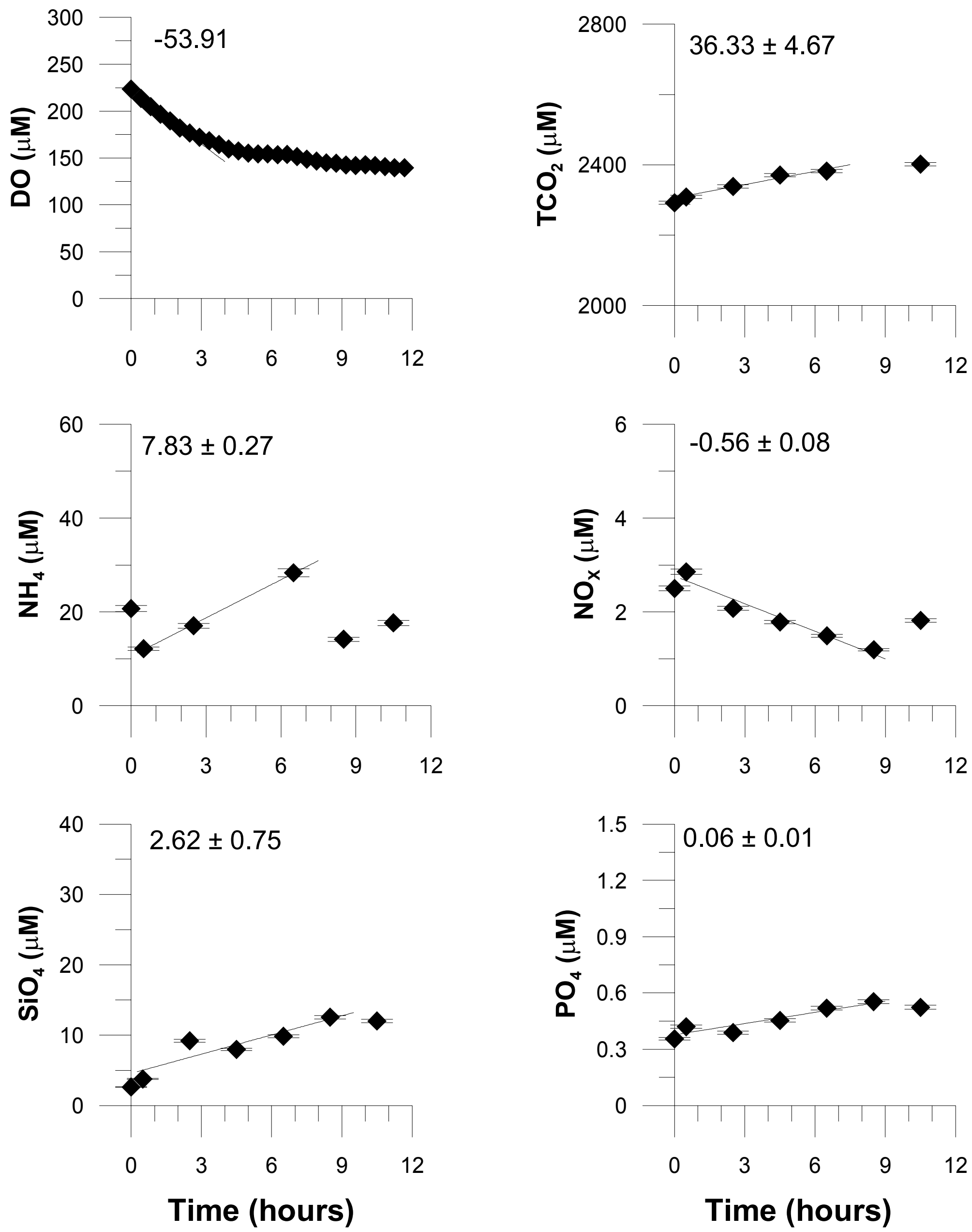
ST9A_2



DO (μM)
N/A
TCO2 (μM)
56.48 ± 7.04
NH4 (μM)
6.47 ± 2.22
NOX (μM)
-0.67 ± 0.05
SiO4 (μM)
5.28 ± 0.32
PO4 (μM)
0.12 ± 0.03
Time (hours)
Time (hours)

