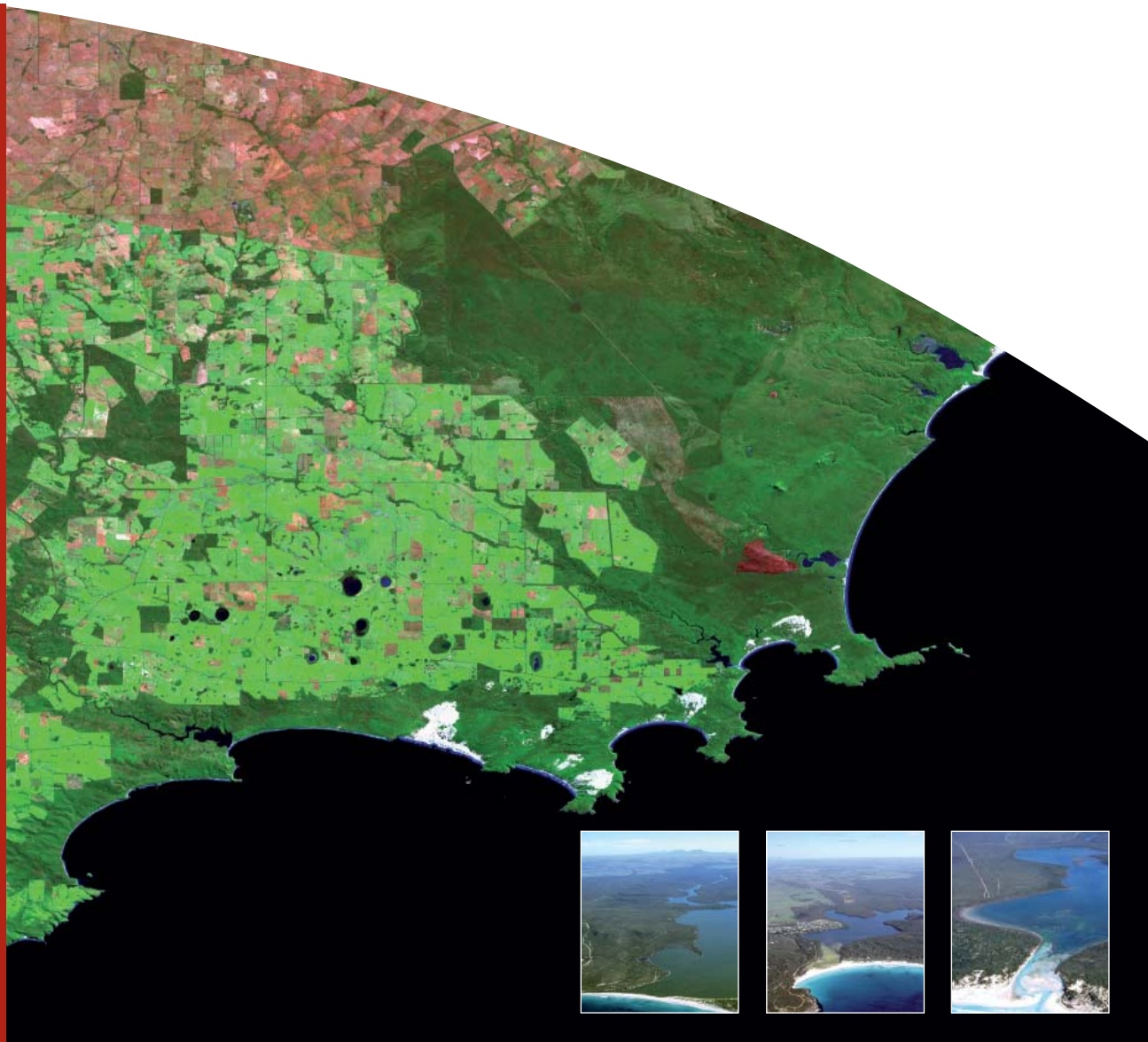
Australian Government
Geoscience Australia

The impact of sediment-water interactions on water quality in Wellstead Estuary, Gordon Inlet, and Beaufort Inlet, south-western Australia

Emma Murray, Ralf Haese, Craig Smith & Emmanuelle Grosjean

Record
2007/03



The impact of sediment-water interactions on water quality in Wellstead Estuary, Gordon Inlet, and Beaufort Inlet, south-western Australia

GEOSCIENCE AUSTRALIA
RECORD 2007/03

Emma J. Murray, Ralf R. Haese, Craig S. Smith, and Emmanuelle Grosjean

Australian Government
Geoscience Australia

Department of Industry, Tourism & Resources
Minister for Industry, Tourism & Resources: The Hon. Ian Macfarlane, MP
Parliamentary Secretary: The Hon. Bob Baldwin, MP
Secretary: Mark Paterson

Geoscience Australia
Chief Executive Officer: Dr Neil Williams

ISSN 1448-2177
ISBN (Print) 978 1 921236 25 9
ISBN (Web) 978 1 921236 26 6

GeoCat # 64912

Bibliographic reference: Murray, E.J., Haese, R.R., Smith, C.S., and Grosjean, E. (2007). The impact of sediment-water interactions on water quality in Wellstead Estuary, Gordon Inlet, and Beaufort Inlet, south-western Australia. Report to the Western Australian Department of Water. *Geoscience Australia Record*. **2007/03**. Commonwealth Government, Canberra.

Executive Summary

Purpose and Background

In early autumn 2006 (14th March to 4th April), Geoscience Australia (GA) conducted a field survey to investigate the major processes controlling water quality in Wellstead Estuary, Gordon Inlet, and Beaufort Inlet. These three estuaries are located near the small township of Bremer Bay, between Albany and Esperance in south-western Australia. The Western Australian (WA) Department of Water (DoW) commissioned this study in partnership with the regional Natural Resource Management (NRM) group; the South Coast Regional Initiative Planning Team (SCRIPT). The DoW aims to improve their water quality monitoring program, incorporating a range of estuary, wetland, and river/catchment projects. This particular project aimed to address critical knowledge gaps in understanding the impact of sediment-water interactions on water quality in each estuary, in particular, to identify the major controls on nutrient abundance and availability. This information will help in setting *Resource Condition Targets* specific to each estuary.

Wellstead Estuary, Gordon Inlet, and Beaufort Inlet: Environmental Setting

Wellstead Estuary, Gordon Inlet, and Beaufort Inlet are similar in several respects. They all have broad, shallow basins (generally <1 m, <0.5 m, and <1.5 m water depths respectively), and a main tributary flowing in from the catchment through a narrow, steep-sided gorge. This channel is relatively sheltered from winds compared to the main basin and has some deep holes in places (up to 7 m water depth). The estuaries and their catchments are all relatively small, especially Wellstead Estuary and Gordon Inlet, which have water and catchment areas less than half that of Beaufort Inlet. Their catchments are similar in terms of geology, climate, and high levels of native vegetation clearance and agricultural activity. Rainfall in the region is generally higher in winter than in summer, with monthly rainfall averages between 20 and 30mm in summer and between 40 and 50mm in winter. All three estuaries are 'wave-dominated' type estuaries, meaning that wave energy has a greater influence in shaping estuary geomorphology than tidal or river energy. Wave dominated estuaries typically have a wave-built sandbar, which restricts or completely blocks water exchange with the ocean, effectively trapping nutrients and sediments carried in by catchment runoff within the estuary basin. Therefore, activities in the catchment, and also nutrient processes within the estuary, strongly influence estuarine water quality and condition. Water quality concerns for Wellstead Estuary, Gordon Inlet, and Beaufort Inlet include known incidences of fish kills, rapid sedimentation, deoxygenation, and algal blooms.

Objectives

The main objective of this study was to:

> ***Determine the impact of sediment-water interactions and the major controls on water quality in Wellstead Estuary, Gordon Inlet, and Beaufort Inlet***

This involved for each estuary, determining the:

1. Magnitude of benthic fluxes, and porewater, and water column metabolite concentrations
2. Processes influencing benthic metabolite fluxes and their effects on water column properties
3. Likely organic matter sources driving benthic metabolite fluxes
4. Denitrification efficiencies and degree of nitrogen fixation

Sampling

In order to achieve the above objectives, we measured benthic nutrient (NH_4^+, NO_X, PO_4^{3-}, SiO_4^{4-}), dissolved oxygen (O_2), nitrogen (N_2), and carbon dioxide (TCO_2) fluxes using benthic chambers. Also, down core distributions of porewater nutrients (NH_4^+, NO_X, PO_4^{3-}, SiO_4^{4-}), salinity, and carbon dioxide (TCO_2), porosity, solid phase phosphate, and chlorophyll a. We measured water column properties including nutrients (NH_4^+, NO_X, PO_4^{3-}, SiO_4^{4-}), chlorophyll a, salinity, and total

suspended matter (TSM), and the type of organic matter by analysing bulk organic matter carbon and nitrogen stable isotopes, biomarkers, and pigments. Sample sites were chosen to represent both basin and channel environments.

It is important to recognize the context within which these measurements were taken (i.e. conditions at the time of the survey), given the very changeable nature of these estuaries and their functioning depending on season, rainfall patterns, local weather conditions, entrance status, and freshwater inflows. As such, the characteristics and key processes influencing water quality may differ to those outlined below given a different set of prevailing conditions. At the time of the survey, Wellstead Estuary and Gordon Inlet were open to the ocean, whereas Beaufort Inlet was closed. Wellstead Estuary had been open since May 2005, and Gordon Inlet and Beaufort Inlet had opened following a heavy rainfall event in mid January 2006, however Beaufort Inlet quickly closed only a few weeks after this. In the two months leading up to the survey, rainfall was substantially above average in January and below average in February. Local weather during the survey was generally dry and sunny.

Impacts of Sediment-Water Interactions on Overall Water Quality

1. Shallowness and Long Water Residence Times

The shallowness of the three estuaries means the ratio of water volume to sediment surface area is very small. Also, when the estuary entrance is closed, the same volume of water remains in contact with the sediments for a long time. These factors result in a strong and immediate coupling between sediment and water column processes. For example, the ratio of nitrogen (N) to phosphorus (P) being released from the sediments appears to determine N : P ratios in the water column. The small size and shallowness of these systems also means that dynamic and changeable factors that affect the activity of microbenthic algae (MBA), such as wind and solar radiation, have a major influence on nutrient fluxes at the sediment-water interface. Additionally, during periods of water exchange with the ocean, and large freshwater flows, these estuaries experience significant and widespread changes to their geochemical and ecological functioning.

2. Productivity of Microbenthic Algae

In these shallow estuaries, sunlight can penetrate the entire water column and illuminate the estuary bottom, allowing plant growth not only in the water (e.g. of phytoplankton, macrophytes and associated epiphytes) but also on the sediment surface (e.g. seagrasses, macro- and microalgae). As a consequence, aquatic plants strongly influence water quality and nutrient processing within these estuaries. Most notably, microbenthic algae (MBA) affect benthic nutrient and gas fluxes in several ways: (1) when assimilating nutrients into biomass, MBA reduce the delivery of nutrients released from organic matter breakdown in surface sediments to the overlying water; (2) phosphorus release is additionally reduced because oxygen produced by the photosynthesising MBA causes rapid formation of ironoxyhydroxides, which adsorb phosphorus, retaining it in the sediments (3) denitrification is reduced since MBA preferably assimilate NO_3^-, thereby, reducing the NO_3^- available for denitrification (4) in the absence of sufficient N, some types of MBA can assimilate N from N_2 gas (N-fixation), which effectively introduces additional N to the system. It follows that, factors that influence MBA productivity, will in turn influence benthic fluxes and water column quality. Such factors change the availability of light and nutrients at the sediment surface and include, water depth, shading by overlying macroalgae and seagrasses, and cloud cover. Moderate to strong winds can also form waves strong enough to resuspend surface sediments, which increases turbidity, lowers light levels, and can physically disturb the MBA layer.

3. Type of Aquatic Plant Growth

As mentioned above, aquatic plants strongly influence water quality in these shallow estuaries. As such, in all three estuaries, most of the labile and non-labile organic material analysed from surface sediments, was found to originate from primary productivity (plant growth) occurring within the estuary, as opposed to organic material washed in from the catchment. Therefore, in addition to the influence of MBA on benthic fluxes, the relative abundance of all different plant types growing in each estuary (e.g. MBA, macrophytes, phytoplankton etc) can influence water quality. For example, given abundant nutrients, macrophytes can outcompete phytoplankton, and grow extensively, filling the entire water column, and creating a large standing stock of organic material. The concern for water quality in this case, is that the macrophytes can then potentially die en-masse following a flood event, bar opening, or during the autumn – winter transition when plants start to die due to light limitation. The sudden load of decaying organic material can lead to anoxia and fish kills.

At the time of the survey, benthic (MBA) primary production was dominant in Wellstead Estuary and Gordon Inlet, whereas water column primary production was dominant in Beaufort Inlet. In Wellstead Estuary, macrophytes are often dense and extensive, and they contribute significantly to the labile organic matter degrading in the sediments along with the epiphytic diatoms associated with the macrophytes and the MBA. Macrophytes and MBA also form the bulk of labile organic matter degrading in the sediments of Gordon Inlet and Beaufort Inlet. Interestingly in Beaufort Inlet, phytoplankton make up a significant proportion of the organic matter in the sediments, however it seems the labile proportion of this is broken down in the water column before reaching the sediment.

Impacts of Sediment-Water Interactions on Overall Water Quality Specific to Each Estuary

Wellstead Estuary

- MBA were well established in the main basin at the time of the survey and the productivity of MBA far outweighed that of phytoplankton in the water column.
- PO_4^{3-} benthic fluxes were negligible in the main basin because of effective P trapping in the sediments enhanced by MBA, whereas in the channel, which lacked an MBA layer, PO_4^{3-} fluxes were significant.
- NH_4^+ benthic fluxes were large in both the main basin and channel.
- DIN : DIP ratios in the water column were very high (> 40) in the main basin, and very low (0.29) in the channel.
- DIN : DIP ratios were likely leading to P limitation of primary production (phytoplankton) in the water column of the main basin and possibly N limitation in the channel, however with plentiful release of NH_4^+ from channel sediments, an abundance of phytoplankton was able to grow here.
- Macrophytes, and their attached epiphytes, are contributing significantly to the basin-wide formation of biomass and are a major source of the organic matter presently decomposing in surface sediments.
- Very low denitrification efficiencies (16-19%) mean sediments were releasing abundant bioavailable N, as NH_4^+, to the overlying watercolumn, and very little N was being lost from the estuary.

Gordon Inlet

- MBA were well established throughout the main basin and channel at the time of the survey and primary productivity was much greater in surface sediments than in the water column.
- MBA were a significant influence, reducing N and P release to the water column, leading to negligible dissolved inorganic N and P concentrations in the water column.

- Cyanobacteria were detected in sampled microbial mats and in surface sediments, indicating that under sunny conditions, N-fixation may be occurring. This is a likely means for overcoming the low levels of dissolved N in the water column.
- Denitrification rates were moderate, with efficiencies of between 27-53% when MBA productivity was suppressed during overcast, windy conditions.

Beaufort Inlet

- Water quality related features differed to those of Wellstead Estuary and Gordon Inlet in several key respects.
- Chlorophyll a inventories indicated that primary productivity was in general much greater in the water column (indicating the dominance of phytoplankton) compared to surface sediments.
- Benthic PO_4^{3-} fluxes were very high and benthic NH_4^+ fluxes were very low, which is likely leading to the very low molar DIN : DIP ratios in the water column, (<4), and N limitation of primary productivity.
- MBA were active at the time of sampling in the main basin and absent, or less active at upper estuary sites. Without the filtering effect of MBA, benthic N and P fluxes were comparatively higher in the upper estuary sites, compared to the main basin.
- In the absence of MBA, denitrification efficiencies were extremely high (82-96%) in the upper estuary, whereas rates of N-fixation were, by far, much greater than denitrification in the main basin. Here, N-fixation was likely the response of MBA to the deficiency in bioavailable N.
- Euglenophytes, a phytoplankton group capable of assimilating dissolved organic N (DON) in lieu of DIN, dominated the phytoplankton community in the main basin.

5B. CONSIDERATIONS FOR MANAGEMENT AND WATER QUALITY MONITORING

1. With high rates of denitrification in Beaufort Inlet, moderate rates in Gordon Inlet, and very low rates in Wellstead Estuary, we recommend reducing N loads from the catchment of particularly Wellstead Estuary, and limiting any increase in N loads from the catchment of Gordon Inlet.
2. With very little P trapping and very high rates of P release from sediments, we recommend reductions in the P load from the catchment of Beaufort Inlet.
3. The abundance of macrophytes in Wellstead Estuary, and their potential to grow rapidly, is of concern. Therefore, in regards to developing *resource condition targets*, we recommend monitoring the abundance of macroalgae in Wellstead Estuary, particularly during the main growth period, and assess the risk of large-scale algal mass decay by accounting for weather conditions, water levels, and bar status. The daily variation in water column dissolved oxygen levels is a possible means for estimating plant biomass in the system, where the larger the difference between day and night time concentrations, the greater the plant biomass.
4. Dense stands of macrophytes are also sometimes present in Gordon Inlet, however the nature of macrophyte growth and decay cycles is poorly known. We recommend monitoring macrophyte abundance in Gordon Inlet, however, at present, it seems that bioavailable N is moderated by MBA, and also by a reasonable level of denitrification when MBA productivity is low.
5. Presently in Beaufort Inlet, the more common occurrence of phytoplankton blooms seems of greater concern, and frequent monitoring of water column Chl-a concentrations in relation to seasonal and local weather conditions may be more relevant. Additionally, the

pre-dominance of euglenophyta is often an indicator for eutrophic conditions and possibly for organic pollution. Since Beaufort Inlet was dominated by euglenophyta at the time of the survey, its waters should be tested for organic pollution and its source identified

6. Importantly for designing future monitoring programs, water column properties, and benthic nutrient and gas fluxes are highly controlled by seasonal and weather conditions, therefore, the interpretation of any environmental data from these shallow estuaries must consider conditions at the time of sampling. Day-to-day differences in weather have immediate effects on water column and flux properties, making it difficult to derive long-term temporal trends from single measurements

Acknowledgements

The authors would like to thank Jon Stratton and Matthew Carey from Geoscience Australia, and Andrew Maughan, Vanessa Forbes, Dave Bloomfield, Helen Astill, Ania Lorenz, and Geoff Bastyan from the WA Department of Water for their assistance with field logistics, sampling, and analysis. Also, Bill Pappas, Liz Webber, and Janet Hope from Geoscience Australia, and Frank Krikowa from Canberra University for sample preparation and analyses (sediment grinding, XRF, stable isotope, and ICP-MS analysis respectively).

In addition, Andrew Maughan provided bathymetry maps, aerial photographs, and background data, and background information and data was also received from Vanessa Forbes.

We thank the WA Department of Water, South Coast Regional Office, and the SCRIPT NRM Group for commissioning this study, and also Malcolm Robb from the WA Department of Water for his support and for final comments on the draft.

From Geoscience Australia, Angie Jaensch prepared the estuary location map and sample site location maps, Maria Bentley designed the report cover, and Alix Post and Chris Hepplewhite provided comments and editing.

Abbreviations and Units

ANZECC	Australian and New Zealand Environment and Conservation Council
Chl-a	Chlorophyll a
C	Carbon
$\delta^{13}C$	Delta ^{13}C
cc	cubic centimetre
cm	centimetre
CO_2	Carbon Dioxide
DIN	Dissolved Inorganic Nitrogen
DIP	Dissolved Inorganic Phosphorus
DO	Dissolved Oxygen
DoW	Department of Water, Western Australian Government
Fe	Iron
GA	Geoscience Australia
H_2S	Hydrogen Sulfide
Kd	Light Attenuation Coefficient
km	kilometre
m	meter
m^{-1}	per metre
mAHD	metres above Australian Height Datum
mg/L	milligrams per litre
mm	millimeters
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
$^{15}N_2$	N_2 labelled with ^{15}N isotope
NH_4^+	Ammonium
NLWRA	National Land and Water Resources Audit
NO_2^-	Nitrite
NO_3^-	Nitrate
$^{15}NO_3^-$	NO_3^- labelled with ^{15}N isotope
NO_X	Nitrate + Nitrite
O_2	Oxygen
P	Phosphorus
PAR	Photosynthetically Active Radiation
PO_4^{3-}	Phosphate
SCRIPT	South Coast Regional Initiative Planning Team
Si	Silica
SiO_4^{4-}	Silicate
TCO_2	Total Carbon Dioxide
TIN	Total Inorganic Nitrogen
TN	Total Nitrogen
TOC	Total Organic Carbon
TP	Total Phosphorus
TSM	Total Suspended Matter
WA	Western Australia
WRC	Water and Rivers Commission, Western Australia (integrated into DoE in 2004)
µg/L	micrograms per litre
µM	micromolar
°C	degrees Celsius

Contents

1. Introduction

1A. RATIONALE FOR THIS INVESTIGATION

Declining water quality in Australian estuaries

Water quality decline and associated problems such as fish kills and toxic algal blooms are a growing concern for Australian estuaries. This is especially so in southern Australia, where estuaries are subject to increasing nutrient inputs from agricultural, urban, and industrial development, and according to the National Land and Water Resources Audit (NLWRA), estuary condition is predominantly 'modified' or 'extensively modified' (NLWRA 2002). In addition, most estuaries in southern Australia are 'wave-dominated', where wave energy is greater than tide and river energy (Ryan *et al*. 2003; NLWRA 2002). This estuary type is more susceptible to eutrophication and water quality problems compared to tide and river dominated estuaries because a characteristic sand bar restricts or totally blocks the entrance, limiting flushing to the ocean and retaining nutrients within the estuary (Harris and Heap 2003).

Water quality concerns for Wellstead Estuary, Gordon Inlet, and Beaufort Inlet

This study investigated the major sediment-water interactions controlling water quality in Wellstead Estuary, Gordon Inlet, and Beaufort Inlet; all located near the small township of Bremer Bay, between Albany and Esperance, south-western Australia (Figure 1-1). These estuaries adjoin the Southern Ocean, where wave action is strong but tidal range is small (microtidal). Average annual rainfall is low (400-600mm), and river flow is only significant after heavy rain. Consequently, the NLWRA classified all three estuaries as 'wave-dominated'. Also, with the clearance of 80%, 60%, and 84% of native vegetation from the catchments of Wellstead Estuary, Gordon Inlet, and Beaufort Inlet respectively, and considerable agricultural activity (evident in Figure 1-1), the NLWRA assessed their condition as 'modified'.

The nature and extent of impacts on Wellstead Estuary, Gordon Inlet, and Beaufort Inlet from catchment clearance and agricultural practices is not well established (WRC 2004; Hodgkin and Clark 1988). However, activities in the catchment are likely to have a strong influence on water quality in the estuaries since they are 'wave-dominated', each with a sand bar blocking water exchange with the ocean for extended periods and classified by Ernest Hodgkin as 'normally closed' (Brearley 2005). There are known incidences of fish kills, rapid sedimentation, deoxygenation, and algal blooms in these estuaries, however it is not known if this is natural or linked to catchment disturbance (WRC 2004).

Needs for estuary management

The South Coast Regional Initiative Planning Team (SCRIPT), who are the regional Natural Resource Management (NRM) group, and the Western Australian (WA) Department of Water (DoW), are responsible for managing estuaries along the south coast of WA, including Wellstead Estuary, Gordon Inlet, and Beaufort Inlet. In order to develop natural resource management strategies, SCRIPT and the DoW require an understanding of the current environmental condition of these estuaries, how they have changed in response to catchment disturbances, and how they might respond to different management approaches. The recently developed *Monitoring and Evaluation Framework for the National Action Plan for Salinity and Water Quality* requires the setting of

Resource Condition Targets for guiding and assessing management actions in achieving desired changes in estuary condition (WRC 2004). These must be measurable and scientifically valid.

In a report commissioned to provide comment on the environmental status of Wellstead Estuary (WRC 2004), the DoW states that existing data and information is inadequate, and ecological process information (for example sediment-water nutrient exchange) is required for determining the current environmental condition of the estuary and to make management recommendations. The report specifically recommends the use of benthic chamber experiments to quantify nutrient exchange between sediments and overlying waters and determine how sediments influence water quality. This will assist in determining the nutrient capacity of the estuary. As such, the DoW commissioned this study in partnership with SCRIPT to conduct an expanded water monitoring program covering a range of estuary, wetland, and river/catchment projects over about 2.5 years. Funded by the *National Action Plan for Salinity and Water Quality*, this program is required to provide background information for setting *Resource Condition Targets*.

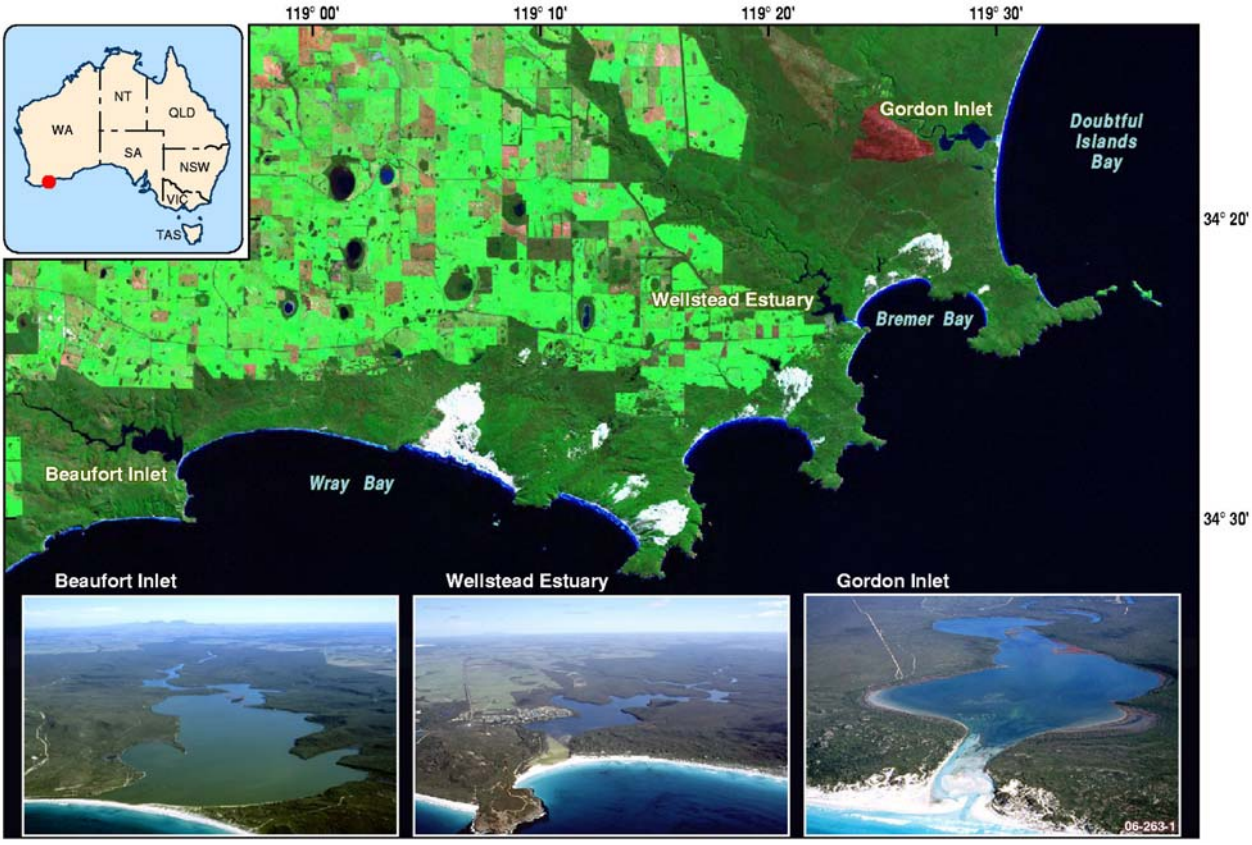


Figure 1-1. Satellite image and aerial views of Wellstead Estuary, Gordon Inlet, and Beaufort Inlet. False colour Landsat 7 ETM+ satellite image from the Australian Greenhouse Office mosaic of Australia; aerial photos from WRC (2001a).

1B. OBJECTIVES

The main objective of this study was to:

Determine the impact of sediment-water interactions and the major controls on water quality in Wellstead Estuary, Gordon Inlet, and Beaufort Inlet

This involved for each estuary, determining the:

1. Magnitude of benthic flux, porewater, and water column metabolite concentrations
2. Processes influencing benthic metabolite fluxes and their effects on water column properties
3. Likely organic matter sources driving benthic metabolite fluxes
4. Denitrification efficiencies and degree of nitrogen fixation

In order to achieve the above objectives, we measured benthic nutrient (NH_4^+, NO_X, , PO_4^{3-}, SiO_4^{4-}), dissolved oxygen (O_2), nitrogen (N_2), and carbon dioxide (TCO_2) fluxes using benthic chambers. Also, down core distributions of porewater nutrients (NH_4^+, NO_X, PO_4^{3-}, SiO_4^{4-}), salinity, and carbon dioxide (TCO_2), porosity, solid phase phosphate, and chlorophyll a. We measured water column properties including, nutrients (NH_4^+, NO_X, PO_4^{3-}, SiO_4^{4-}), chlorophyll a, salinity, and total suspended matter (TSM), and the type of organic matter by analysing bulk organic matter carbon and nitrogen stable isotopes, biomarkers, and pigments. Sample sites were chosen to represent both basin and channel environments.

1C. THE IMPORTANCE OF SEDIMENT-WATER INTERACTIONS

Biogeochemical and physical processes occurring in estuary sediments play an important role in controlling estuarine water quality. As such, this study focussed on measuring the release and uptake of nutrients and other solutes at the sediment-water interface (benthic fluxes), as well as the change in porewater and solid phase constituents with depth in the sediments. The breakdown of organic matter in sediments, and the resulting exchange of oxygen, carbon dioxide, and nutrients (nitrogen and phosphorus) with the overlying water can influence water column conditions (for example oxygen levels) and also supplement nutrient supply from the catchment (Figure 1-2, green arrows; Jørgensen 1996). Plants utilise nutrients available in the water column, and when nutrient input from the catchment and/or the sediments is excessive, eutrophic conditions may develop, involving prolific plant growth and the possibility of toxic blue-green algae blooms, low dissolved oxygen levels, and fish kills.

The magnitude of benthic fluxes is an indicator of the amount of biological activity and organic matter breakdown in the sediments. Figure 1-2 is a simplified illustration of organic matter breakdown and nutrient cycling in wave-dominated type estuaries. Nutrients in runoff from the catchment can enter an estuary and stimulate plant growth, for example that of phytoplankton and macroalgae in the water column, and microbenthic algae on the sediment surface. Bacteria subsequently break down these plants when they die and settle to the bottom sediments. The resulting flux of nutrients to the overlying water from organic matter breakdown is a source of nutrients for further plant growth. Nitrogen is released in various forms (NH_4^+, NO_x, and N_2), as well as phosphorus (PO_4^{3-}), and if diatoms (a type of microalga with cell walls made of silica) are present, silicate (SiO_4^{4-}) is released. The bacteria consume oxygen, when available, during respiration to oxidise the organic material. If organic matter supply to the sediment is excessive, for example, under eutrophic conditions following an algae bloom, the bacteria can use up all the available oxygen, creating anoxic conditions and possibly causing a fish kill.

In addition to organic matter breakdown (a respiration process), plant productivity (photosynthesis), for example that of microbenthic algae (MBA) or macroalgae on the sediment surface, can have a significant impact on oxygen, carbon, and nutrient fluxes and therefore water quality. Photosynthesis during daylight hours produces oxygen and consumes carbon dioxide. MBA and macroalgae also take up nutrients both from the sediments (released from the breakdown of organic matter) and from the water column (Figure 1-2).

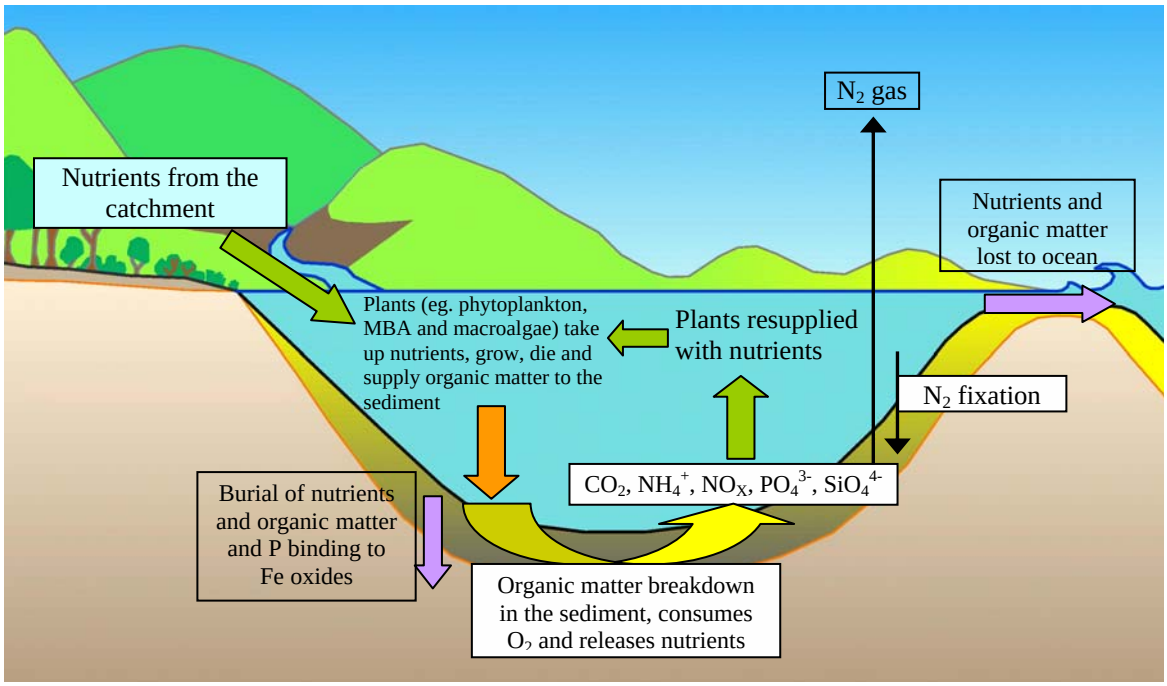


Figure 1-2. Schematic diagram of nutrient cycling in wave-dominated type estuaries. Green arrows indicate nutrient supply to plants, the orange arrow indicates organic matter supply to the sediment, the yellow arrow represents organic matter breakdown, the black arrows show N loss through denitrification, and N supply through N fixation, and the purple arrows show loss of nutrients and organic matter to the ocean (often very limited in wave-dominated estuaries) and burial in the sediments, and loss of P through binding with iron oxides in the sediment.

Processes of nutrient loss and gain

Denitrification

Denitrification is an important control on eutrophication because this process of organic matter breakdown releases the nutrient nitrogen (N) as N_2 gas, which plants cannot use directly; N_2 gas is eventually lost from the estuary into the atmosphere (Figure 1-2, long black arrow; Seitzinger 1990). The degree to which denitrification is occurring in the sediments can indicate the susceptibility of an estuary to eutrophication. In some estuaries, the capacity for nitrogen removal is limited because ammonification and dissimilatory nitrate reduction dominate nitrogen cycling, producing bioavailable ammonium (NH_4^+) as opposed to N_2 gas.

Phosphorus binding to iron oxides

Binding of the nutrient phosphorus (P) to iron oxides present in the sediment is also a possible control on eutrophication (Figure 1-2, down-pointing purple arrow). Many studies have shown that iron oxides strongly influence pore water phosphate (PO_4^{3-}) concentrations and the flux of phosphate

to the overlying water (eg. Sundby *et al*. 1992). The capacity of the sediment to 'trap' phosphorus depends on the amount of iron oxide available, and this is dependant on the amount of iron in the sediments arriving from the catchment, and the oxygen status of the sediments in the estuary. Under anoxic conditions, iron oxides are reduced and dissolved phosphate is released into the pore waters and overlying waters. Generally, the surface sediments are oxidised and effectively trap phosphorus if iron is available, however, deeper sediments are often anoxic (reduced), where iron oxides dissolve, releasing any bound phosphorus.

Burial and ocean exchange

Nutrients and organic matter can also be lost from estuaries through water exchange with the ocean and burial in the sediments (Figure 1-2, purple arrows). However, the restricted entrances of many wave-dominated estuaries limit water exchange with the ocean, trapping nutrients within the estuary. Also, sedimentation rates are usually not rapid enough to bury a significant fraction of organic material before it is broken down (Haese *et al*. submitted).

Nitrogen fixation

Nitogen fixation is the conversion of atmospheric nitrogen (N_2) into a bioavailable form of nitrogen, ammonium (NH_4^+), which is immediately assimilated into biomass. This process can counteract nitrogen removed via denitrification and potentially serve as a source of nitrogen to estuaries. Only certain types of bacteria can fix nitrogen, in estuaries cyanobacteria (blue-green algae) are the most common form.

1D. WATER QUALITY ISSUES IN WELLSTEAD ESTUARY, GORDON INLET, AND BEAUFORT INLET

The nature and extent of impacts from extensive catchment clearance and agriculture on the environmental condition of Wellstead Estuary, Gordon Inlet, and Beaufort Inlet is not well established, however, known incidences of fish kills, rapid sedimentation, deoxygenation, and algal blooms are potential responses to catchment disturbance and indicators of environmental decline. Wellstead Estuary, Gordon Inlet, and Beaufort Inlet all have a wave-built sand bar blocking water exchange with the ocean for extended periods, therefore catchment-derived nutrients and sediments are retained within the estuary, and changes in the catchment are likely to cause changes in the estuary and have a significant influence on water quality.

Table 1-1 summarises the general water quality conditions in Wellstead Estuary, Gordon Inlet, and Beaufort Inlet. Much of this information was compiled using data and reports associated with the WA Water and Rivers Commission (now within the Department of Water) water quality monitoring program, which has involved physical, chemical, and biological sampling of around five to eight sites within each estuary, every three months since 1997 (WRC 1999; WRC 2001b; WRC 2004). The discussion below, which highlights the known water quality concerns for each estuary, also draws on the work of Hodgkin and Clark (1987; 1988), and the summary of Brearley (2005).

Wellstead Estuary has shallow, clear waters, soft sediments, and a nutrient-retentive environment ideal for benthic macrophytes. Benthic macrophytes often thrive in the estuary, forming extremely dense beds covering extensive areas of the main basin and growing in height to fill almost the entire water column. The biomass of macrophytes within the estuary varies widely over time, with huge increases to the point of collapse, then almost complete loss of submerged aquatic vegetation when the ocean bar opens. Macrophytes can be a nuisance for boating and cause unpleasant odours when decaying on the shoreline. Currently there have been no studies to quantify any link in macrophyte growth to increases in nutrients from the catchment following vegetation clearance and agriculture.

Table 1-1. Summary of water quality characteristics of Wellstead Estuary, Gordon Inlet, and Beaufort Inlet. Compiled from WRC (2004), WRC (2001b), WRC (1999), and Brearley (2005). ANZECC guidlines: Australian and New Zealand Guidelines for Freshwater and Marine Water Quality (ANZECC 2000).

Wellstead Estuary	Salinity	Ranges from fresh to more than double seawater salinity (7->70ppt) but generally around seawater salinity, varying between 30-40ppt. Water column usually well mixed with little difference in top and bottom water salinities, sediment porewater salinities very low (0.3-2.6ppt) compared to overlying water, suggesting a freshwater source, possibly groundwater
	Dissolved Oxygen	Variable, ranging from 0-158% saturation, but anoxia rare, water column generally well oxygenated with little vertical stratification, DO conc. highest in winter, lowest in late summer
	Nitrogen	Highly variable, total N ranging between 0.11-3.2mg/L and ammonia <0.005-0.7mg/L, median total N slightly higher than ANZECC guidelines but generally lower than other estuaries in the region, N conc. highest in late summer
	Phosphorus	Generally low compared to other estuaries in region, total P median 0.04mg/L, total P is mainly of particulate form rather than dissolved
	Plantlife	Macrophytes dominate, often extremely dense, low phytoplankton biomass, Chl-a conc low compared to other estuaries in region, microphytobenthic communities likely important
Gordon Inlet	Salinity	Usually >seawater salinity except after rain, often double seawater salinity in late summer, channel and upper basin can become stratified, permanently stratified and hypersaline, >75ppt in bottom of some deep holes in channel
	Dissolved Oxygen	Surface waters throughout estuary usually above 100% saturation, usually higher in the lower basin than upper basin and channel, sometimes stratification and low DO in bottom waters of channel and upper basin, bottom waters permanently anoxic in some deep holes in the channel
	Nitrogen	Total N is moderate to high and exceeds ANZECC guidelines, whereas dissolved inorganic N is low, suggesting N is predominantly in particulate or dissolved organic form, except in the bottom of some deep holes in the channel which have extremely high dissolved inorganic N, 27mg/L.
	Phosphorus	Total P is moderate to high and exceeds ANZECC guidelines, whereas dissolved inorganic P is low, suggesting P is predominantly in particulate or dissolved organic form, except in the bottom of some deep holes in the channel which have extremely high dissolved inorganic P, 4mg/L.
	Plantlife	Phytoplankton is abundant with some of the highest Chl-a conc. measured in the region, the estuary experiences phytoplankton blooms, Ruppia is the dominant macrophyte and is often very dense in the lower basin
Beaufort Inlet	Salinity	Usually around seawater salinity, 25-40ppt, highest in late summer, basin usually well mixed, deep holes in channel often highly stratified and saline >70ppt,
	Dissolved Oxygen	Usually reasonably well oxygenated in basin surface waters, however basin bottom waters can often become deoxygenated, deep holes in channel often strongly stratified with low DO or anoxic bottom waters
	Nitrogen	Total N is moderate to high and exceeds ANZECC guidelines, whereas dissolved inorganic N is low, suggesting N is predominantly in particulate or dissolved organic form, except in the bottom of some deep holes in the channel which have extremely high dissolved inorganic N, 14mg/L.
	Phosphorus	Total P is moderate to high and exceeds ANZECC guidelines, whereas dissolved inorganic P is low, suggesting P is predominantly in particulate or dissolved organic form, except in the bottom of some deep holes in the channel which have extremely high dissolved inorganic P, 2.4mg/L.
	Plantlife	Phytoplankton is abundant with some high Chl-a conc. compared to other estuaries in the region, the estuary often experiences large phytoplankton blooms, some dense patches of macrophytes were observed during this study

Fish kills are known to occur in Wellstead Estuary, for example, there was a major fish kill in early May 2005, immediately after the bar opened (Geoff Bastyan pers. comm. 28/06/2006), and also in mid December 2001. WRC (2004) describes the conditions leading to the 2001 fish kill, which began with a long period of high water levels (22 months at around 2 m depth) and a massive increase in macrophyte biomass as the plants grew to fill the available water column. Broadscale deoxygenation and the fish kill followed when the bar finally broke and water levels suddenly dropped by 1 m. At the time, the macrophytes were in a state of decline, and dissolved oxygen levels were low, associated with decaying organic matter. The drop in water levels exposed the macroalgae and also further reduced the amount of available dissolved oxygen.