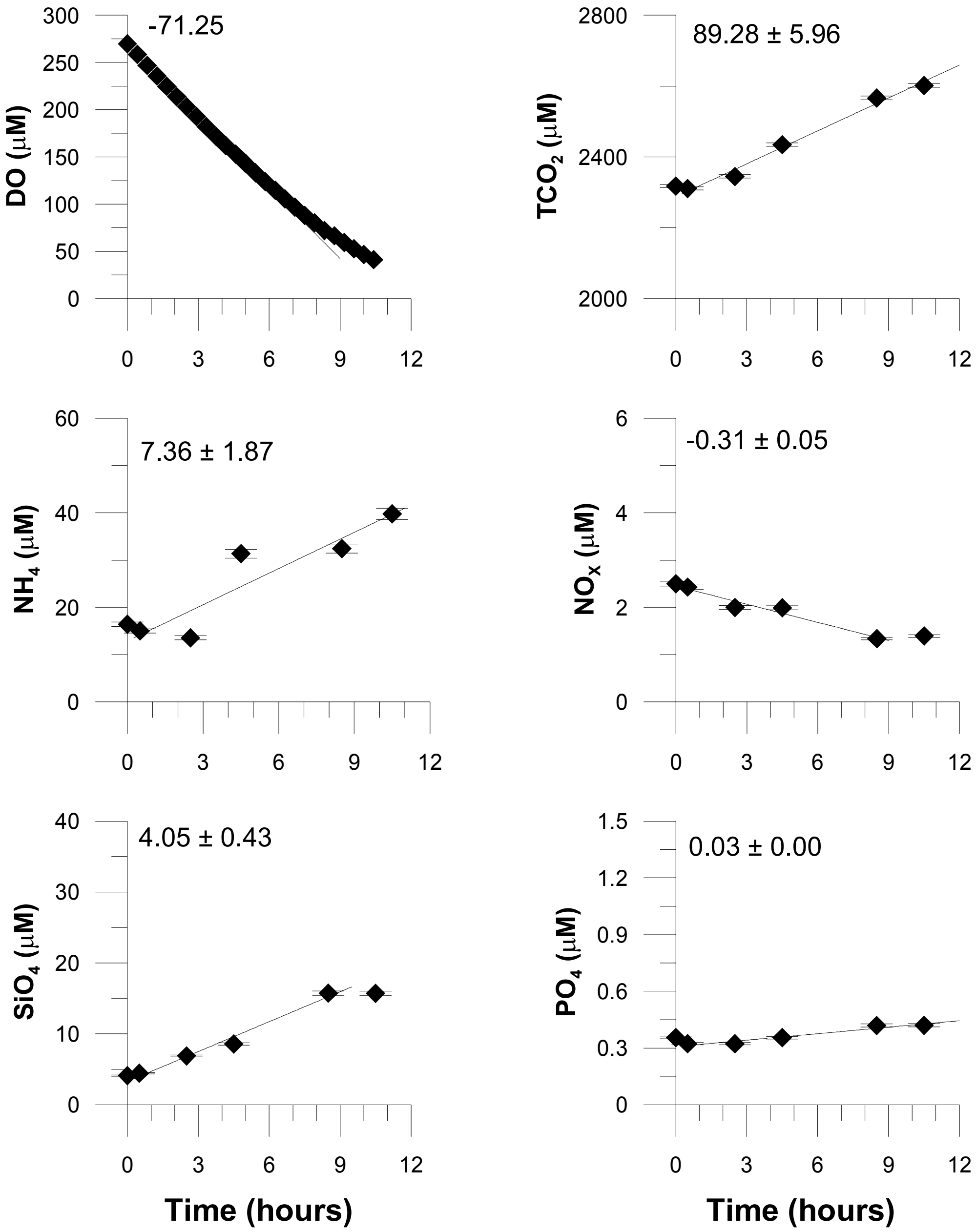
Dark

ST9A_3


-53.91
DO (μM)
36.33 ± 4.67
TCO2 (μM)
7.83 ± 0.27
NH4 (μM)
-0.56 ± 0.08
NOX (μM)
2.62 ± 0.75
SiO4 (μM)
0.06 ± 0.01
PO4 (μM)
Time (hours)
Time (hours)

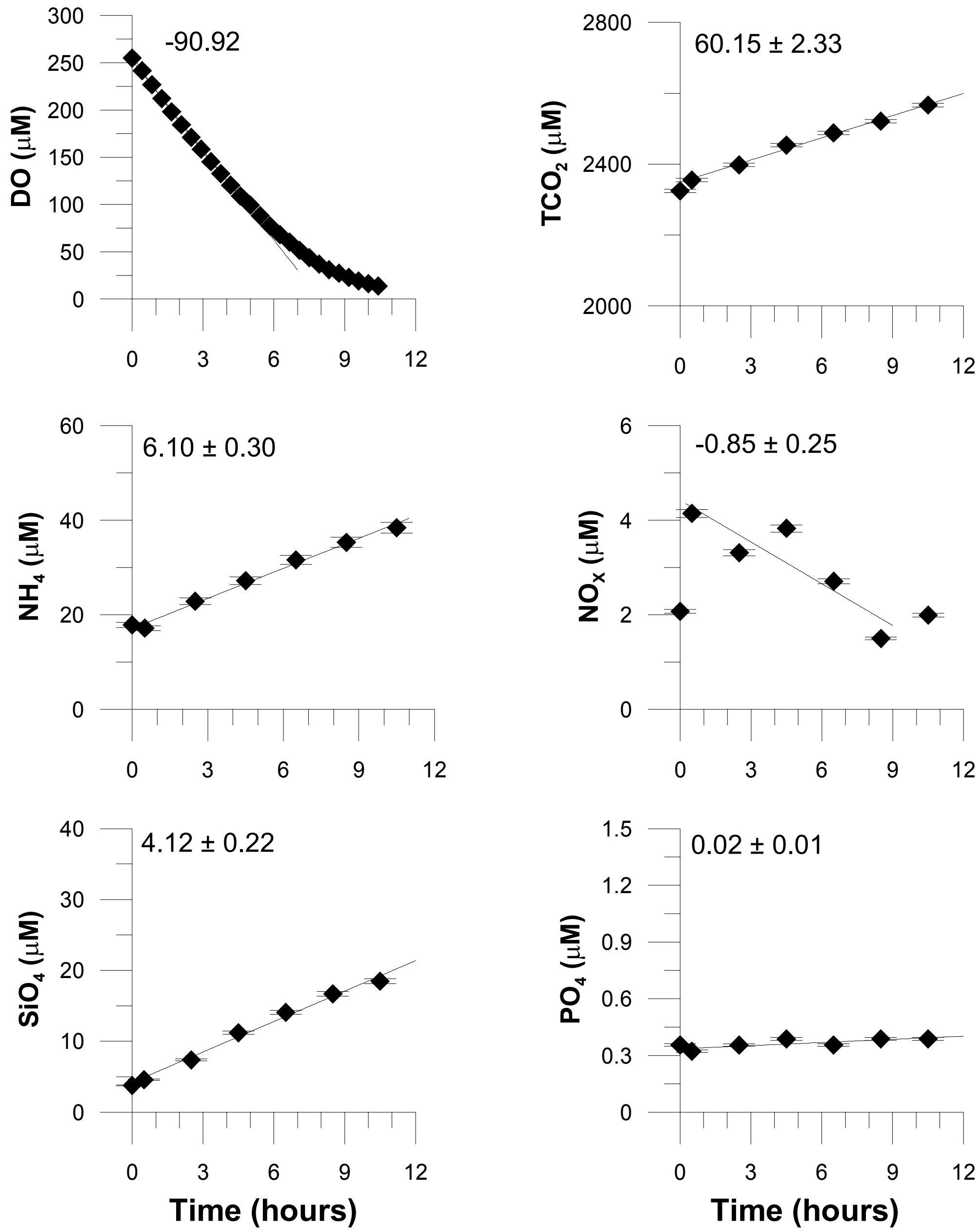
Dark

ST10B_1


-71.25
DO (µM)
300
250
200
150
100
50
0
0
3
6
9
12
89.28 ± 5.96
TCO_2 (µM)
2800
2400
2000
7.36 ± 1.87
NH_4 (µM)
60
40
20
-0.31 ± 0.05
NO_X (µM)
6
4
2
4.05 ± 0.43
SiO_4 (µM)
40
30
20
10
0.03 ± 0.00
PO_4 (µM)
1.5
1.2
0.9
0.6
0.3
Time (hours)
Time (hours)