Phytoplankton blooms and dense macrophyte beds are known to occur in Gordon Inlet (Table 1-1). However, the estuary is more isolated and less visited than Wellstead Estuary and Beaufort Inlet, and fish kills, algal blooms, and other water-quality related events may have occurred but gone unnoticed. One issue of concern are the deep holes (4-5 m deep) in the river channel draining into the estuary. These holes are permanently stratified, and the bottom waters are anoxic, hypersaline, and have very high dissolved nutrient concentrations (Table 1-1). The impact of the water in these holes on the main estuary basin is unknown.

Beaufort Inlet has known incidences of fish kills, phytoplankton blooms, and rapid sedimentation. There were at least nine fish kills in the estuary between 1936 and 2000 (Brearley 2005). The exact cause of these is unknown, but may be attributed to high salinities and temperatures, algal blooms, and deoxygenation. Similarly to Gordon Inlet, the deep holes (5-10 m deep) in the river channel draining into the estuary are a concern, as they are also often stratified and have anoxic, hypersaline bottom waters with high dissolved nutrient concentrations (Table 1-1). Sedimentation is also an issue, for example, in January 1982, floods in the Pallinup River deposited an estimated 100 000 tonnes of sediment into Beaufort Inlet, representing a layer of sediment 25 mm in depth over the entire basin area.

1E. ENVIRONMENTAL SETTING

This section provides a brief summary of the environmental and biophysical features of Wellstead Estuary, Gordon Inlet, and Beaufort Inlet. Only information considered relevant to this investigation is presented, including that which assists with data interpretation, and which provides a useful context for the results. For more detail about the estuaries and their catchments refer to the following documents from which much of this summary was sourced:

Brearley, A. (2005). *Ernest Hodgkin's Swanland: estuaries and coastal lagoons of southwestern Australia*. Ernest Hodgkin Trust for Estuary Education and Research and National Trust of Australia (WA). University of Western Australia Press, Crawley, Western Australia.

Hodgkin, E.P. and Clark, R. (1987). Wellstead Estuary, the estuary of the Bremer River, An inventory of information on the estuaries and coastal lagoons of south Western Australia. *Estuarine Studies Series No*. **1**. Environmental Protection Authority, Government of Western Australia, Perth.

Hodgkin, E.P. and Clark, R. (1988). Beaufort Inlet and Gordon Inlet, Estuaries of the Jerramungup Shire, An inventory of information on the estuaries and coastal lagoons of south Western Australia. *Estuarine Studies Series No*. **4**. Environmental Protection Authority, Government of Western Australia, Perth.

Water and Rivers Commission (2004). Situation Paper for the Wellstead Estuary, South Western Australia. *Department of Environment, Water Resource Management Series* No WRM **x**. Government of Western Australia. Perth

Wellstead Estuary, Gordon Inlet, and Beaufort Inlet are fed by the Bremer, Gairdner, and Pallinup Rivers respectively (Table 1-2). Beaufort Inlet is the largest system, with a catchment area over six times larger than that of Wellstead Estuary, and almost three times larger than that of Gordon Inlet. Beaufort Inlet also has the largest water area; more than double that of Wellstead Estuary and Gordon Inlet. All three estuaries are similar in physical form, comprising a broad, shallow basin, connected to the catchment via a narrow channel within a deeply incised valley. Of particular note, is the shallowness of the main basin of these estuaries, with water depths ranging between 1.5 m in Beaufort Inlet, to less than 0.5 m in Gordon Inlet. Sometimes Gordon Inlet almost completely dries

out. The channel of each estuary is also generally shallow, however there are deep holes in places, some up to 10 m deep (Table 1-2).

All three estuaries can remain closed to the ocean for several years at a time (referred to by Ernest Hodgkin as "normally closed" estuaries) and will usually only open after particularly heavy rainfall. The three estuaries and their catchments are in a region of relatively low rainfall (between 400 and 600 mm annually). Generally, most rain falls during winter months, however, infrequent summer storms can contribute significantly to annual precipitation, and flooding which is large enough to breach the estuary mouth can occur any time of the year. Notably however, the height, width, and ocean exposure of the sand bar at the mouth of each estuary differs, resulting in differences in the frequency and duration of sand bar openings (Table 1-2). The bar of Beaufort Inlet is higher and less sheltered from ocean swells than Wellstead Estuary and Gordon Inlet. Therefore, Beaufort Inlet only stays open for a few weeks at a time, whereas Gordon Inlet and Wellstead Estuary often stay open for months and years respectively, which is longer than most other estuaries in the region.

Table 1-2. Physical characteristics of Wellstead Estuary, Gordon Inlet, and Beaufort Inlet.

Estuary	Main Tributary	Catch-ment Area[1]	Water Area[2]	Catch-ment Cleared[1]	General Basin Depth[3]	General Channel Depth[3]	Estuary Mouth Sandbar	Mouth Openings[4]	
								Frequ-ency	Duration
Wellstead Estuary	Bremer River	720km^2	3km^2	80%	<1m	0.5-1.5m, some deep 2.5m holes	Relatively low, ~ 1-2m	Highly variable, open 5 times 1993-2004, can open any season	Anywhere between a month and a year, open longer than other estuaries in region
Gordon Inlet	Gairdner River	1 770km^2	3km^2	60%	<0.5m	1-2m, some deep 4-5m holes	Relatively low, <1.5m	Opens every 3-5 years	Generally a few weeks or months but sometimes for 2-3 years, open relatively longer than other estuaries in region
Beaufort Inlet	Pallinup River	4 800km^2	7km^2	84%	<1.5m	1-2m, some deep 5-10m holes	Relatively high, up to 3.5m, allowing a large range in water levels in basin	Highly variable, from every 1-2 years to 12 years	Opens only briefly, bar rapidly rebuilds within weeks

[1] From WRC (2001a)

[2] From NLWRA (2002)

[3] From this study and WRC bathymetry maps (see Figure 2-1, Figure 2-2, and Figure 2-3)

[4] Summarised from Brearley (2005)

Evaporation in the main basin of each estuary is high and salinities can vary hugely (Table 1-1) depending on freshwater inflow, bar status, and season. This restricts the number of species of flora and fauna able to survive in the estuaries to those able to survive large changes in salinity. Water levels can also vary significantly, with Beaufort Inlet having the largest range in possible water levels due to its relatively high sand bar.

The catchment geology of all three estuaries is very similar, and the channel portion of each estuary is sheltered within a steep-sided gorge, which cuts through the relatively soft, Plantagenet Group siltstones and sandstones. These flat-bedded marine sediments consist of clays, sand, and many silica sponge spicules. Native vegetation clearance for agriculture, mainly for sheep farming and some cropping, in the catchments of Wellstead Estuary, Gordon Inlet, and Beaufort Inlet is significant (80%, 60%, and 84% respectively). Most of this is in the upper and middle catchment, with native vegetation in the immediate area around each estuary remaining largely intact. Most vegetation clearance occurred very rapidly over a short and intensive period of broadscale removal in the 1950s and 1960s. The soils in the region are highly leached and naturally very nutrient poor. To compensate for this, farmers relied on fertiliser application of superphosphate following vegetation clearance, and later also on nitrogen application. This has likely increased nutrient loads to the estuaries.

Sheet and gully erosion following vegetation clearance has probably increased the amount of sediment mobilised in the catchments and reaching the estuaries. The annual sediment yield to Wellstead Estuary, Gordon Inlet, and Beaufort Inlet, estimated from spatial modelling (Prosser *et al*. 2001) is 3.6, 4.1, and 27.0 kT $year^{-1}$ respectively. This represents an estimated 14 to 18 fold increase in sediment yield since European settlement of the region.

2. Methods

2A. SAMPLING STRATEGY

In March 2006, Geoscience Australia (GA) conducted a field survey to investigate Wellstead Estuary, Gordon Inlet, and Beaufort Inlet. The field program involved water column, benthic chamber, and sediment sampling at selected sites in each estuary. Table 2-1 outlines the specific type of sampling undertaken at each site. All three estuaries comprise a broad, shallow basin fed by a deeper, narrow channel, as outlined in Table 1-2 in the previous chapter, and described in Section 1E. *Environmental Setting*. Sites in each estuary were chosen to encompass these two distinct environments (Table 2-1; Figure 2-1; Figure 2-2; and Figure 2-3). Where possible, WA Department of Water, water quality monitoring sites were used (Table 2-1), in order to allow the Department to interpret the results of this investigation alongside their existing data.

Table 2-1. Sampling site details and type of sampling undertaken at each site.
1. Site identification (ID) code;
2. Corresponding WA Department of Water (DoW) site ID code;
3. Description used throughout this report to identify the general environment of each site;
4. Water column sampling undertaken i.e. dissolved oxygen, salinity, and temperature profiles (Profile); surface water samples (SWS) for nutrient, chlorophyll a, and total suspended matter analysis; also surface water samples for pigments (Pigments), and biomarkers (BM);
5. Type of chambers deployed (i.e. either dark or light) and the chamber ID number (in brackets);
6. Sediment sampling undertaken i.e. coring (Cores) for sediment profiles of pore water nutrient, carbon dioxide, and chlorophyll a analysis and solid phase carbon and nitrogen stable isotope and phosphate and aluminium analysis and surface sediments for biomarkers (BM) and pigments (Pigments).

Estuary	Site ID[1]	DoW Site ID[2]	General Environ.[3]	Lat. °S	Long. °E	Water Column[4]	Chambers Deployed[5]	Sedi-ment[6]
Wellstead Estuary	WE9	WE005	Channel	-34.3656	119.3663	Profile SWS	Dark (3) Light (6)	Cores BM
	WE8	WE003	Basin	-34.3759	119.3712	Profile SWS	Dark (4, 7) Light (9)	Cores BM
	WE7		Basin	-34.3859	119.3718	Profile SWS	Dark (4, 7) Light (9)	Cores BM
	WE6	WE001	Basin	-34.3877	119.3845	Profile SWS	Dark (3) Light (6)	Cores BM
Gordon Inlet	GO6		Channel	-34.2840	119.4538	Profile SWS	Dark (3) Light (6)	Cores BM
	GO7	GOI005	Channel	-34.2819	119.4603	Profile SWS	Dark (4, 7) Light (9)	Cores BM
	GO8	GOI004	Basin	-34.2901	119.4652	SWS	Dark (4, 7) Light (9)	Cores BM
	GO9	GOI003	Basin	-34.2876	119.4736	SWS	1 Dark (3) 1 Light (6)	Cores BM
Beaufort Inlet	BE12		Channel	-34.4606	118.8541	SWS Pigments		
	BE11		Channel Hole	-34.4587	118.8616	SWS Pigments		
	BE10	BEA005	Channel Hole	-34.4546	118.8619	Profile SWS Pigments BM		Cores BM Pigments
	BE6	BEA003a	Channel	-34.4526	118.8737	Profile SWS Pigments BM		Cores BM
	BE9		Channel	-34.4542	118.8758	Profile SWS	Dark (3) Light (6)	Cores
	BE7		Channel/Basin Entrance	-34.4568	118.8787	Profile SWS	Dark (4, 7) Light (9)	Cores
	BE8		Basin	-34.4584	118.8839	SWS	Dark (3, 4, 7) Light (6, 9)	Cores

2A1. Site Selection

In Wellstead Estuary, sites WE6, WE7, and WE8 were chosen to represent conditions within the main basin, whereas site WE9 was chosen to represent channel conditions (Figure 2-1; Table 2-1). The sediments of both the basin and channel comprised homogenous grey/black mud with a layer of green macro/micro-algae on the surface.

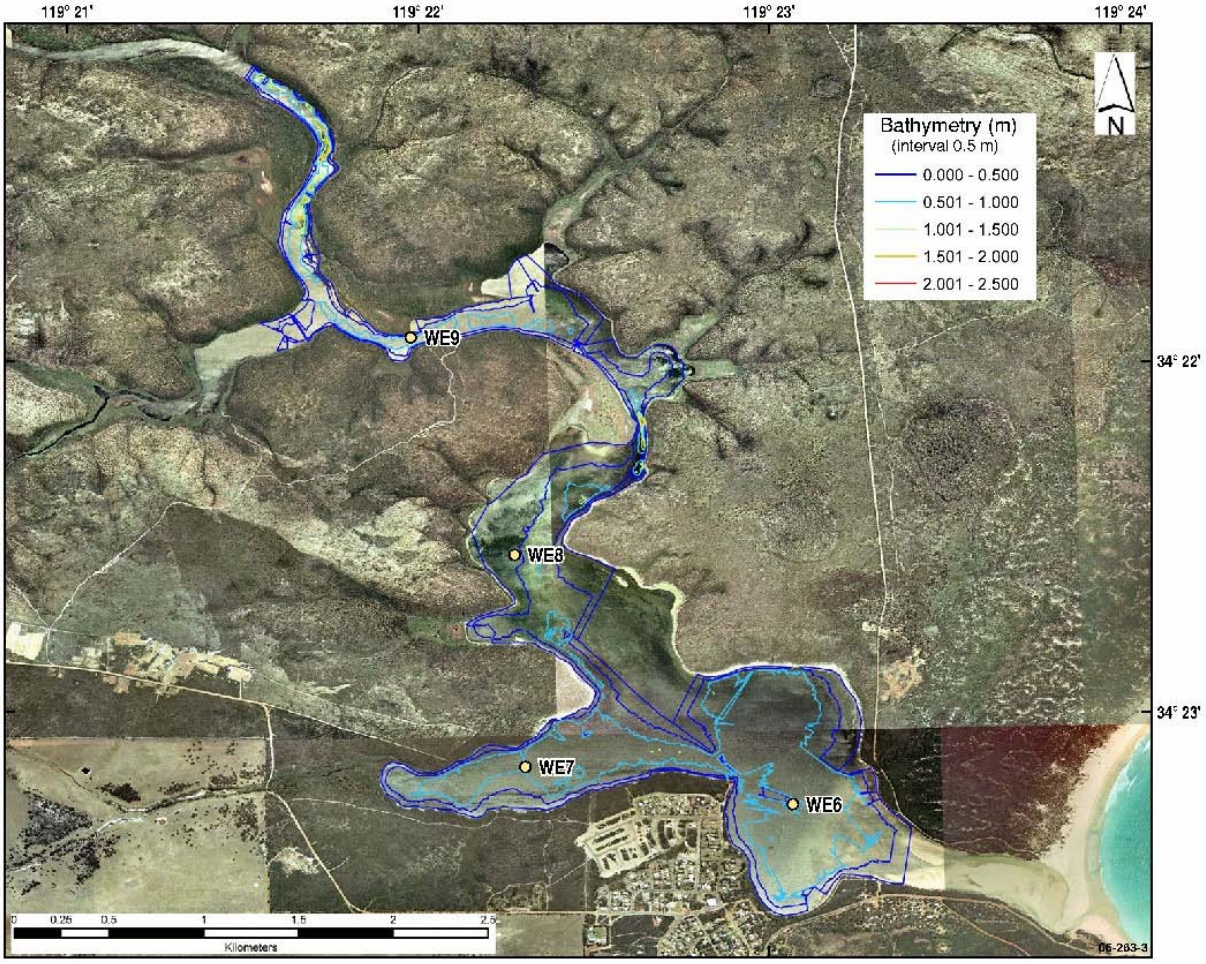


Figure 2-1. Wellstead Estuary bathymetry and sampling site locations. Bathymetry is in mAHD (metres above Australian Height Datum). Bathymetry source: Department of Water, WA Government. Aerial photo source: Department of Land Information, WA Government.

In Gordon Inlet, sites GO8 and GO9 were chosen to represent the main basin, and sites GO6 and GO7, the narrow, deeper channel (Figure 2-2; Table 2-1). The sediments of both the channel and basin comprise a layer of homogenous black mud over homogenous grey mud. Phototrophic microbacterial mats were observed on the sediment surface within the channel.

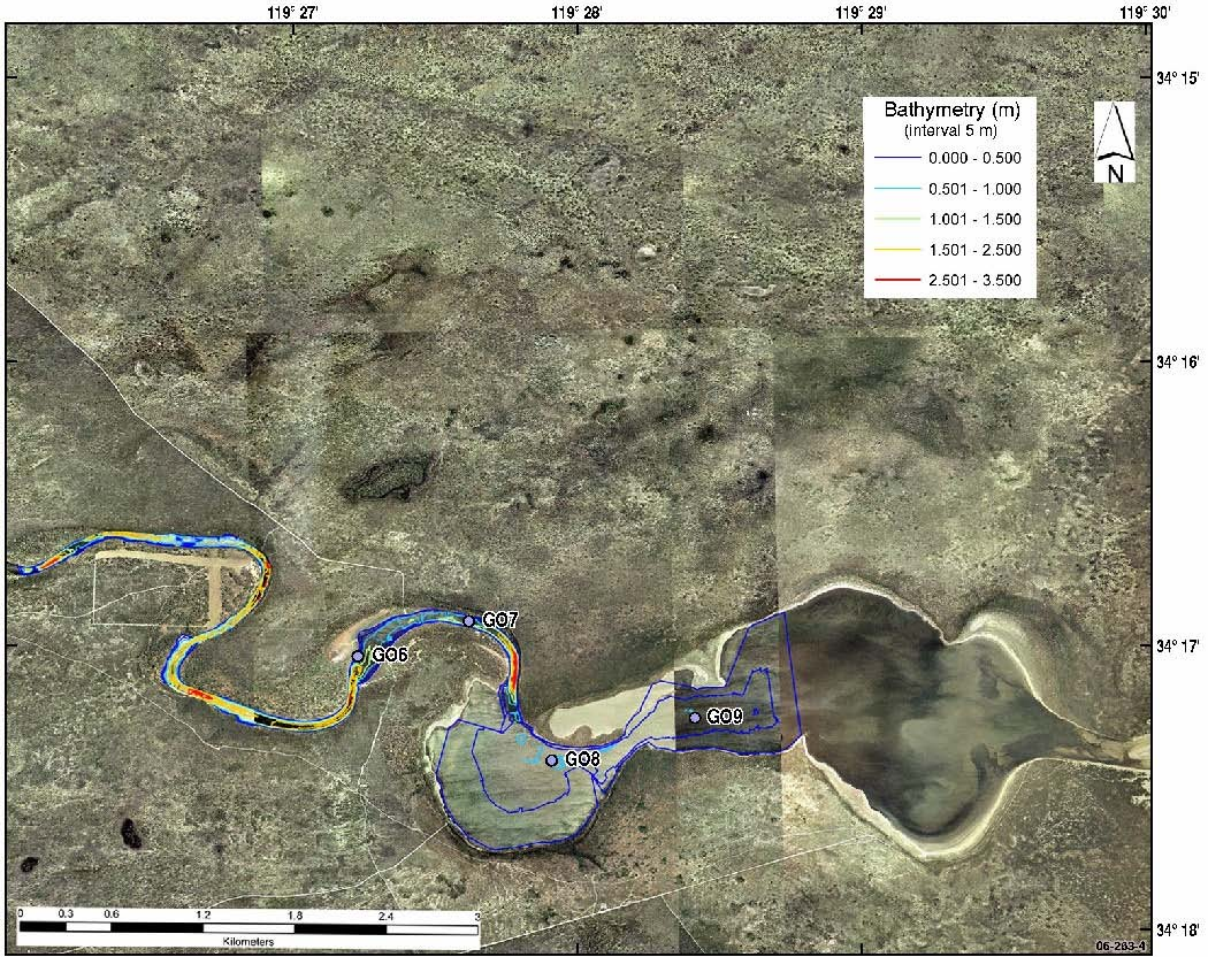


Figure 2-2. Gordon Inlet bathymetry and sampling site locations. Bathymetry is in mAHD (metres above Australian Height Datum). Bathymetry source: Department of Water, WA Government. Aerial photo source: Department of Land Information, WA Government.

In Beaufort Inlet, site BE8 was chosen to represent conditions in the central basin, sites BE9, BE6, and BE12, conditions in the channel, sites BE10 and BE11 conditions in some deep holes in the channel, and site BE7, the transition between the channel and basin (Figure 2-3; Table 2-1). Note that Figure 2-3 does not show BE12. This site is upstream of BE11 and just outside the western extent of the map. The sediments of both channel and basin comprise a surface layer of light brown sediment overlying black mud.