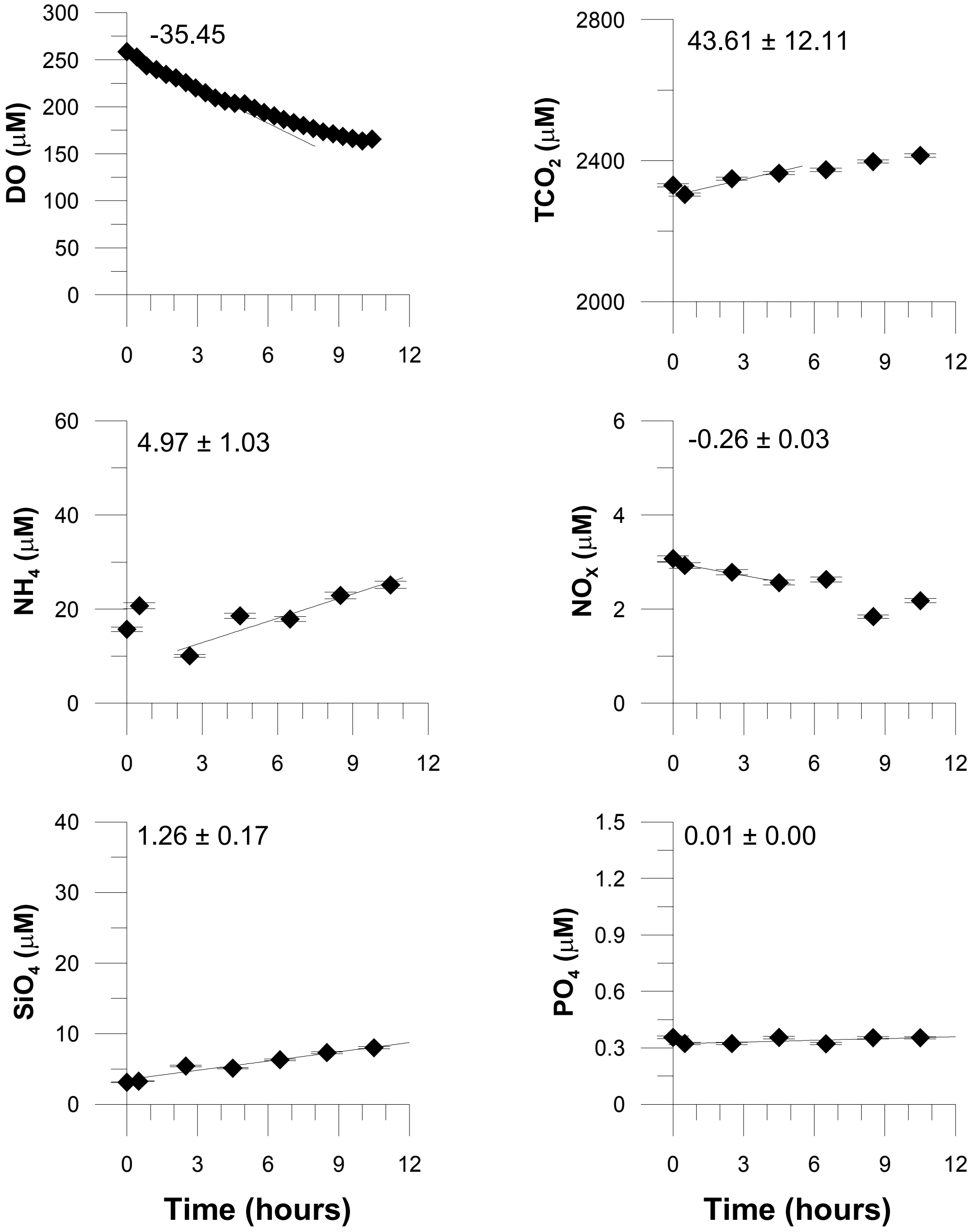
Dark

ST10B_2


-90.92
DO (μM)
60.15 ± 2.33
TCO2 (μM)
6.10 ± 0.30
NH4 (μM)
-0.85 ± 0.25
NOX (μM)
4.12 ± 0.22
SiO4 (μM)
0.02 ± 0.01
PO4 (μM)
Time (hours)
Time (hours)

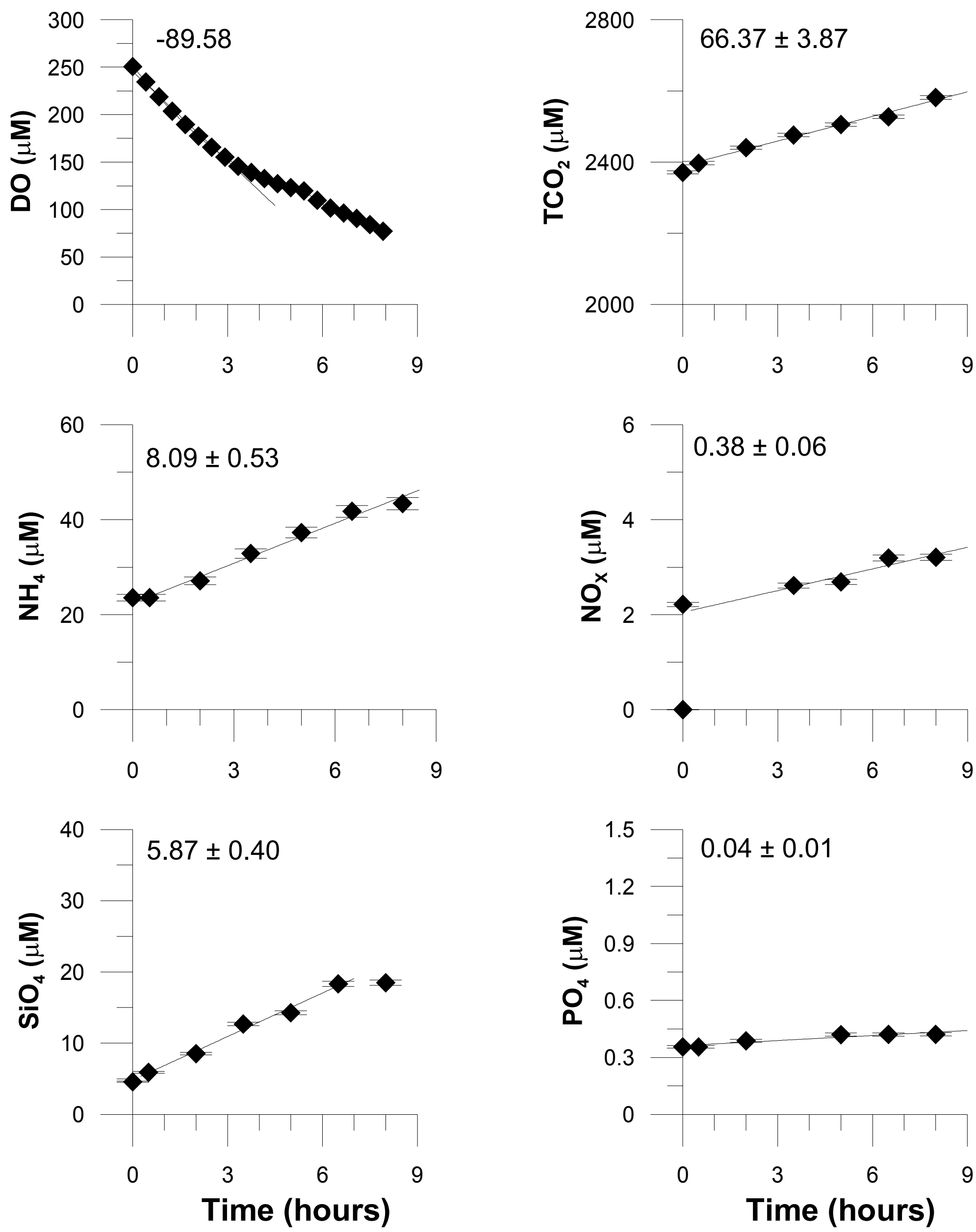
Dark

ST10B_3


-35.45
DO (μM)
43.61 ± 12.11
TCO2 (μM)
4.97 ± 1.03
NH4 (μM)
-0.26 ± 0.03
NOX (μM)
1.26 ± 0.17
SiO4 (μM)
0.01 ± 0.00
PO4 (μM)
Time (hours)
Time (hours)