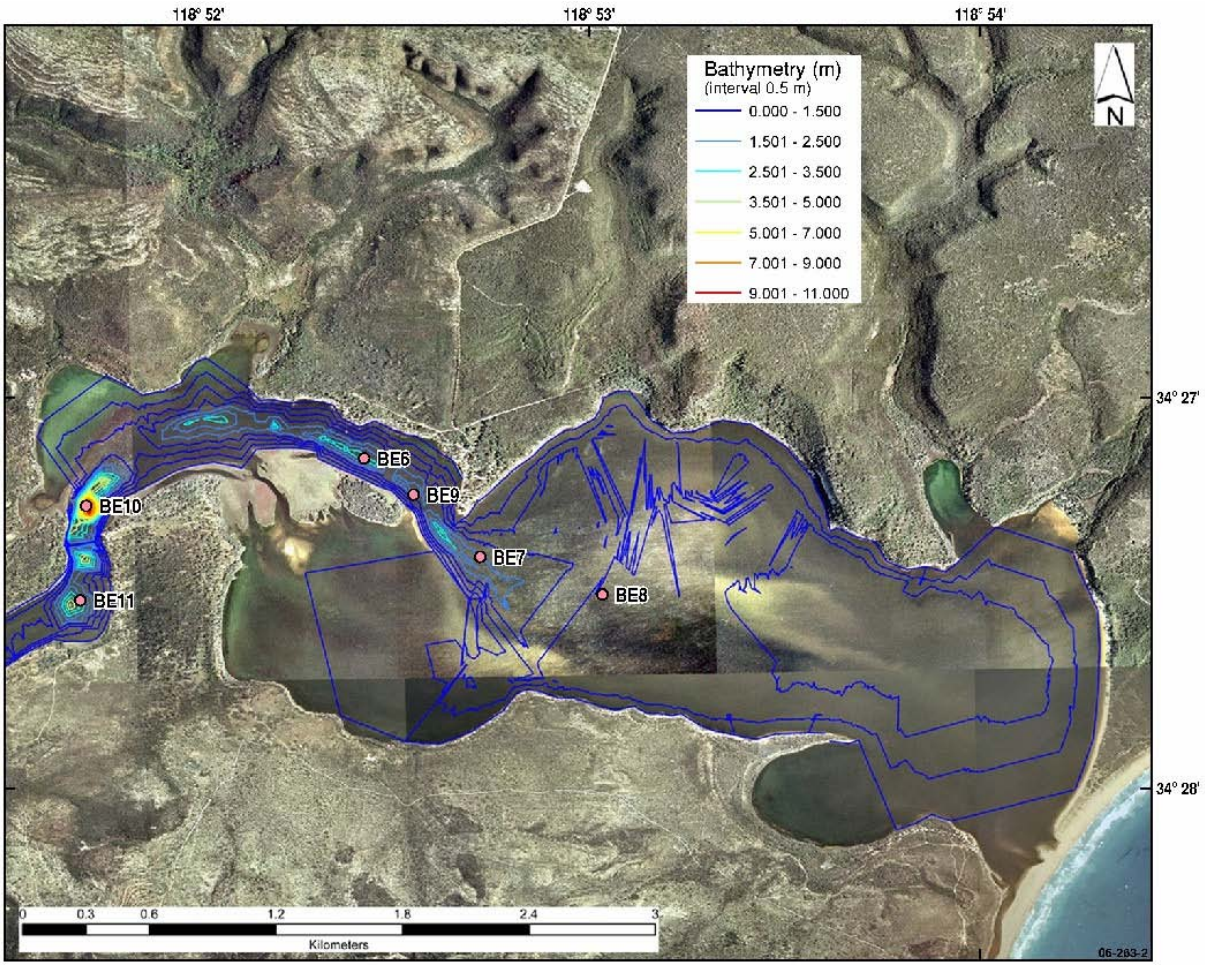


Figure 2-3. Beaufort Inlet bathymetry and sampling site locations. Bathymetry is in mAHD (metres above Australian Height Datum). Bathymetry source: Department of Water, WA Government. Aerial photo source: Department of Land Information, WA Government.

2B. SAMPLING METHODS

The following sections briefly describe the methods used for water column, benthic chamber, and sediment sampling. See Appendix 1 for more detail regarding benthic chamber operations, and Appendix 2 for detailed sediment core sampling procedures. Appendix 3 outlines the analytical methods for determining total carbon dioxide (TCO_2), ammonia (NH_4^+), nitrate + nitrite (NO_X), silicate (SiO_4^{4-}), phosphate (PO_4^{3-}), dissolved N_2, chlorophyll a (Chl-a), total suspended matter (TSM) concentrations, pigments, carbon and nitrogen stable isotopes, biomarkers, sediment solid phase phosphorus and aluminium concentrations. Appendix 4 gives the methods for calculating benthic fluxes and denitrification efficiencies.

2B1. Water Column

Water column was performed to determine the general water column conditions prevailing in each estuary at the time of the survey. This included surface water levels of nutrients and total suspended matter, light attenuation, and whether the water column was well mixed or stratified in relation to salinity, dissolved oxygen and/or temperature.

Surface water samples were taken from all sites for nutrient (NH_4^+, NO_X, SiO_4^{4-}, PO_4^{3-}), Chl-a, pigments, and TSM determination (Table 2-1; see Appendix 3 for analytical methods). Discrete surface water samples were collected in 1L plastic bottles. Samples for nutrient analysis were filtered using 0.45 μm filters and refrigerated until analysed, within 48 hours, at the NMI laboratories in Perth. Surface water samples for TSM and Chl-a were vacuum filtered using 0.45 μm filters and analysed within 24 hours. The filters used for Chl-a analysis were kept frozen until extraction in 20 mL of 90 % acetone. The extracted samples were shaken vigorously, placed in an ultrasonic bath, centrifuged and analysed by fluorometry.

Depth profiles of temperature, salinity and dissolved oxygen (DO) in the water column were measured at selected sites (Table 2-1) using a YSI 600XLM sonde. The average vertical light attenuation was also measured if sufficient sunlight was available at the time of sampling. Photosynthetically active radiation (PAR) was measured at several depth intervals throughout the water column using a quantum sensor LI-COR light meter (LI-250A) and the average vertical light attenuation coefficient (K_d) was calculated from the PAR profiles.

2B2. Benthic Chambers

Nutrient (NH_4^+, NO_X, SiO_4^{4-}, PO_4^{3-}), O_2, and TCO_2 fluxes were measured at the sediment-water interface using benthic chambers (Figure 2-4) according to the methods of Berelson *et al*. (1998). Fluxes were calculated from the change (either positive or negative) in metabolite concentrations over time inside each benthic chamber (see Appendix 4 for calculation). Two types of benthic chambers were deployed at each site, one type was blacked out to stop sunlight entering (*dark* chambers), and the other was transparent to sunlight (*light* chambers). The dark chambers recorded oxygen consumption and nutrient release from respiration processes, whereas light chambers recorded *net* oxygen flux (production minus consumption) and nutrient release from both respiration and photosynthesis.

Benthic chambers were deployed at all four sites in Wellstead Estuary, all four sites in Gordon Inlet, and three of the seven sites in Beaufort Inlet (Table 2-1). At each site, either two chambers (1 light and 1 dark) or three chambers (2 dark and 1 light) were deployed. The central basin site in Beaufort

Inlet was one exception (BE8), where five chambers were deployed (3 dark and 2 light). Chambers at each site were typically deployed less than 5 m apart.
Timing of sample draws from each chamber involved: an initial water sample representing ambient conditions (bottom water) taken immediately before lid closure; a sample draw taken 30 minutes after lid closure; then, a sample drawn every 0.5 to 1.5 hours, with the last sample taken up to 8 hours after lid closure. Appendix 1 describes chamber specifications in more detail, as well as sample draw, sample handling, and sub-sampling procedures. Sample draws from each chamber were analysed for NH_4^+, NO_X, nitrogen gas (N_2), pH, alkalinity, PO_4^{3-}, and SiO_4^{4-} using the procedures outlined in Appendix 3. TCO_2 concentrations were calculated using two methods; the Gran titration method using alkalinity and pH measurements, and, as a direct measurement of Dissolved Inorganic Carbon (DIC). These are described in Appendix 3. YSI data loggers recorded O_2 concentrations, salinity, and temperature both inside and outside each chamber. Appendix 4 explains how benthic fluxes and denitrification efficiencies were calculated from the raw benthic chamber data.

At one site in each estuary, the chambers were injected (spiked) with nitrogen isotopes (labelled $^{15}NO_3$ and $^{15}N_2$) for denitrification and nitrogen fixation experiments. The results of these experiments are not reported here, however, nitrogen isotope injections can affect benthic flux results. Therefore, this study considered the possibility of artefacts when interpreting the benthic flux results of injected chambers. At site WE7, chamber 4 (dark) was spiked with labelled $^{15}N_2$, and chambers 7 (dark) and 9 (light) were spiked with labelled $^{15}NO_3$. The same protocol was followed at site GO7. At site BE8, chamber 7 (dark) was spiked with labelled $^{15}N_2$, and chambers 4 (dark) and 9 (light) were spiked with labelled $^{15}NO_3$

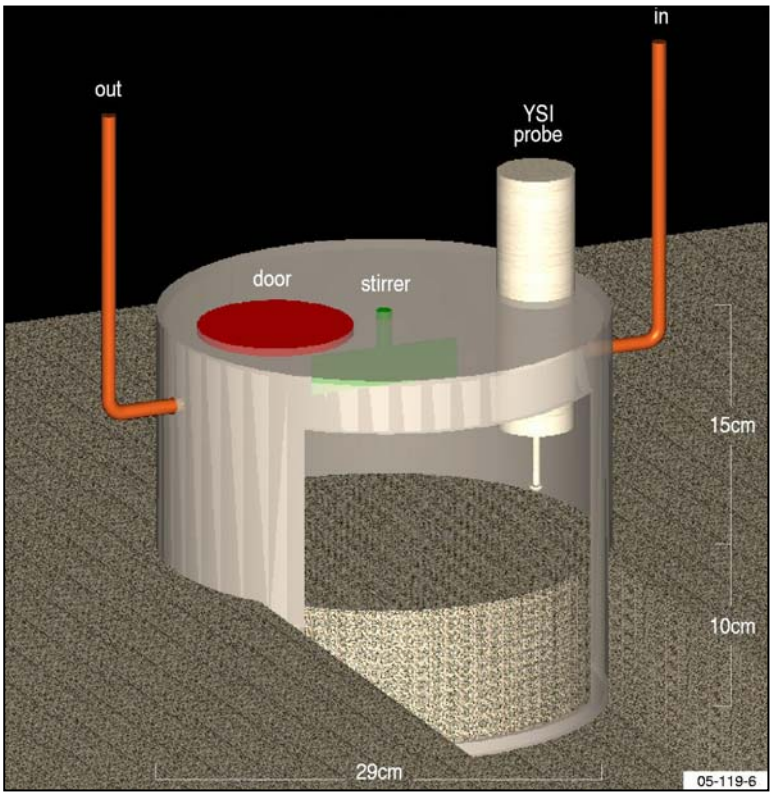


Figure 2-4. Schematic diagram of a benthic chamber experimental set-up.

2B3. Sediment Sampling

Sediment cores were collected at all sites except two channel sites in Beaufort Inlet (BE11 and BE12; Table 2-1). Two sediment cores were taken from each coring site; one for porewater and solid phase analysis and the other for porosity, chlorophyll-a, and carbon and nitrogen stable isotope analysis.

We collected these cores using a manually operated corer (Figure 2-5), which we pushed into the soft sediment using a long pole (pole corer; see Appendix 2 for more detail). The depth of sediment collected varied between 20 and 50 cm depending on how far the core barrel could be pushed into the sediment. Cores were sliced into 1 to 2 cm depth intervals and centrifuged to separate porewaters from the solid phase. Porewaters were analysed for PO_4^{3-}, NO_X^-, NH_4^+, SiO_4^{4-}, and TCO_2 using the methods outlined in Appendix 3. Note that TCO_2 was measured using a DIC analyser rather than the alkalinity titration method used for the lower concentration benthic chamber samples. We also measured the sediment porosity of each depth interval (see Appendix 2). Surface sediment samples were also collected at several sites for biomarker analysis (Table 2-1).

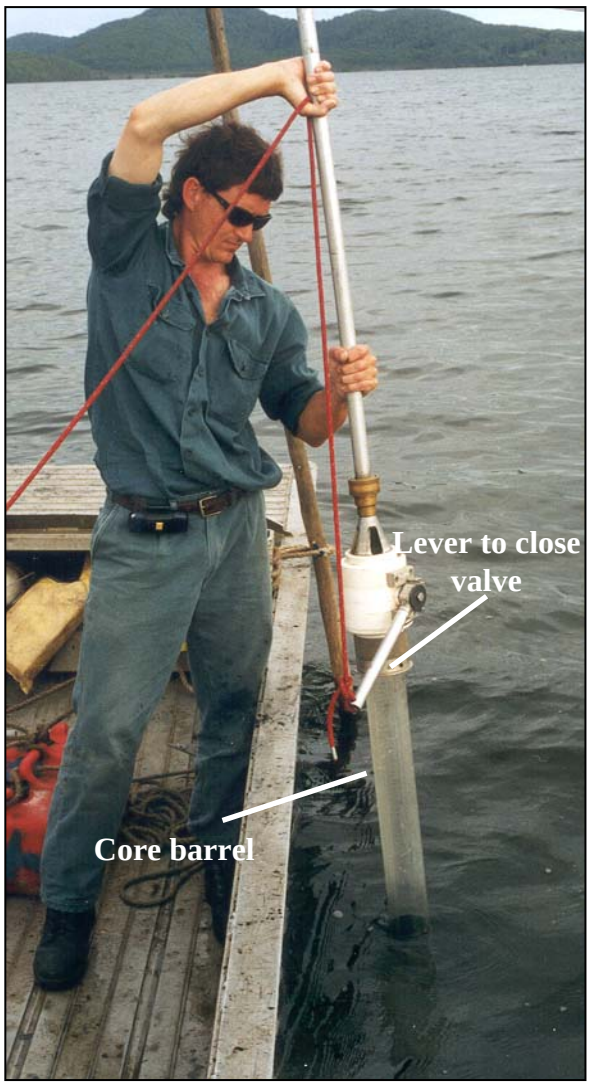


Figure 2-5. Collecting a sediment core using a pole corer.

3. Results

At the time of sampling (14th March to 4th April 2006), Wellstead Estuary and Gordon Inlet were open to the ocean, whereas Beaufort Inlet was closed to the ocean. Wellstead Estuary had been open since May 2005, and Gordon Inlet and Beaufort Inlet had opened following a heavy rainfall event in mid January 2006, however Beaufort Inlet quickly closed only a few weeks after this (Geoff Bastyan pers. comm. 28/06/2006).

The weather during the survey was generally dry and sunny. However, there were some overcast days, and the day sites GO8 and GO9 in the basin of Gordon Inlet were sampled, it was rainy with very strong winds. On most sampling days, a strong wind would develop by the afternoon.

Water column, benthic flux, sediment, and pore water properties measured at sites in the three estuaries are outlined below. See Table 2-1 in Chapter 2 for a summary of the specific type of sampling undertaken at each site, and Figure 2-1, Figure 2-2, and Figure 2-3, for maps showing the location of each sampling site.

3A. WATER COLUMN

The water columns of Wellstead Estuary, Gordon Inlet, and Beaufort Inlet were generally well-mixed during the time of the survey. That is, surface and deep water properties (temperature, dissolved oxygen, and salinity) did not differ significantly (Table 3-1). This is probably because of the shallowness of these estuaries, which are typically less than 1.5 m deep, leading to effective vertical mixing of the water column by wind driven waves. The only sites where surface and deeper water properties differed markedly were the two channel sites in Gordon Inlet (GO6 and GO7), which were sampled under calm, fine weather conditions, and are also relatively sheltered from the prevailing winds compared to the main basin, and the deep hole in the channel of Beaufort Inlet (BE10).

Despite all three estuaries being similar in respect of having a well-mixed water column, specific water column properties differed significantly between estuaries and also within each estuary (Table 3-1). The outline below describes the water column characteristics measured in each estuary during the survey. Note that temperature, dissolved oxygen, and salinity were measured at the surface and at depth by lowering a YSI sonde, whereas samples analysed for nutrient concentrations and other parameters were only taken from surface waters. The light attenuation coefficient (K_d), was only possible to derive for sites where cloud cover was minimal at the time of sampling.

Table 3-1. Water column properties and surface water nutrient concentrations. Sites are arranged in order from most upstream to most downstream. Temp.=temperature; DO=dissolved oxygen; Sal.=salinity; NH_4^+=ammonia; NO_X=oxidised nitrogen; PO_4^{3-}=phosphate; SiO_4^{4-}=silicate; Chl-a=chlorophyll a; TSM=total suspended matter; K_d=average vertical light attenuation coefficient; n.d.=no data; b.d.l.=below detection limit

Site ID	General Environ	Depth (m)	Temp. (°C)	DO (%)	Sal.	NH_4^+ (µM)	PO_4^{3-} (µM)	SiO_4^{4-} (µM)	NO_X (µM)	Chl-a (µg/l)	TSM (mg/l)	K_d (m^{-1})
WE9	Channel	Surface 0.9	23.0 22.5	90.2 79.4	30.3 30.4	2.50	8.57	385.52	b.d.l.	11.52	76.89	n.d.
WE8	Basin	Surface 0.7	22.7 22.7	72.8 69.7	35.6 35.5	12.85	0.26	124.62	b.d.l.	3.99	54.40	n.d.
WE7	Basin	Surface 0.8	20.0 20.0	80.8 79.3	36.4 36.3	11.42	0.29	78.33	b.d.l.	2.09	55.60	1.4
WE6	Basin	Surface 0.9	19.8 19.8	87.9 86.1	36.9 36.9	16.42	0.26	49.86	b.d.l.	2.51	39.43	1.0
GO6	Channel	Surface 1.0 1.7	23.6 23.1 23.0	98.5 84.0 69.0	31.1 31.5 34.9	b.d.l.	b.d.l.	103.25	9.28	5.61	46.22	n.d.
GO7	Channel	Surface 1.0 1.3	23.9 22.3 22.8	87.6 50.9 46.0	32.6 35.6 36.4	b.d.l.	b.d.l.	92.57	b.d.l.	3.36	46.00	n.d.
GO8	Basin	Surface	n.d.	n.d.	35.0	b.d.l.	b.d.l.	60.53	b.d.l.	2.34	76.00	n.d.
GO9	Basin	Surface	n.d.	n.d.	35.0	b.d.l.	b.d.l.	46.29	b.d.l.	4.97	134.17	n.d.
BE12	Channel	Surface	n.d.	n.d.	n.d.	1.99	0.16	24.57	b.d.l.	n.d.	16.50	n.d.
BE11	Channel Hole	Surface	n.d.	n.d.	n.d.	1.86	0.26	23.85	b.d.l.	n.d.	25.20	n.d.
BE10	Channel Hole	Surface 8.0	18.9 18.8	102.0 30.9	18.3 18.5	1.86	0.19	23.14	b.d.l.	n.d.	22.33	n.d.
BE6	Channel	Surface 1.2 2.5	17.5 17.5 17.3	100.2 100.4 96.0	18.8 18.7 18.5	1.36	0.45	25.28	b.d.l.	23.44	22.80	1.9
BE9	Channel	Surface 1.0	18.9 18.6	112.5 110.0	18.6 18.5	1.86	0.23	23.85	b.d.l.	25.44	16.83	1.7
BE7	Channel/ Basin Entrance	Surface 1.3	18.9 18.9	110.7 106.0	18.4 18.4	0.93	0.23	20.65	b.d.l.	18.84	50.40	1.6
BE8	Basin	Surface	n.d.	n.d.	n.d.	1.14	0.19	19.23	b.d.l.	22.69	18.00	n.d.

3A1. Wellstead Estuary

A distinct salinity gradient, where salinities increased with increasing distance downstream, was found between the channel site (WE9), and the lower estuary site (WE6; Table 3-1). Salinities in the main basin (sites WE6, WE7, and WE8) exceeded normal marine water, suggesting significant evaporation during the recent past. Interestingly, there were also NH_4^+ and SiO_4^{4-} gradients between the channel (WE9) and lower estuary (WE6), with NH_4^+ concentrations increasing, and SiO_4^{4-} concentrations decreasing with increasing distance downstream. In the main basin (sites WE6, WE7, and WE8), DIN : DIP ratios (= NH_4^+/PO_4^{3-}) were consistently high (40 – 63), whereas in the channel (WE9), DIN : DIP was very low (0.29), and SiO_4^{4-} and Chl-a concentrations were also much higher. Total suspended matter concentrations in both the channel and main basin varied between 40 and almost 80 mg/l, which under normal weather conditions is very high, indicating constant resuspension of fine sediments by wind-driven waves from the estuary bottom.

3A2. Gordon Inlet

The water column of Gordon Inlet was distinctive in that NH_4^+ and PO_4^{3-} concentration levels were below detection limit at all sites (Table 3-1). NO_X concentrations were also all below the detection limit, except for the channel site (GO6), which had high NO_X concentrations and was the only site in all three estuaries with NO_X concentrations above the detection limit. Similarly to Wellstead Estuary, SiO_4^{4-} concentrations decreased with increasing distance downstream. Also, there was an increasing salinity gradient between the channel (sites GO6 and GO7) and the lower estuary (sites GO8 and GO9) for surface waters. Salinity increased with depth at each of the channel sites. Despite the depletion of dissolved nutrients in the main basin, Chl-a concentrations in the range 2 to 6 µg/l were measured. Total suspended matter concentrations were high (46 mg/l) in the channel (sites GO6 and GO7), even though they were measured during calm weather. Elevated total suspended matter concentrations (76 - 134 mg/l) in the main basin (sites GO8 and GO9) were measured during stormy weather.

3A3. Beaufort Inlet

Water column properties in Beaufort Inlet were relatively homogeneous, with little difference in concentrations throughout the channel and basin (Table 3-1). Salinity was in the range 18.3 to 18.8, and NH_4^+, PO_4^{3-}, and SiO_4^{4-} concentrations were in the ranges 0.9 to 2.0, 0.16 to 0.45, and 19.2 to 25.3, respectively. Due to low NH_4^+ and relatively high PO_4^{3-} concentrations, DIN : DIP ratios were consistently low (3 to 8). Chl-a concentrations were very high (19 to 25 µg/l), reflecting abundant water column algae biomass and explaining the observed dissolved oxygen supersaturation (100 to 112 %) from O_2 produced during photosynthesis in surface waters. Total suspended matter concentrations ranged between 16 and 25 mg/l at all sites except BE7, which had a concentration more than twice that of the other sites (50 mg/l).

At site BE10, located in a deep hole in the channel, depth profiles of temperature, salinity, and oxygen were taken to detect changes with depth (Figure 3-1). Temperature was not changing with depth (data not shown), but salinity showed a slight gradual increase with depth down to 4 m and then remained constant to the bottom. Similar to other sites in Beaufort Inlet, the surface water was slightly supersaturated in oxygen. However, particularly below a depth of 3 m, oxygen decreased gradually to very low concentrations in the bottom water, indicating a high sediment oxygen demand and no or very little re-supply of oxygen through vertical mixing. The lack of vertical mixing has also likely led to the slight increase in salinity, where high density water, formed by evaporation in shallow areas, has migrated to the nearest depression.

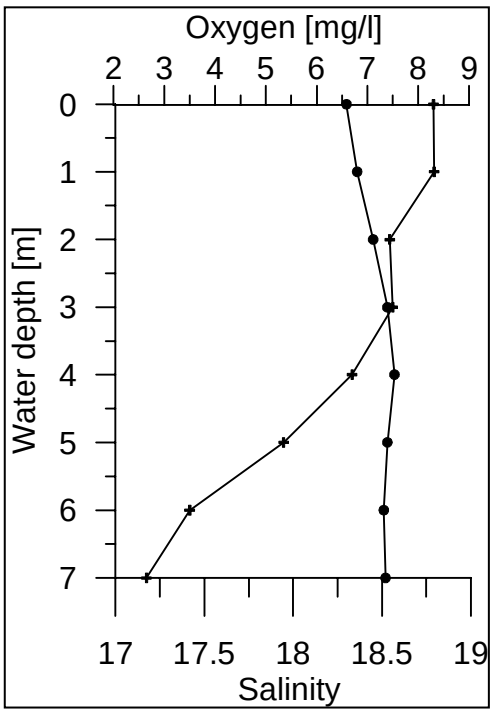


Figure 3-1. Changes in dissolved oxygen (crosses) and salinity (dots) levels with depth in the water column at site BE10 in a deep hole in the channel of Beaufort Inlet.

3A4. Differences between Estuaries

Salinities in Wellstead Estuary and Gordon Inlet were close to typical marine water (between 30 and 37), whereas Beaufort Inlet was brackish, with salinities between 17 and 19. Also, surface water salinities of Wellstead Estuary and Gordon Inlet increased with increasing distance downstream, along with increasing NH_4^+, and decreasing SiO_4^{4-} concentrations. These properties are a reflection of entrance status at the time of the survey, where Wellstead Estuary and Gordon Inlet were open to the ocean and their waters increasingly influenced by tidal exchange, with increasing proximity to the ocean. Salinities in Gordon Inlet also increased with depth at each site, indicating the presence of a tidally driven salt wedge. During the sampling period, Beaufort Inlet was closed, and the water column influenced by freshwater inflows and subsequent vertical and horizontal mixing. Beaufort Inlet had been closed to the ocean entrance for over a month prior to the survey and the water column throughout Beaufort Inlet had become relatively homogeneous.

Chl-a concentrations in Wellstead Estaury and Gordon Inlet were typically below 5 µg/l, while Beaufort Inlet had Chl-a concentrations of 19 µg/l and higher. The high Chl-a concentrations in Beaufort Inlet are also reflected in oxygen concentrations above saturation levels (100 – 112% saturation). Dissolved nutrient concentrations also differed markedly. NH_4^+ concentrations were low in Beaufort Inlet (0.9 – 1.9 µmol/l), and relatively high in Wellstead Estuary (typically 11.4 – 16.4 µmol/l). Whereas the nutrient concentrations were below detection limit (NH_4^+: 0.7 µmol/l, NO_x: 0.07 µmol/l, PO_4^{3-}: 0.15 µmol/l) in Gordon Inlet, with the exception of one NO_x sample. The highest total suspended matter concentrations were measured in samples taken from Gordon Inlet (sites GO8 and GO9), which were taken during a very windy and rainy day.

3B. BENTHIC FLUXES

The magnitude and range of benthic fluxes for different solutes varied greatly both within and between the Wellstead Estuary, Gordon Inlet, and Beaufort Inlet (Table 3-2). These flux rates are given in mmol m^{-2} day^{-1} in both table (Table 3-2) and graph (Figure 3-2 to Figure 3-8) formats and are described on a solute-by-solute basis. The y-axis scale on the graphs for each different solute is kept the same to allow for comparisons between estuaries, for example, the y-axis for TCO_2 is always between 200 and -200 mmol m^{-2} day^{-1} (Figure 3-3).

For a general discussion of the meaning and context of benthic fluxes and their influence on estuarine water quality, see Chapter 1 *The importance of sediment-water interactions.* Also, see Appendix 4 for benthic flux calculation methods, and Appendix 5 for the solute versus time plots used to calculate benthic flux rates. Section 2B2 *Benthic Chambers* explains the difference between *light* and *dark* chambers.

Table 3-2. Benthic flux rates for all sites in mmol m^{-2} day^{-1}. Sites are arranged in order from most upstream to most downstream. Positive values represent a flux out of the sediment (release), whereas negative values represent a flux into the sediment (uptake). (*) benthic chamber spiked with $^{15}NO_3$,. (^) benthic chamber spiked with $^{15}N_2$.

Site ID	General Environ	Chamber #	Chamber Type	O_2	TCO_2	NH_4^+	NO_X	N_2	PO_4^{3-}	SiO_4^{4-}
WE9	Channel	3	Dark	-221.2	80.7	7.5	0.0	0.5	0.06	3.4
		6	Light	-22.6	22.1	14.3	0.0	-2.7	0.17	14.1
WE8	Basin	4	Dark	-108.8	69.2	3.6	0.0	2.6	0.00	4.0
		7	Dark	-51.6	103.5	5.5	0.0	0.9	0.00	17.0
		9	Light	-11.1	29.3	5.9	0.0	0.2	0.00	9.8
WE7	Basin	4	Dark	-106.8	151.2	11.3	0.0	12.0^	0.03	6.3
		7	Dark	-84.0	95.4	9.7	-4.1*	-2.1	0.00	5.4
		9	Light	47.3	14.5	6.6	-3.0*	-1.0	0.00	6.2
WE6	Basin	3	Dark	-133.1	69.1	2.9	0.0	0.2	0.00	9.2
		6	Light	41.5	-65.7	3.2	0.0	-6.4	0.03	13.3
GO6	Channel	3	Dark	-16.7	3.2	-0.2	0.0	-3.5	0.00	0.8
		6	Light	44.5	-56.8	0.0	0.0	-1.6	0.00	10.0
GO7	Channel	4	Dark	-67.0	64.7	0.0	0.0	8.2^	0.00	15.9
		7	Dark	-56.2	54.2	3.3	-1.4*	2.2	0.00	13.0
		9	Light	44.2	-109.7	0.0	-2.7*	-9.3	0.00	7.3
GO8	Basin	4	Dark	-77.0	108.5	7.6	0.0	3.4	0.00	8.4
		7	Dark	-70.4	93.7	4.1	0.0	2.9	0.00	8.5
		9	Light	-62.1	117.4	0.1	0.0	-1.0	0.00	10.3
GO9	Basin	3	Dark	-64.0	86.5	1.3	0.0	0.6	0.02	10.3
		6	Light	-86.6	88.5	0.6	0.0	1.6	0.02	8.0
BE9	Channel	3	Dark	-48.4	19.9	0.0	0.3	4.3	0.15	2.6
		6	Light	-12.3	-64.0	0.0	0.0	2.6	0.15	2.7
BE7	Channel/ Basin Entrance	4	Dark	-53.8	56.5	0.0	1.2	8.9	0.45	4.9
		7	Dark	-37.8	66.8	0.0	1.8	7.3	0.33	5.0
		9	Light	-43.2	117.5	0.2	2.4	11.0	0.54	11.4
BE8	Basin	3	Dark	-36.4	52.7	-0.8	0.0	0.7	0.06	3.0
		6	Light	89.6	-185.7	4.2	0.3	-31.8	0.19	1.7
		4	Dark	-47.7	49.2	1.5	-1.7*	2.9	0.13	4.2
		7	Dark	-108.3	94.6	0.0	0.0	4.0^	-0.02	0.2
		9	Light	16.7	-42.7	0.4	-2.8*	-6.9	0.12	4.9

3B1. Oxygen

Oxygen (O_2) uptake at the sediment surface, representing respiration, was generally higher in Wellstead Estuary than in Gordon Inlet and Beaufort Inlet, with the highest rate measured in a dark chamber deployed in the channel (WE9-3; Table 3-2; Figure 3-2). A high O_2 uptake rate, comparable to those in Wellstead Estuary, was also measured in a dark chamber deployed in the basin of Beaufort Inlet (BE8-7).

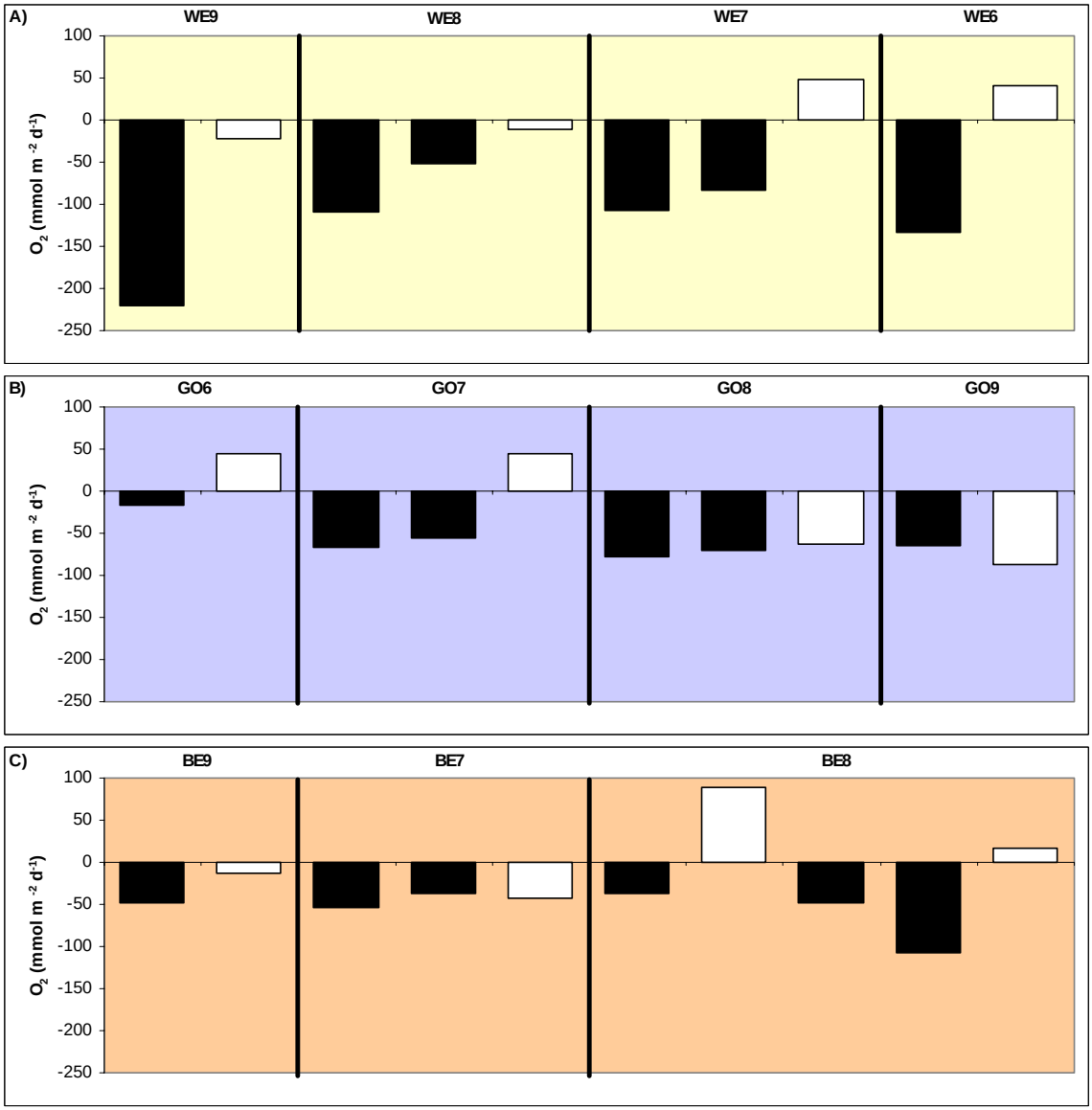


Figure 3-2. O_2 fluxes in Wellstead Estuary (A), Gordon Inlet (B), and Beaufort Inlet (C) in mmol m^{-2} day^{-1}. Black bars represent benthic flux rates derived from dark chamber incubations and white bars represent benthic flux rates from light chamber incubations. The bars are arranged, left to right, from the most upstream site to the most downstream site.

O_2 flux rates in light chambers, which allow both photosynthesis (O_2 release) and respiration to occur, were highest in the basin of Beaufort Inlet (BE8), followed by the basin of Wellstead Estuary (WE7 and WE6), and the channel of Gordon Inlet (GO6 and GO7; Figure 3-2). These were the only sites with positive O_2 fluxes, therefore the only sites that were photosynthesis dominated at the time of sampling. All other sites, that is, the channel in Wellstead Estuary (WE9), basin in Gordon Inlet (GO8 and GO9), and sites BE9 and BE7 in Beaufort Inlet were respiration dominated. Note that the weather was overcast and stormy during sampling of sites GO8 and GO9 in the basin of Gordon Inlet and may have limited photosynthesis.

3B2. Carbon Dioxide

In dark chambers, carbon dioxide (TCO_2) release at the sediment surface, representing respiration, was generally moderate to high at all sites in Wellstead Estuary, moderate in the basin of Gordon Inlet (GO8 and GO9), and low to moderate at sites BE7 and BE8 in Beaufort Inlet (Table 3-2; Figure 3-3). TCO_2 release from the sediment (respiration) in dark chambers was generally lowest in the channel of Gordon Inlet (GO6 and GO7) and site BE9 in the channel of Beaufort Inlet. The magnitude of TCO_2 release in dark chambers is an indicator of the amount of labile organic matter degrading in the sediment. TCO_2 flux rates in dark chambers do not differ significantly between the three estuaries or between sites within each estuary, except for perhaps the two channel sites GO6 and BE9, which have the lowest TCO_2 release rates compared to all other sites. .

TCO_2 uptake in light chambers, indicating photosynthesis was dominant over respiration, was recorded in the basin of Wellstead Estuary (WE6), the channel of Gordon Inlet (GO6 and GO7) and the basin (BE8) and channel (BE7) of Beaufort Inlet.

In summary, based on both O_2 release and TCO_2 uptake rates in light chambers, photosynthesis dominated in the channel of Gordon Inlet, and sites BE9 and BE8 in Beaufort Inlet, whereas respiration generally dominated throughout Wellstead Estuary, in the basin of Gordon Inlet, and site BE7 in Beaufort Inlet. O_2 release in light chambers at sites WE7 and WE6 and TCO_2 uptake in the light chamber at WE6 indicates photosynthesis can dominate at particular times and locations in the basin of Wellstead Estuary.

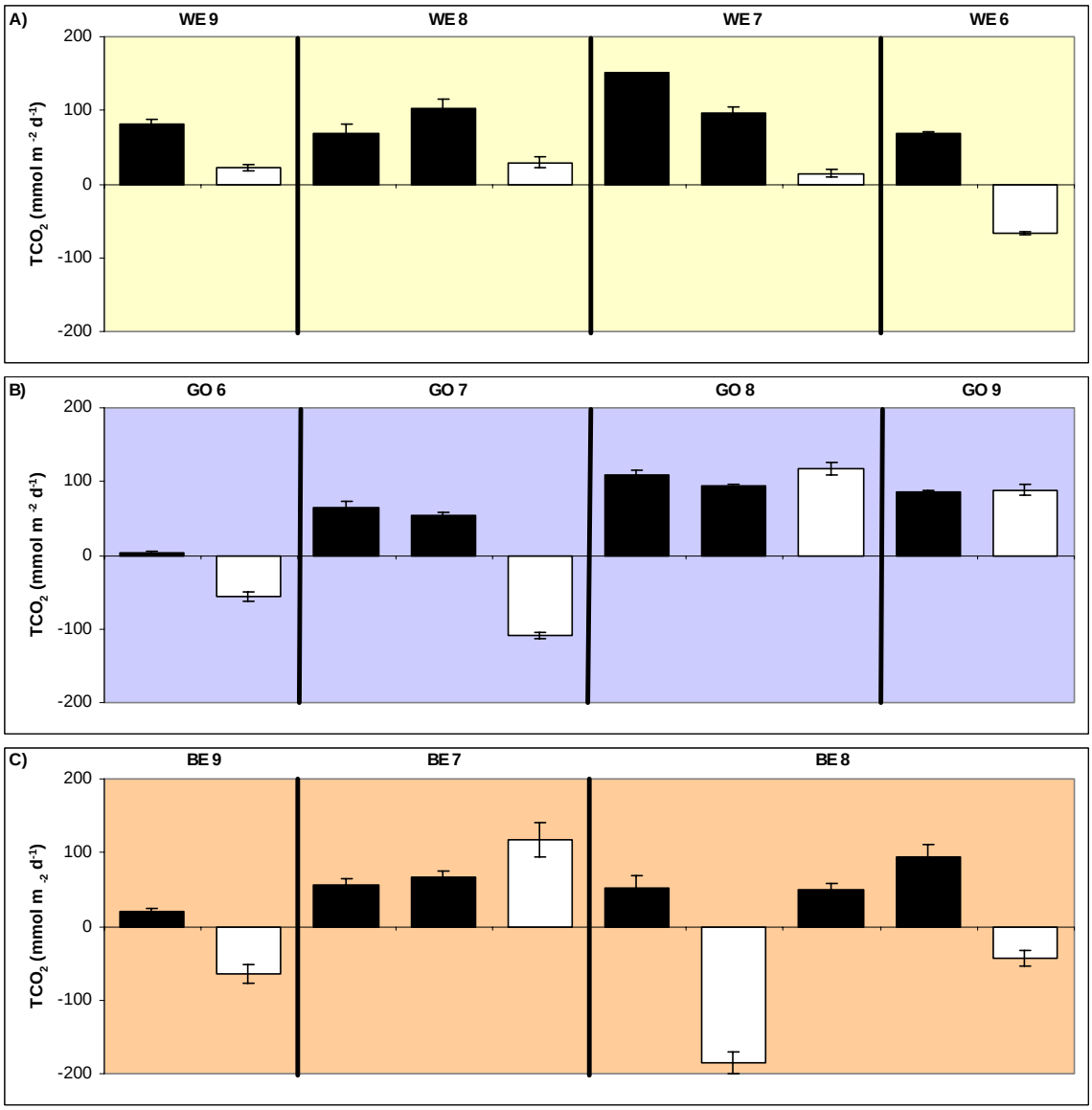


Figure 3-3. TCO_2 fluxes in Wellstead Estuary (A), Gordon Inlet (B), and Beaufort Inlet (C) in mmol m^{-2} day^{-1}. Black bars represent benthic flux rates derived from dark chamber incubations and white bars represent benthic flux rates from light chamber incubations. The bars are arranged, left to right, from the most upstream site to the most downstream site.

3B3. Ammonia

Release of ammonia (NH_4^+) from the sediment was generally high at all sites in Wellstead Estuary and much lower in Gordon Inlet and Beaufort Inlet (Table 3-2; Figure 3-4). The channel site in Wellstead Estuary (WE9) had the highest NH_4^+ fluxes, followed by WE7 in the basin. NH_4^+ release was close to zero for all sites in Gordon Inlet and Beaufort Inlet except for GO8 in the basin of Gordon Inlet and one chamber (BE8-6) in the basin of Beaufort Inlet.