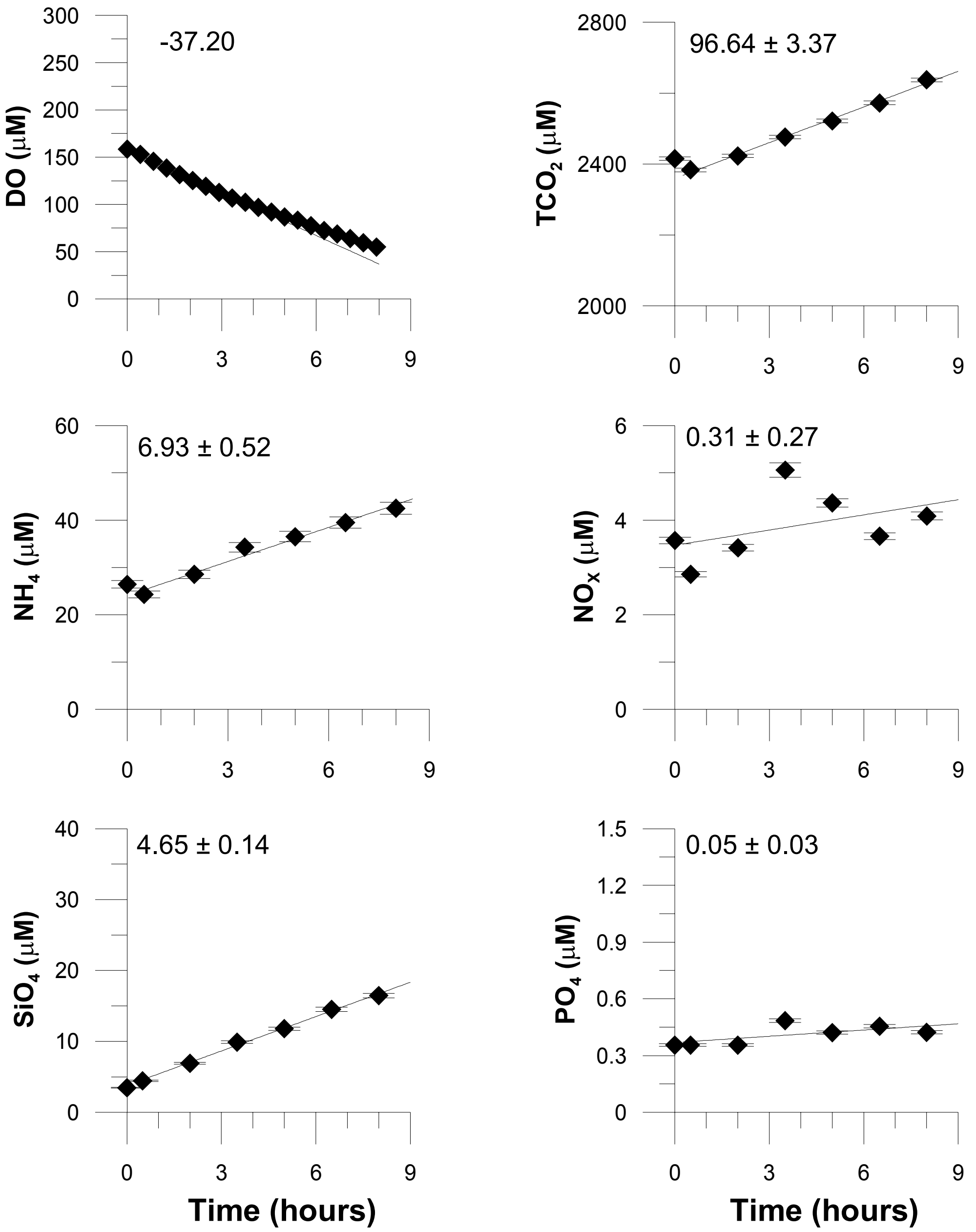
Light

ST10A_1

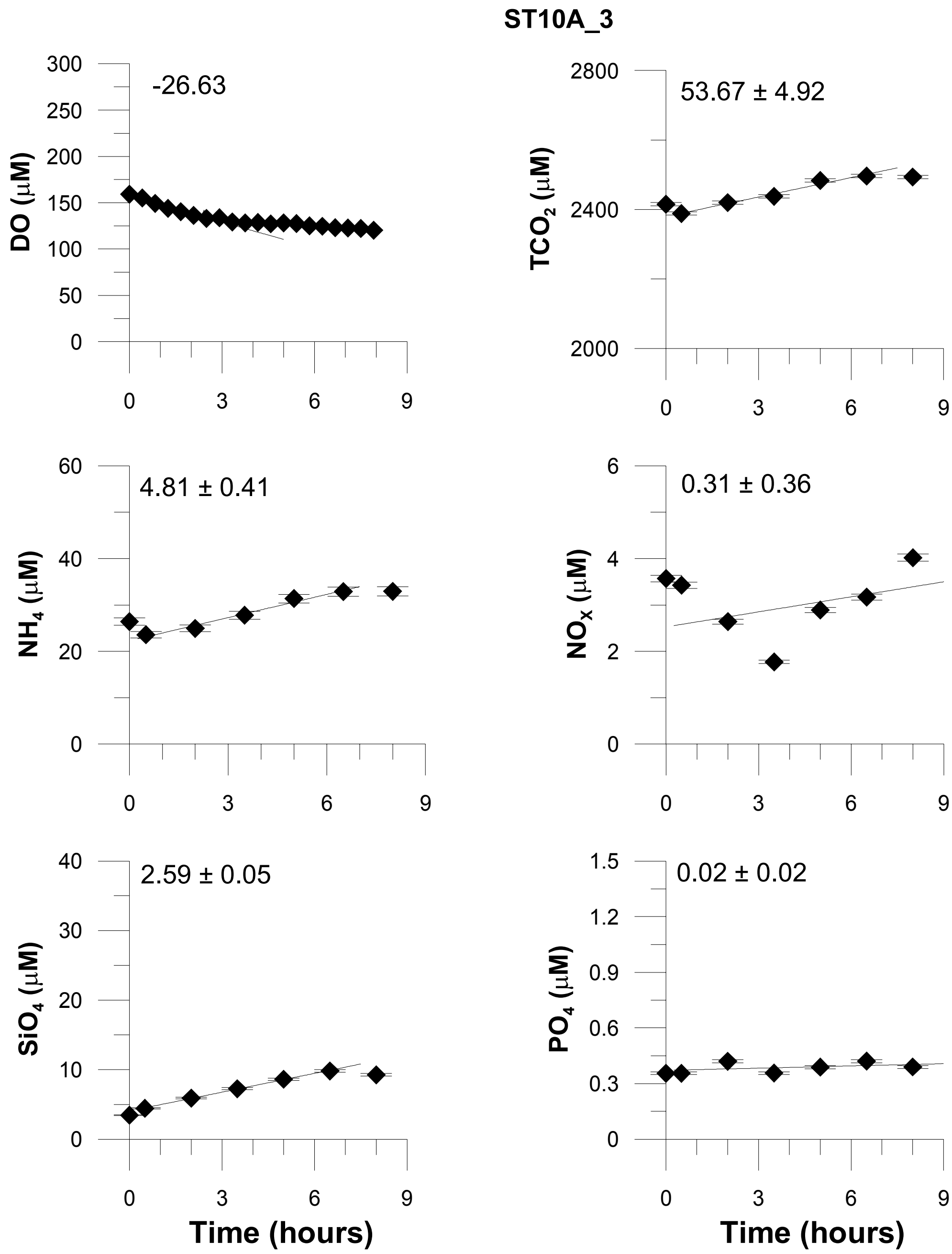


Light

ST10A_2



Light


ST10A_3
DO (μM)
-26.63
TCO2 (μM)
53.67 ± 4.92
NH4 (μM)
4.81 ± 0.41
NOX (μM)
0.31 ± 0.36
SiO4 (μM)
2.59 ± 0.05
PO4 (μM)
0.02 ± 0.02
Time (hours)
Time (hours)