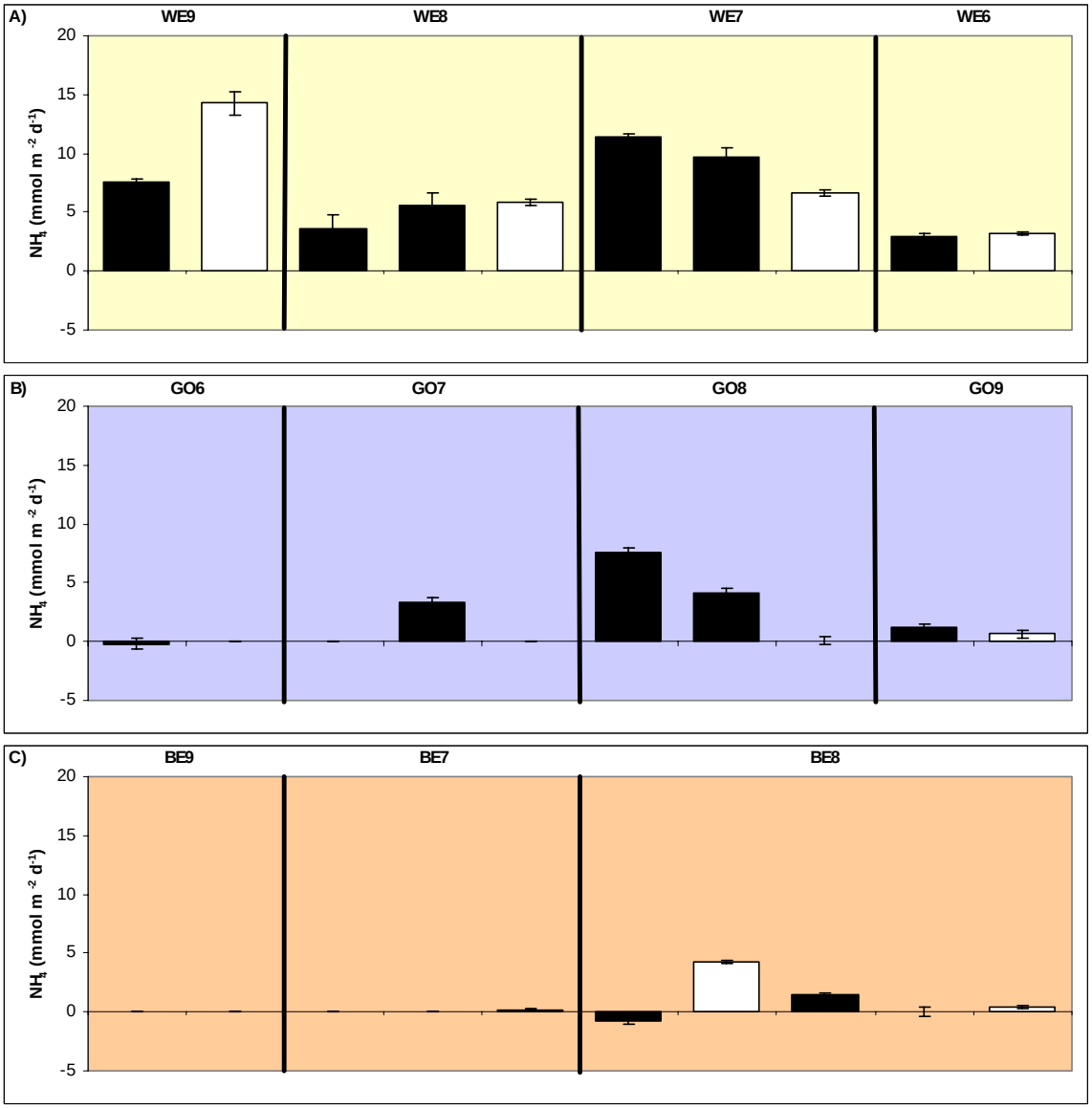


Figure 3-4. NH_4^+ fluxes in Wellstead Estuary (A), Gordon Inlet (B), and Beaufort Inlet (C) in mmol m^{-2} day^{-1}. Black bars represent benthic flux rates derived from dark chamber incubations and white bars represent benthic flux rates from light chamber incubations. The bars are arranged, left to right, from the most upstream site to the most downstream site.

3B4. Oxidised Nitrogen

Oxidised nitrogen (NO_X) fluxes were close to zero at all sites in all three estuaries, disregarding chambers injected with labelled $^{15}NO_3$ (Table 3-2; Figure 3-5). The uptake of NO_X recorded in these chambers probably represents diffusion of the NO_X spike into the sediment. BE7 at the channel/basin entrance of Beaufort Inlet was the only site with significant NO_X fluxes with release rates of between 1.2 and 2.4 mmol m^{-2} day^{-1}. Note that the labelled $^{15}NO_3$ injections were part of a supplementary investigation, the results of which are not reported here.

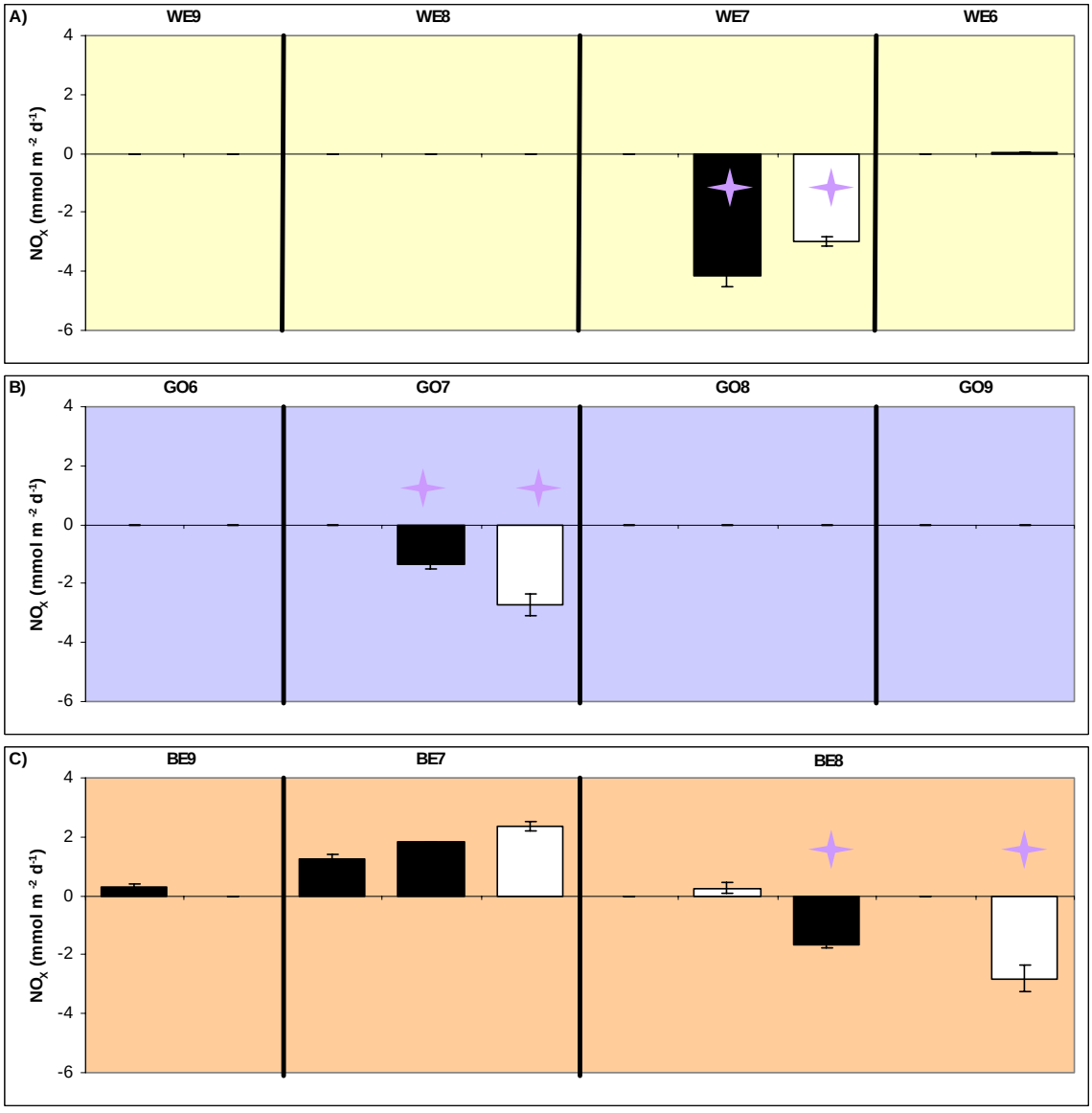


Figure 3-5. NO_X fluxes in Wellstead Estuary (A), Gordon Inlet (B), and Beaufort Inlet (C) in mmol m^{-2} day^{-1}. Black bars represent benthic flux rates derived from dark chamber incubations and white bars represent benthic flux rates from light chamber incubations. The bars are arranged, left to right, from the most upstream site to the most downstream site. Chambers spiked with labelled $^{15}NO_3$ are marked with a star.

3B5. Nitrogen Gas

Nitrogen gas (N_2) fluxes in light chambers were either close to zero or strongly negative at all sites in all three estuaries except for BE7 in Beaufort Inlet, which had high rates of N_2 release in both light and dark chambers (Table 3-2; Figure 3-6). Site BE8 in the basin of Beaufort Inlet had the highest rates of N_2 uptake, followed by GO7 in the channel of Gordon Inlet, and WE6 in the basin of Wellstead Estuary.

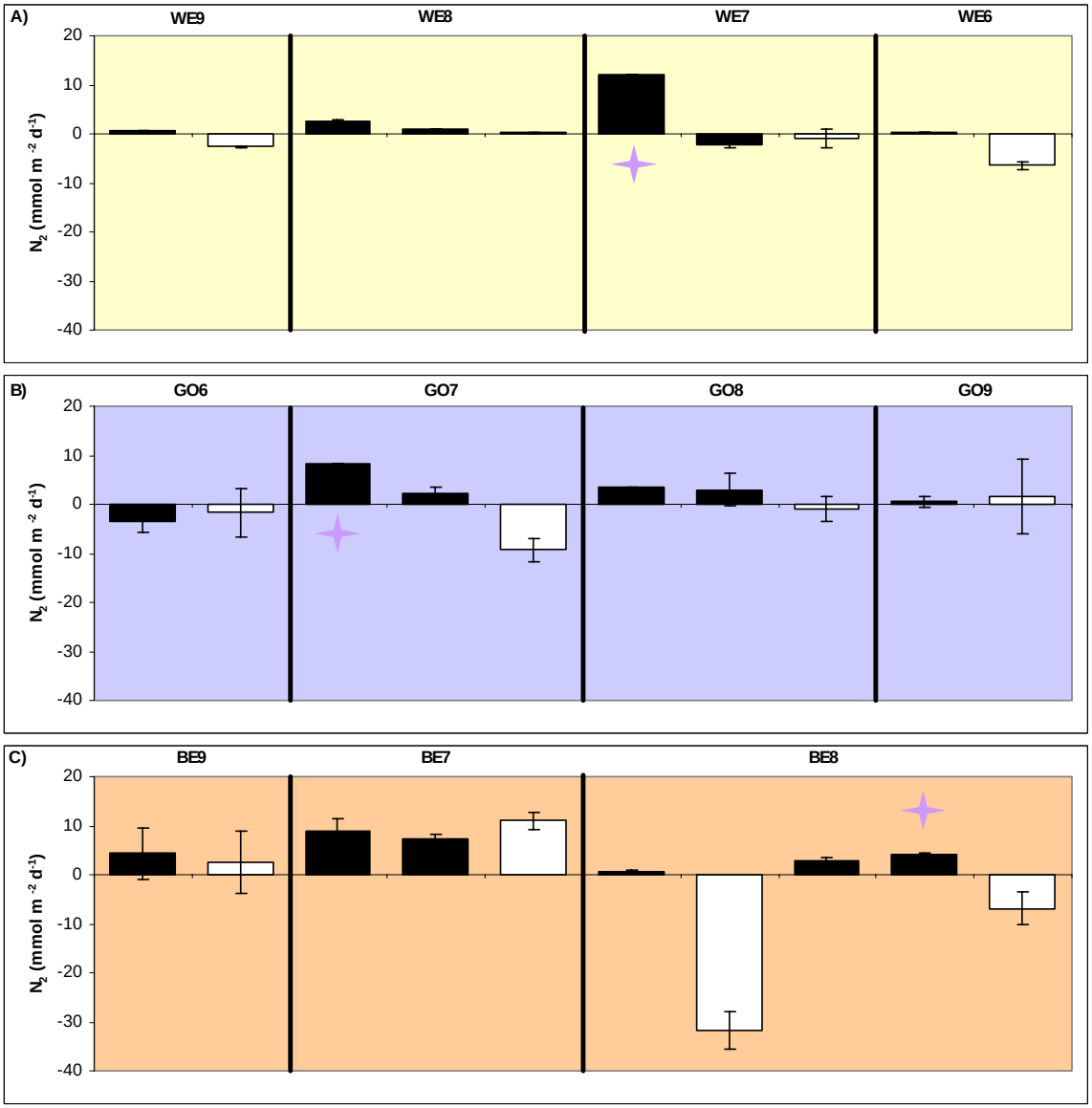


Figure 3-6. N_2 fluxes in Wellstead Estuary (A), Gordon Inlet (B), and Beaufort Inlet (C) in mmol m^{-2} day^{-1}. Black bars represent benthic flux rates derived from dark chamber incubations and white bars represent benthic flux rates from light chamber incubations. The bars are arranged, left to right, from the most upstream site to the most downstream site. Chambers spiked with labelled $^{15}N_2$ are marked with a star.

N_2 fluxes in dark chambers were either close to zero or strongly positive at all sites in all three estuaries. BE7 had the highest average rates of N_2 release of any site, followed by WE7 in the basin of Wellstead Estuary, and GO7 in Gordon Inlet. BE9, GO8, and WE8 also had moderate average N_2 release rates. Note that some chambers were injected with labelled $^{15}N_2$ as part of a supplementary investigation, the results of which are not reported here. These injections do not appear to have affected N_2 fluxes.

3B6. Phosphate

The rate of phosphate (PO_4^{3-}) release from the sediments at all three sites in Beaufort Inlet were very high, especially site BE7, where rates were between 0.3 and 0.5 mmol m^{-2} day^{-1} (Table 3-2; Figure 3-7). This was in contrast to Wellstead Estuary and Gordon Inlet, where all sites recorded zero PO_4^{3-} flux except site WE9 in the channel of Wellstead Estuary with PO_4^{3-} release rates of between 0.1 and 0.2 mmol m^{-2} day^{-1}.

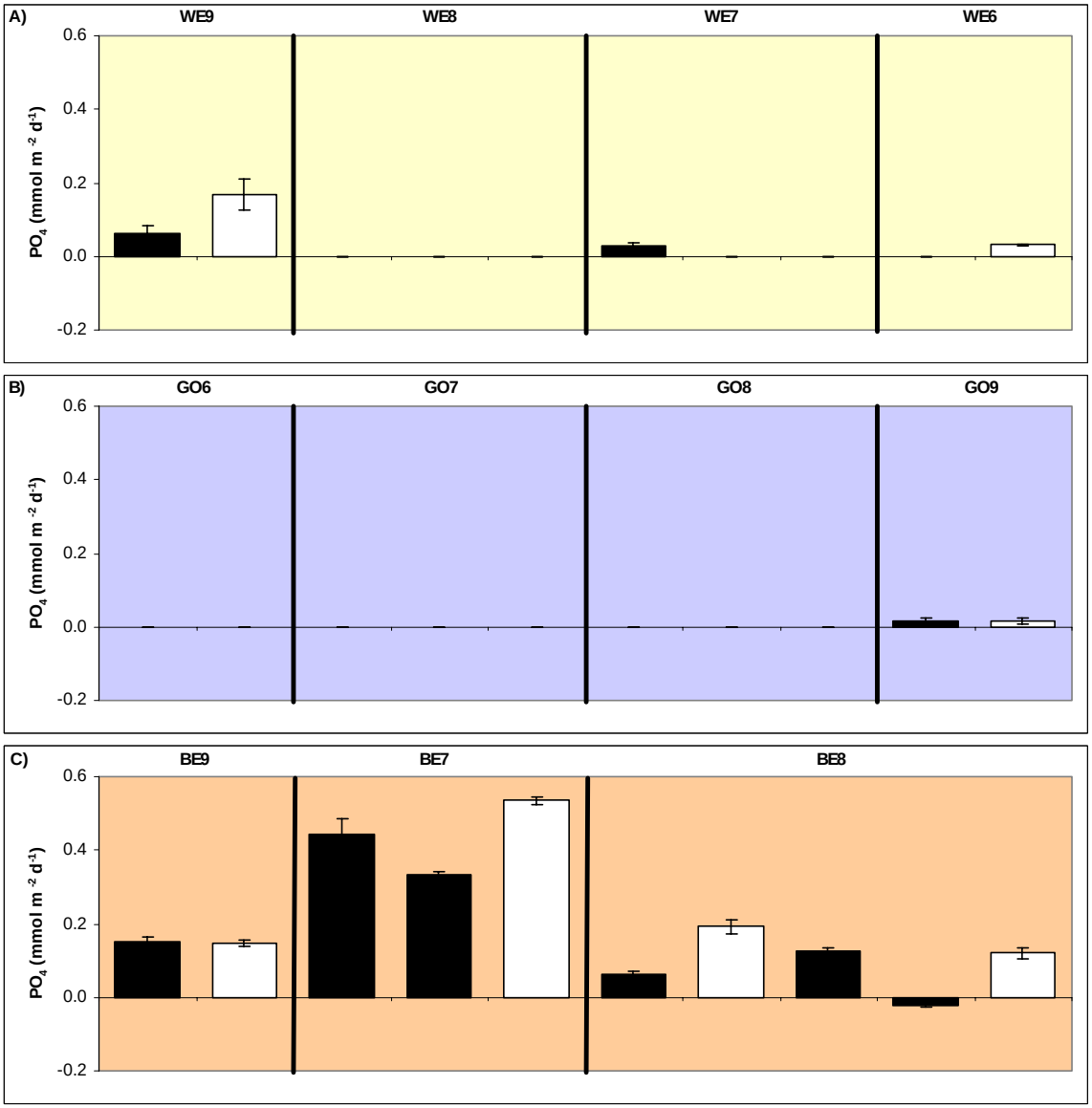


Figure 3-7. PO_4^{3-} fluxes in Wellstead Estuary (A), Gordon Inlet (B), and Beaufort Inlet (C) in mmol m^{-2} day^{-1}. Black bars represent benthic flux rates derived from dark chamber incubations and white bars represent benthic flux rates from light chamber incubations. The bars are arranged, left to right, from the most upstream site to the most downstream site.

3B7. Silicate

All sites in all three estuaries recorded a release of silicate (SiO_4^{4-}) from the sediment (Table 3-1; Figure 3-8). However, the magnitude of SiO_4^{4-} fluxes was extremely variable, with rates often varying significantly between chambers at the same site. As a general summary, SiO_4^{4-} release rates were larger in Wellstead Estuary and Gordon Inlet than in Beaufort Inlet.

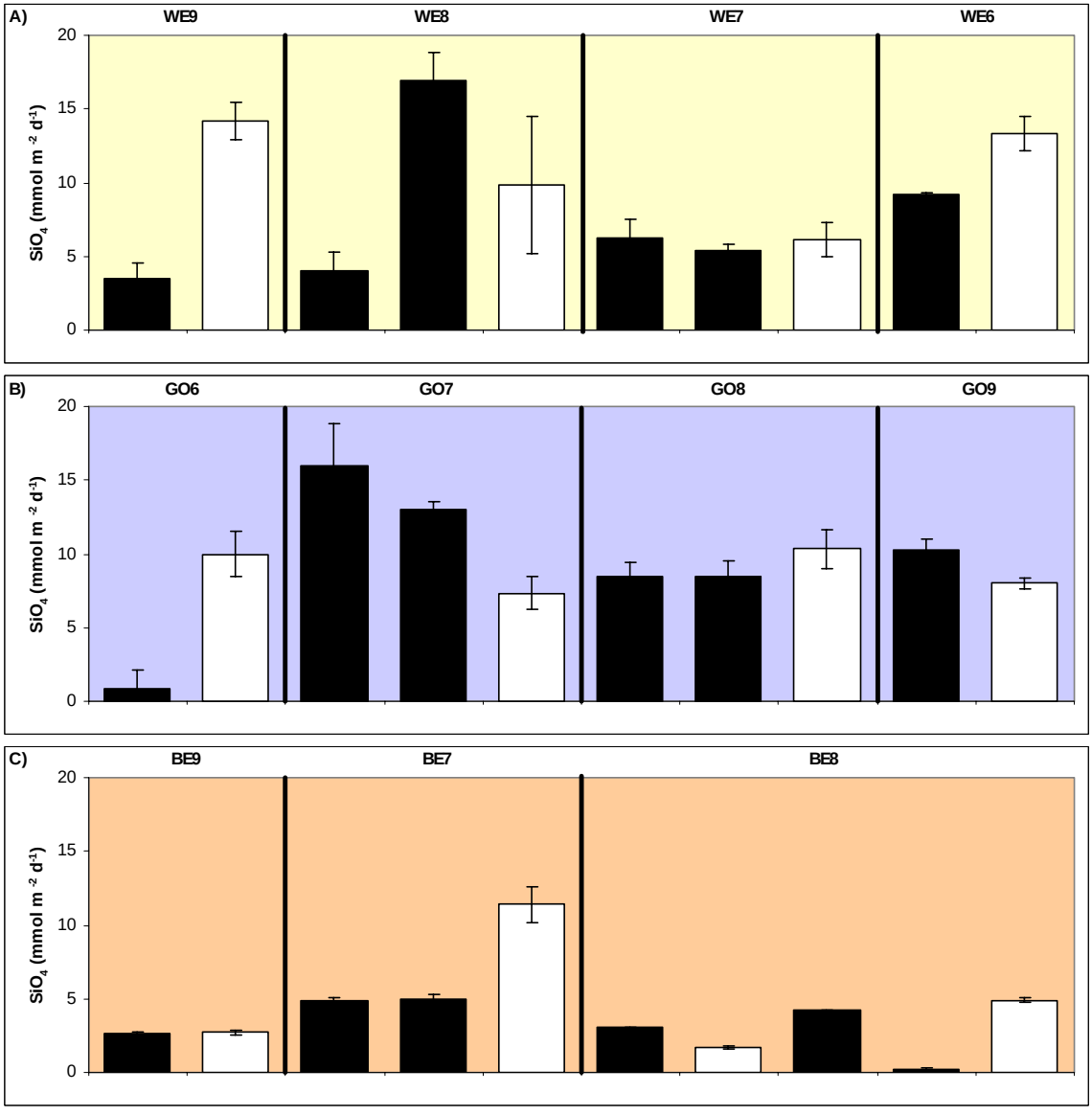


Figure 3-8. SiO_4^{4-} fluxes from Wellstead Estuary (A), Gordon Inlet (B), and Beaufort Inlet C) in mmol m^{-2} day^{-1}. Black bars represent benthic flux rates derived from dark chamber incubations and white bars represent benthic flux rates from light chamber incubations. The bars are arranged, left to right, from the most upstream site to the most downstream site.

3C. POREWATER AND SEDIMENT COMPOSITION

Vertical profiles of porewater solutes are presented in Appendix 6. These profiles reflect the depth and intensity of organic matter breakdown (mineralization) in sediments. During the process of mineralization, carbon, nitrogen, and phosphorus are released from particulate organic matter as TCO_2, NH_4^+, and PO_4^{3-} respectively. SiO_4^{4-} also builds up in porewaters due to the dissolution of siliceous diatom frustules. Nitrate (NO_3^-) and nitrite (NO_2^-), collectively termed NO_X, may form in porewaters by secondary processes, particularly nitrification ($NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O$).

Concentration gradients with depth indicate the transport of solutes by molecular diffusion from the depth of highest concentration to the depth of lowest concentration. A discrete maximum in TCO_2 or nutrient concentration observed as a peak in the depth profile indicates the depth of maximum production of these solutes. Constant concentrations with depth indicate that the observed solute is neither produced nor consumed. The degree of build-up of a given porewater solute can be expressed as the porewater pool size (see section *4B. Nutrient and Chl-a Pool Sizes*). Molecular diffusion and bioirrigation are two modes of solute exchange between the porewaters and water column. The solute flux by bioirrigation (the activity of fauna living in the sediment) typically exceeds the molecular diffusion flux several fold. Note that benthic flux measurements measure the *total* net solute flux across the sediment-water interface. In contrast to nutrient gradients in porewater profiles, salinity gradients reflect mixing between two water bodies with different composition.

Sediment depth profiles of Chlorophyll-a (Chl-a) are used to reveal the presence of microbenthic algae (MBA). When light penetrates to the sediment surface, MBA can photosynthesise, and the resulting enrichment in Chl-a can be compared to Chl-a in the water column.

When sediments have the capacity to retain phosphorous, a distinct enrichment in mineral-bound total phosphorous (TP) can be measured. In order to eliminate variations in TP due to changes in the original composition of sediments, TP is normalised to the aluminium concentration.

3C1. Wellstead Estuary

The sediments of Wellstead Estuary are generally very muddy with porosities of 90% or higher. Salinity steadily increases with depth starting with a salinity of 35 in the bottom water and reaching ~ 40 at about 20 cm depth. Nutrient porewater concentrations changed little with depth in the top 5 cm of sediment in the main basin (sites WE6, WE7, and WE8), whereas concentration gradients below this depth were consistently very steep. This pattern is likely related to intense bioirrigation in surface sediments, which inhibits the build-up of high solute concentrations. At sites WE6 and WE7, the steep concentration gradients extend into sediments deeper than ~ 15 cm, indicating the process of organic matter breakdown is continuous in these deeper sediments. At sites WE8 and WE9, maximum concentrations are reached asymptotically below 15 cm, indicating that the most reactive sediment is found in this upper layer.

The basin sites (WE6, WE7, and WE8) are characterized by a strong enrichment in Chl-a at the sediment surface, indicating the importance of photosynthesis by MBA. Observations of MBA were also made in the field, where cores from some sites had a thick layer of MBA on their surface (Figure 3-9). At the channel site (WE9), however, there was no Chl-a enrichment in the surface layer. Notably, depth profiles of solid phase TP, normalised according to aluminium concentration, show a similar pattern to Chl-a profiles. The basin sites (WE6, WE7, and WE8) show a distinct

enrichment in surface sediments, whereas the channel site (WE9) does not. Interestingly, the largest TP enrichment is found along with the largest Chl-a enrichment, namely at site WE6.

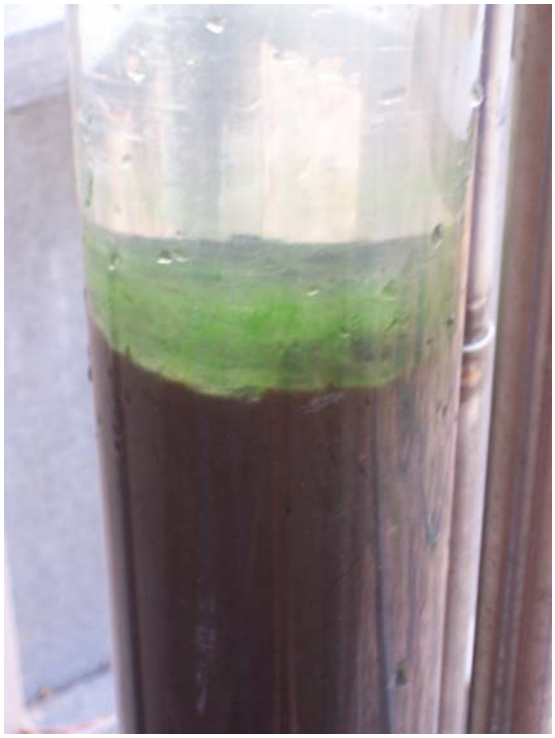


Figure 3-9. Photograph of sediment core from site WE6 in the basin of Wellstead Estuary showing abundant microbenthic algae at the sediment surface.

3C2. Gordon Inlet

Porewater profiles from Gordon Inlet reveal particularly steep concentration gradients in the top 5 cm of sediment, and show little change below this depth. Maximum concentrations in the upper 35 cm are not particularly high, e.g. PO_4^{3-} concentrations typically do not exceed 50 µM, indicating rather moderate rates of organic matter decomposition. Similar to Wellstead Estuary, the Chl-a depth profiles are characterized by an enrichment at the sediment surface, indicating growth of MBA. However, the surface layer of the main basin is not as enriched in Chl-a as in Wellstead Estuary. TP/Al ratios are higher in all surface sediments compared to deeper sediments (background values), suggesting some capacity to bind mobilized P. However, the steep porewater PO_4^{3-} gradients in surface sediments indicate that the P trapping capacity is smaller than in the main basin of Wellstead Estuary. Likewise to Wellstead Estuary however, salinity increases steadily with depth, giving evidence for the presence of a hypersaline fluid in deeper sediments.

3C3. Beaufort Inlet

Porewater profiles from sites BE7 and BE8 in the basin of Beaufort Inlet, are very similar. They show linear increases in NH_4^+ and PO_4^{3-} concentration with depth, and both sites reach similar maximum concentrations, i.e.. ~1800 µM NH_4^+ at 35 cm. The channel site (BE6) is different. Porewater profiles of all solutes at this site show distinct changes in concentration gradients between 5 and 10 cm, which is likely related to a very recent sediment deposition event. This event is

evidenced by the abrupt change in sediment colour at about 5 cm depth (Figure 3-10), reflecting the presence of ironoxyhydroxides (brown) in the upper part, and ironsulfides (black) in the lower part. The patchy mixing of these two sediment types is a result of bioturbation, which has also led to the formation of little mounds at the sediment surface. Salinity at Site BE6 increased with depth in the sediment, reaching a maximum salinity of 90 between 20 and 35 cm. Neither Chl-a nor sediment-bound P is enriched at the sediment surface at sites BE6, BE7, and BE8. BE9 is the only site with a distinct enrichment of both these variables.

Figure 3-10. Photograph of a core from site BE6 in the channel of Beaufort Inlet showing a distinct change in colour at ~5 cm depth. The brown coloured sediment is likely deposited very recently. Bioturbation is gradually mixing this layer with the underlying sediment.

3D. ORGANIC GEOCHEMISTRY

3D1. Bulk Organic Matter

The nitrogen (N) versus carbon (C) stable isotopic results from Wellstead Estuary and Gordon Inlet are similar, and plot together as a cluster (Figure 3-11), whereas the Beaufort Inlet results differed significantly from those of Wellstead Estuary and Gordon Inlet, and plot as a separate, distinct cluster. $\delta^{13}C$ values from Beaufort Inlet ranged between -25 and -26.5 and were relatively 'lighter' than those of Wellstead Estuary and Gordon Inlet, which ranged between -18 and -21. This clustering possibly reflects the different types of plants growing in the estuaries, where benthic primary productivity (MBA and macrophytes) predominates in Wellstead Estuary and Gordon Inlet, and water column primary productivity (phytoplankton) predominates in Beaufort Inlet. However, there are numerous parameters that can influence N and C stable isotopic compositions (Cloern *et al.* 2002), and it is difficult to determine what exactly has led to these particular compositions.

There were no significant differences between surface sediments and samples taken in the water column, which suggests that organic matter in surface sediments is primarily derived from estuarine primary production. If significant terrestrial organic matter were present in surface sediments of Wellstead Estuary and Gordon Inlet, lower $\delta^{13}C$ values would be expected.

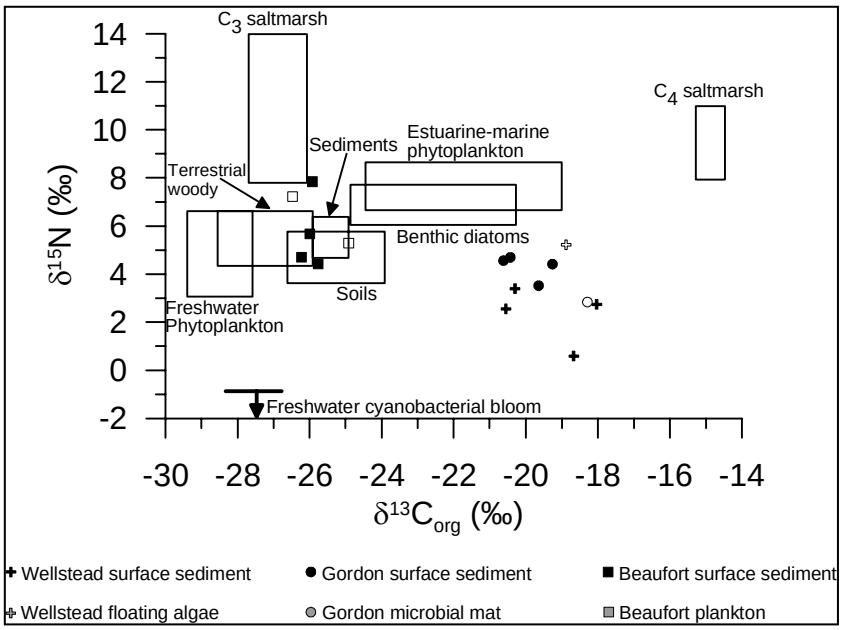


Figure 3-11. Stable isotopic compositions of carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) of the bulk organic matter from surface sediments (solid symbols) and fresh plant material (open symbols) from each estuary. The plot shows these results relative to areas representing typical isotopic compositions of organic matter from different sources (from Cloern et al. 2002).

3D2. Compound Specific Studies

Wellstead Estuary

Lipid composition in floating algae

The biomarkers distribution in floating macroalgae collected in the basin of Wellstead Estuary is dominated by phytol, a degradation product mainly derived from chlorophylls a and b, and sterols (Appendix 7: Figure A; Table A). These algae present quite a diverse distribution of sterols. Cholesterol, brassicasterol, 24-methylenecholesterol, stigmasterol, sitosterol and 28-isofucosterol are the main sterols detected. Brassicasterol is commonly considered as a proxy for diatom abundances (Calvo *et al*. 2004; Schubert et al. 1998) but can also arise from other microalgae such as haptophytes or cryptophytes (Volkman et al. 1998). It is likely that the floating algae collected in Wellstead Estuary is associated with epiphytic diatoms. In addition, a series of linear n-alkan-1-ols showing an even-over-odd carbon predominance in the range C22-C26 indicates inputs from terrigenous plants (Eglinton and Hamilton 1967).

Lipid composition in surface sediments

The surface sediment at site WE6 exhibits a biomarker distribution quite similar to the one displayed by the floating algae collected at Wellstead Estuary, as evidenced by the sterols and in particular, the presence of C_{29} Δ5,24(28)Z in high proportion (Appendix 7: Figure B; Table A). In addition to the contribution of these algae to the sedimentary organic matter, the presence of dinosterol and brassicasterol in relatively large quantities attest to dinoflagellates and diatoms inputs. Dehydrocholesterol is also reasonably abundant and can be attributed to diatoms or rhodophytes.

The biomarker content of surface sediments at the other three sites in Wellstead Estuary were also analysed, however they did not show the distribution displayed by the filamentous algae.

Gordon Inlet

Lipid composition in microbial mats

The organic extract of the microbial mat collected at Gordon Inlet is largely dominated by *n*-heptadecene and sitosterol (Appendix 7: Figure C; Table A). Other less prominent compounds are *n*-heptadecane, phytadienes, fatty acids C16:1 and C16:0 and a variety of sterols, mainly dehydrocholesterol, cholesterol, brassicasterol, stigmasterol and isofucosterol. An unknown sterol eluting before sitosterol corresponding to a C_{29} dienol is also detected.

The relative high abundance of *n*-heptadecene and the occurrence of *n*-heptadecane can probably be attributed to cyanophytes, as they have been shown to be the predominant hydrocarbons in cyanobacteria (Gelpi *et al*. 1970) and cyanobacterial mats (Boudou *et al*. 1986; Grimalt *et al*. 1992). Hopanoids or methylbranched alkanes, which are common constituents of cyanobacteria (Summons *et al*. 1999; Gelpi *et al*. 1970; Koster *et al*. 1999), were not detected. The absence of hopanoids is most likely related to the methodology used here, as bacteriohopanepolyols are not GC-amenable due to their high polarity and their analysis requires cleavage of vicinal diols with periodic acid to produce GC-amenable primary alcohols (Rohmer *et al*. 1984).

The variety of the sterols distribution likely reflects the diverse eukaryotic community in these mats. The possibility that some of these sterols and in particular the predominant sitosterol derived from cyanobacteria cannot be ruled out but is controversial (Volkman 2005), as sterols present in cyanobacterial cultures were suggested to come from contaminating organisms such as yeasts or fungi (Summons *et al*. 2001). However, sitosterol has been shown to be present in high proportions

in some cyanobacteria, although concentrations per cell are low (Volkman 1986) and was found to be a major constituent of cyanobacterial mats (Boon *et al*. 1983). On the other hand, this sterol is commonly associated with higher plants (Volkman 1986) and can also be produced by microalgae such as diatoms or raphidophytes (Volkman *et al*. 1998). Higher plants commonly give rise to linear alkan-1-ols presenting an even-over-odd carbon predominance in the range C_{22}-C_{30} (Eglinton and Hamilton 1967), which are present here only in very minor amounts, and therefore might not be the main contributors to sitosterol.

Lipid composition in surface sediments

The biomarker distribution at site GO8, in the main basin of Gordon Inlet, is dominated by sterols (Appendix 7: Figure D; Table A), presenting a very similar pattern to the one seen in the microbial mat collected in the channel. Indeed, the sedimentary sterols are present in the same proportions as in the microbial mat and are characterized by the predominance of sitosterol and presence of the distinctive unknown C_{29} sterol corresponding to a dienol. The same pattern is apparent in the surface sediment at site GO9, also located in the main basin, with a lesser relative abundance of sitosterol. In addition to the contribution of microbial mats to these sediments, some higher plants and dinoflagellates inputs are detected through the occurrence of even carbon C_{22}-C_{28} alkan-1-ols and dinosterol respectively. C_{27} and C_{29} 5β-stanols deriving from human and herbivores faeces are also observed in abundances that are relatively larger than what is observed for Beaufort Inlet.

At sites GO6 and GO7 in the channel, the contribution from microbial mats is not as obvious as at sites GO8 and GO9 (Appendix 7: Figure E; Table A). Although sitosterol is present, it does not dominate the sterol distribution as at sites GO8 and GO9. Main sterols include cholesterol, cholestanol, brassicasterol, stigmasterol, sitosterol and dinosterol. Dinosterol and 4α,24-dimethylcholestan-3β-ol point to dinoflagellates inputs (Volkman 2003).

Beaufort Inlet

Surface waters

Phytoplankton identification and the composition of pigments was determined for surface waters at four sites in Beaufort Inlet (BE6, BE10, BE11, BE12), all located within the channel. The lipid composition of surface waters at sites BE6 and BE10 was also determined.

Microscopic identification of phytoplanktonic communities

The euglenophyte Eutreptiella is dominant both numerically and by biovolume followed by mixed small Cryptophyte flagellates (Plagioselmis, Leucocryptos, Teleaulax) (Figure 3-12).

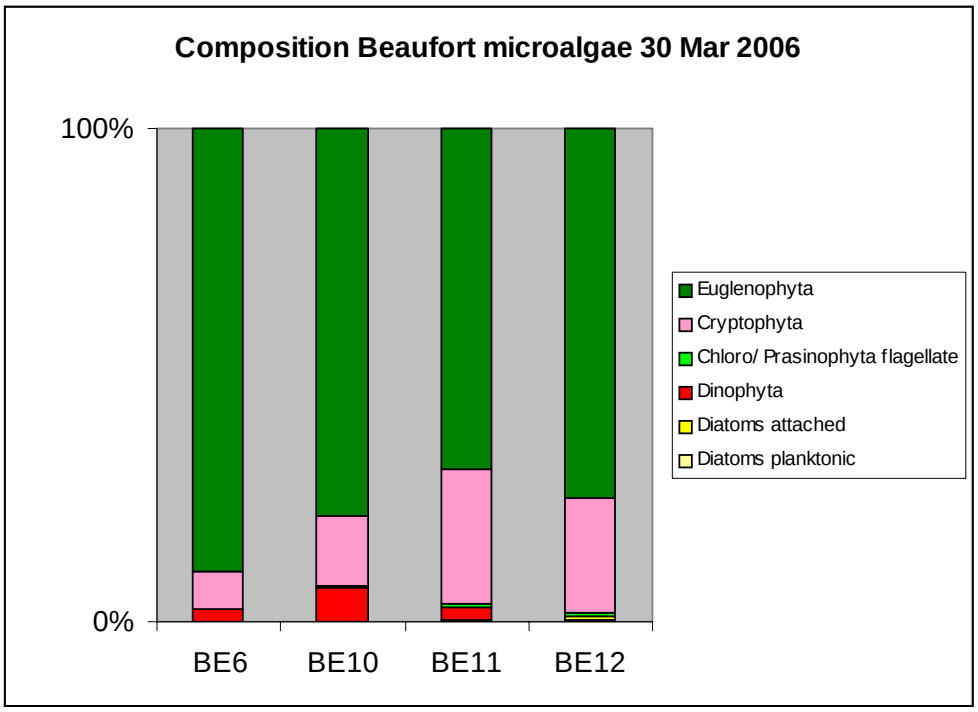


Figure 3-12. Relative composition of microalgae in surface waters of Beaufort Inlet.

Pigments

Twelve pigments were identified from the water column: chlorophyll *a* and its epimer, chlorophyll *b* and its epimer, chlorophyll c_2, peridinin, neoxanthin, diadinoxanthin, fucoxanthin, alloxanthin, diatoxanthin and β,β-carotene. Additionally, a pigment eluting before chlorophyll *b* and showing absorption maxima at 457 and 487 nm has been tentatively identified as eutreptiellanone.

Maximum absolute concentrations for all pigments with the exception of fucoxanthin are observed at site BE10 (Figure 3-13). Concentrations are fairly similar for the three other sites. Overall, the concentrations are particularly high suggesting the surface water samples were collected during or towards the end of a bloom.

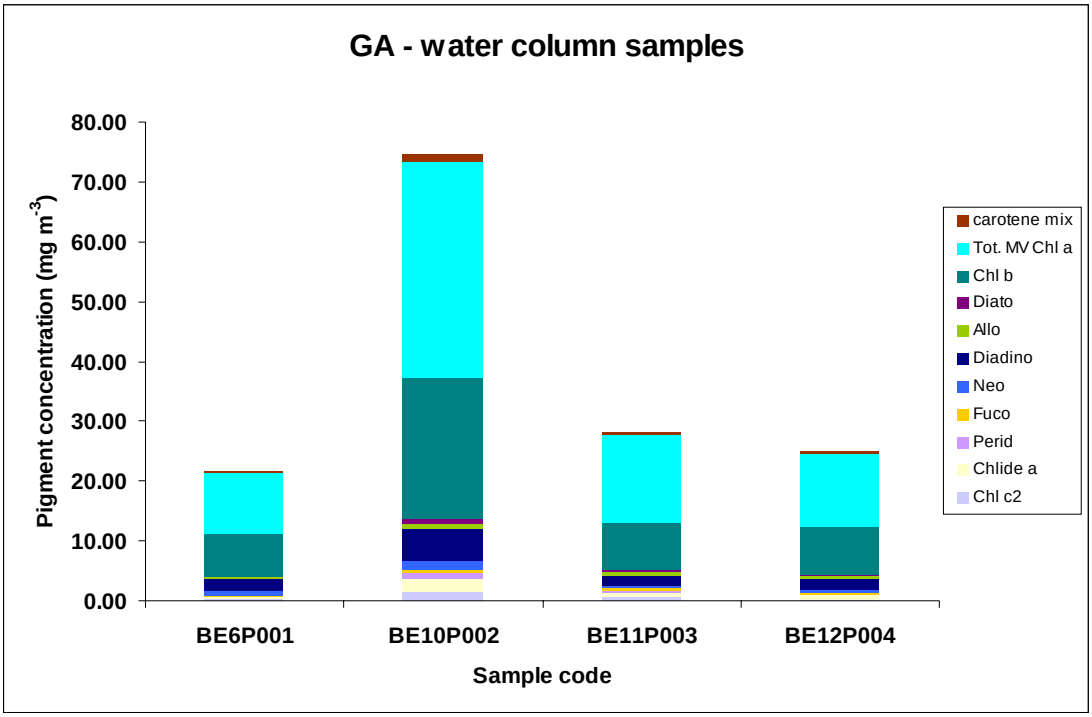


Figure 3-13. Absolute concentrations of pigments in mg/m^3 present in the water column of Beaufort Inlet at sites BE6, BE10, BE11, and BE12. For abbreviations refer to Table 3-3

Table 3-3. Abbreviations used for pigments in Figure 3-13 toFigure 3-17.

Allo	Alloxanthin
Astax	Astaxanthin
But-Fuco	19'-butanoyloxyfucoxanthin
Canthax	Canthaxanthin
Chl b	Chlorophyll b
Chl c2	Chlorophyll c2
Chlide a	Chlorophyllide a
Diadino	Diadinoxanthin
Diato	Diatoxanthin
Fuco	Fucoxanthin
Lut	Lutein
MgDVP	Magnesium 3,8-divinylphaeoporphyrin a5 monomethyl ester
Mix	Mixture
Neo	Neoxanthin
Perid	Peridinin
Phide a	Phaeophorbide-a
Phytin	Phaeophytin
Pras	Prasinoxanthin
Pyro-Phide a	Pyrophaeophorbide-a
Pyrophytin	Pyrophaeophytin
Tot. MV Chl a	Total monovinyl chlorophyll a
Zea	Zeaxanthin

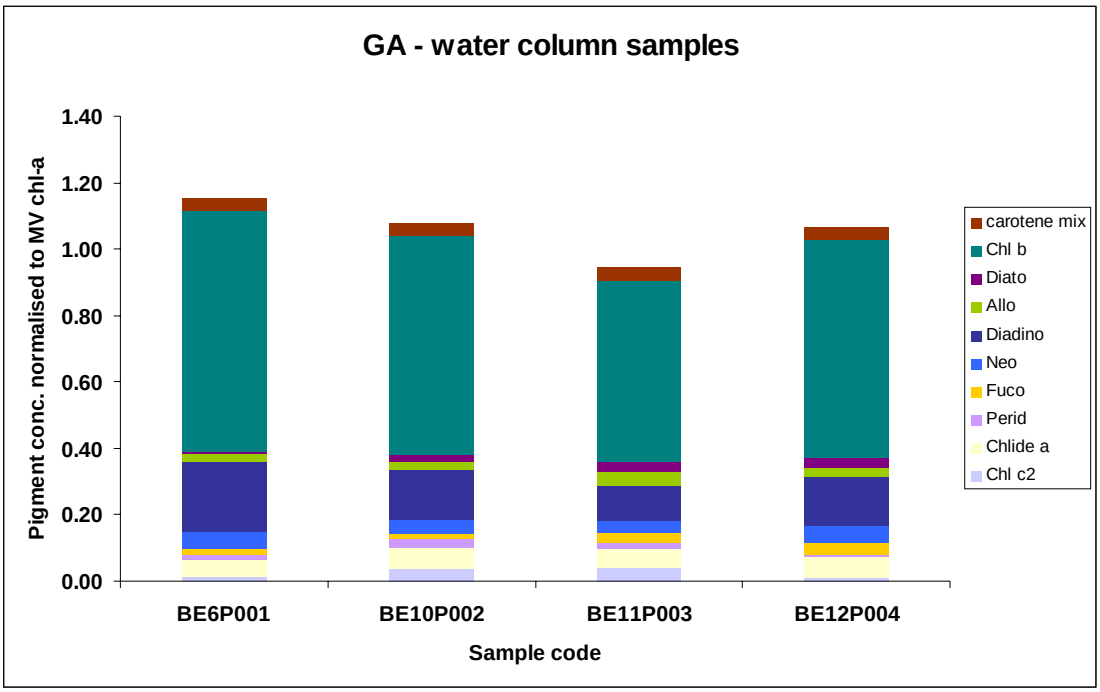


Figure 3-14. Pigment concentrations normalised to Monovinyl Chorophyll a (MV Chl-a) in the water column of Beaufort Inlet at sites BE6, BE10, BE11, and BE12. For abbreviations refer to Table 3-3

The pigment composition illustrated in Figure 3-14 and in particular, the high levels of chlorophyll *b* and diadinoxanthin, together with the occurrence of neoxanthin and β,β-carotene, point to a strong dominance of euglenophytes in the water column of Beaufort Inlet. This is also suggested by the detection of the pigment eutreptiellanone, which has been isolated from the euglenophyte Eutreptiella (Fiksdahl *et al*. 1984).

The low abundances of peridinin, fucoxanthin and alloxanthin suggest small amounts of dinoflagellates, diatoms and crytophytes respectively, which all contribute to the observed chlorophyll c_2. The water column samples are so dominated by euglenophyte pigments that it is reasonable to assert that euglenophytes probably make up around 90% of the population, as shown also by microscope analysis. The pigment composition did not indicate presence of cyanophytes in the surface waters.

Lipids

Phytoplankton extracts present identical biomarker distributions at sites BE6 (Appendix 7: Figure E; Table A) and BE10 largely dominated by polyunsaturated fatty acids (PUFAs) which are usually considered as planktonic biomarkers.

The main PUFA has been tentatively identified as C20:5(n-3) fatty acid. C14:0, C16:0, C16:1 fatty acids are also detected and other tentatively identified polyunsaturated fatty acids include C16:4, C18:4 and C22:6(n-3) fatty acids. The main sterols present are cholesterol, 24-methylenecholesterol and 24-methylcholesterol detected in relatively low amounts when compared to fatty acids. The simplicity of the sterol distribution points to a single major species dominating the surface waters.

The pigment analyses of the surface water sample at site 10 indicated a large predominance of euglenophytes algae in the water column (up to 90%) and the fatty acid composition should reflect the same algal group (Volkman, personal communication). However, only a very few studies have been dedicated to the lipids composition in euglenophytes and therefore, there is not enough data available in the literature to assert whether the fatty acid distribution in our surface water sample reflects euglenophytes inputs.

Dinoflagellates contain large amounts of C16:0, C18:4(n-3) and C22:6(n-3) fatty acids and diatoms have a fatty acid assemblage dominated by C14:0, C16:0, C16:1(n-7) and 20:5(n-3) fatty acids (Viso and Marty 1993). Therefore, diatoms and dinoflagellates, which were found to represent the rest of the algal population from pigments analyses in the surface waters of Beaufort Inlet, could contribute to a small extent to the observed fatty acids.

Surface sediments

The composition of pigments in the surface sediments of site BE10, and the composition of lipids in the surface sediments of sites BE6 and BE10, both located in the channel of Beaufort Inlet, were determined.

Pigments

The pigment composition of the MBA in surface sediments is quite diverse (Figure 3-15 and Figure 3- 16). The biomarker ratio plot (Figure 3- 16) indicates that diatoms (fucoxanthin) are a significant part. Diadinoxanthin, lutein and chlorophyll *b* suggest presence of chlorophytes and euglenophytes, whereas alloxanthin indicates cryptophytes. The zeaxanthin could indicate a small amount of cyanophytes, but some or all of the zeaxanthin could originate from the chlorophytes. One of the surface sediments at site BE10 contains prasinoxanthin indicating prasinophytes. The astaxanthin and canthaxanthin are pigments usually indicative of copepod carpaces, but are also found in some green algae.

Degradation pigments (phaeophorbide-*a* and pyrophaeophorbide-*a*, phaeophytins-*a,b* and pyrophaeophytins-*a,b*) are more abundant in the surface sediments than the chlorophyll *a* from living cells (Figure 3-17), indicating a large number of dead or grazed cells in the benthos.

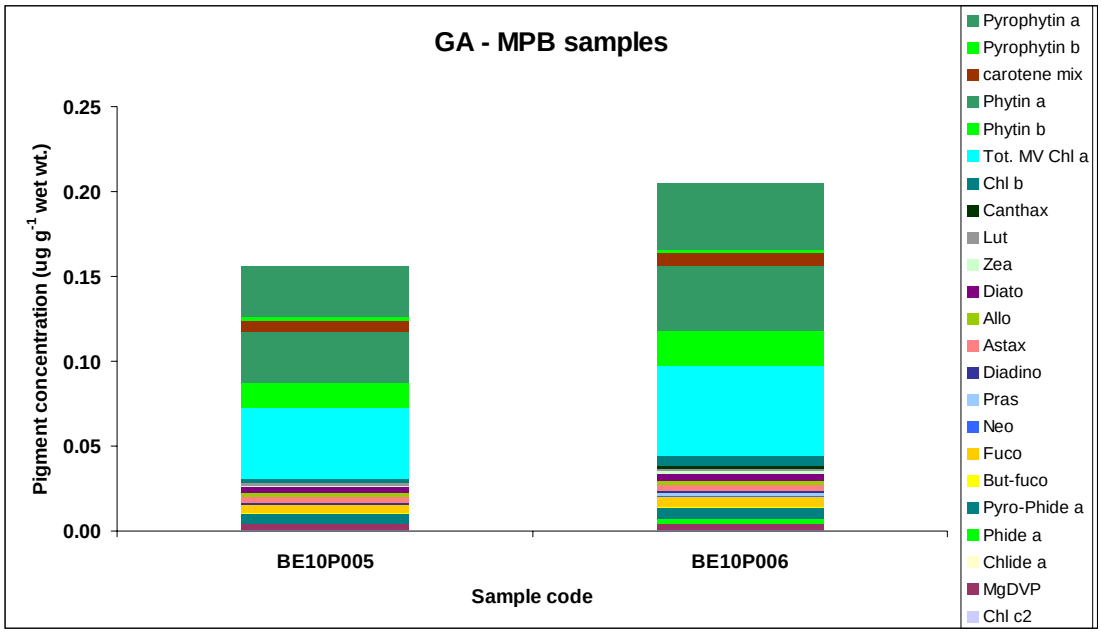


Figure 3-15. Absolute concentrations of pigments in µg/g sediment present in the surface sediments of Beaufort Inlet at site BE10. For abbreviations refer to Table 3-3

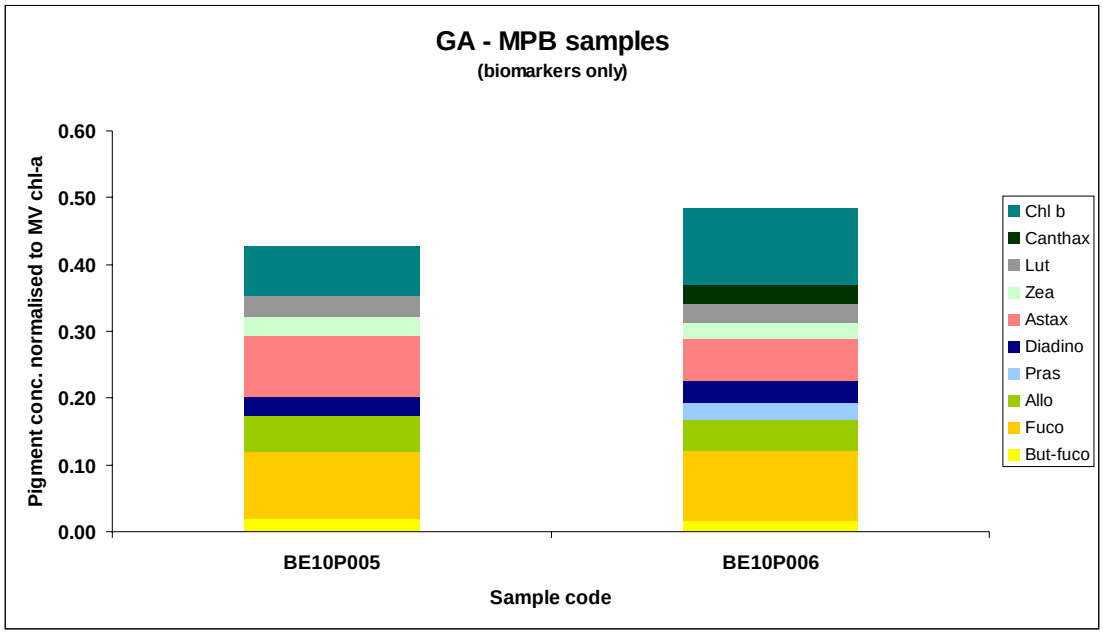


Figure 3- 16. Pigment concentrations normalised to Monovinyl Chorophyll a (MV Chl-a) in the surface sediments of Beaufort Inlet at site BE10. For abbreviations refer to Table 3-3

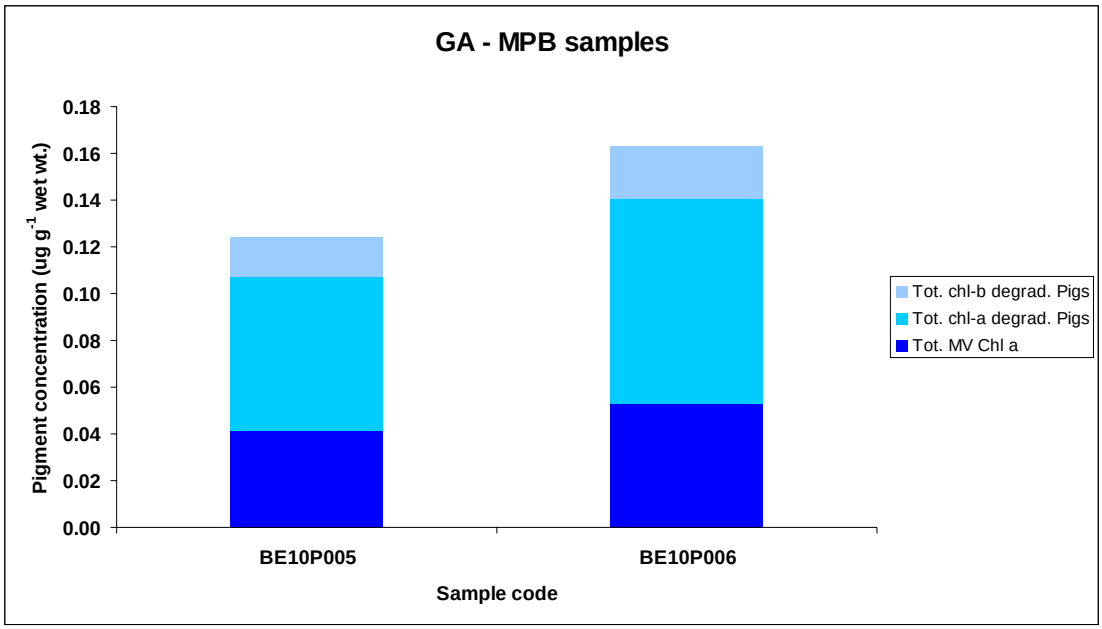


Figure 3-17. Degradation pigments from chlorophylls a and b and MV chlorophyll a concentrations in the surface sediments of Beaufort Inlet at site BE10. For abbreviations refer to Table 3-3

Lipids

Biomarker distribution in the surface sediment of Beaufort Inlet at site BE6 is dominated by 16:0 and 16:1 fatty acids, even carbon straight-chain alkan-1-ols ranging from C_{22} to C_{28}, cholesterol and and C_{32} 1,15-diol (Appendix 7: Figure F; Table A). Various other sterols are identified, among which cholestanol, brassicasterol, 24-methylcholesterol, sitosterol, stigmasterol and dinosterol. The wide variety of sterols is in agreement with pigments results showing much more diverse algal inputs in contrast to the water column. The occurrence of dinosterol provides evidence for contribution from dinoflagellates to the surface sediment (Volkman *et al*. 1998). Brassicasterol is commonly considered as a proxy for diatom abundances (Calvo *et al*. 2004; Schubert *et al*. 1998) but can also arise from other microalgae such as haptophytes or cryptophytes (Volkman *et al*. 1998). Cholesterol can derive from a variety of planktonic organisms including animals as well as diverse microalgae among which are diatoms and dinoflagellates. Some steroidal ketones with a carbonyl group at C-3 derived from microbial transformation processes of sterols are also present.

The source of long-chain alkyl diols such as C_{32} 1,15-diol is still a matter of debate but is likely microalgal. Eustigmatophyte microalgae from the genus *Nannochloropsis* have been found to biosynthesize long-chain alkyl diols but their distributions differ quite substantially from the ones observed in sediments (Volkman *et al*. 1992; Versteegh *et al*. 1997) and consequently, another yet unidentified algal source has been suggested (Gelin *et al*. 1999). The latter hypothesis applies to our samples as no indication for eustigmatophytes were detected from the pigment analyses of surface sediment. The occurrence of C_{30}, C_{32} and C_{33} hopanols points to bacterial inputs.

Detection of taraxerol, germanicol and β-amyrin indicate higher plant inputs, which is also suggested by the high proportion of straight-chain alkan-1-ols.

The surface sediment at site BE10 has a fairly similar biomarker distribution to site BE6 (Appendix 7: Figure G; Table A). As main differences, the sediment at site BE10 presents a much higher

relative abundance of cholesterol and lesser terrestrial input. Both sediments present in low abundances 5β-stanols usually associated with faecal material: coprostanol and epicoprostanol, mainly derived from human feces, and 24-ethylcoprostanol and 24-ethylepicoprostanol, derived from herbivores faeces. 24-ethylcoprostanol and 24-ethylepicoprostanol coelute with other compounds on the GC column which makes their identification more difficult.

Surface sediments at both sites of Beaufort Inlet did not show any PUFAs, which were the main components of the water column samples at these sites. PUFAs are very labile and very sensitive to oxidation, therefore rapidly degraded after cell lysis, which might explain their absence in the sediments.

4. Discussion

4A. MAJOR FACTORS INFLUENCING BENTHIC FLUXES

Microbenthic algae (MBA) can influence the release and uptake of nutrients, oxygen, and carbon dioxide at the sediment surface; and the presence of MBA at sites in Wellstead Estuary, Gordon Inlet, and Beaufort Inlet appeared to have a major effect on the benthic fluxes measured during the survey. The activity of MBA is in turn influenced by light and nutrient availability at the sediment surface, and turbulence and turbidity created in the water column by wind-driven waves. The dynamic nature of MBA productivity and these other influencing factors means that benthic fluxes are very changeable depending on local weather conditions, incoming freshwater flows, and entrance status (i.e. either open or closed to the ocean). This section explains more specifically, how MBA and these other factors are likely influencing benthic fluxes at different sites in Wellstead Estuary, Gordon Inlet, and Beaufort Inlet.

Photosynthesis creates organic matter, whereas respiration breaks down organic matter. In shallow estuaries, photosynthetic microalgae and cyanobacteria (both may be referred to as MBA) often inhabit the sediment surface. When photosynthesising, MBA *produce* organic matter and oxygen, and *consume* nutrients and carbon dioxide. Conversely, respiration processes, both that carried out by MBA for energy and that of bacteria when breaking down dead organic matter, *consume* organic matter and oxygen, and *release* carbon dioxide and nutrients. Respiration occurs during both daylight and night-time, whereas photosynthesis requires light and only occurs during daylight. Therefore, the productivity of MBA at the sediment surface can influence the daily (24-hour) consumption and production of organic matter, oxygen (O_2), carbon dioxide (TCO_2), and nutrients (N, P, and Si). For further background information about processes occurring at the sediment-water interface, see Section 1C. *The Importance of Sediment-Water Interactions.*

O_2 and TCO_2 benthic fluxes (Figure 3-2 and Figure 3-3) indicated that photosynthesis dominated over respiration processes in the channel of Gordon Inlet, and at sites BE9 and BE8 in Beaufort Inlet. In contrast, respiration dominated in the basin of Gordon Inlet, at site BE7 in Beaufort Inlet, and generally throughout Wellstead Estuary. However, significant O_2 release and TCO_2 uptake at some sites in the basin of Wellstead Estuary indicated that photosynthesis can at times dominate here.

Figure 4-1 illustrates the dominance of either photosynthesis or respiration at different sites by plotting the net daily (24-hour) TCO_2 flux; calculated as half the average flux measured in dark chambers (i.e. the flux over 12-hours of night) plus half the flux measured in light chambers (i.e. the flux over 12-hours of day), as there were equal hours of day and night during the sampling period. In Wellstead Estuary, Gordon Inlet, and Beaufort Inlet, sites with net photosynthesis likely had high MBA productivity; while those with net respiration likely had some inhibiting factor, for example light availability, limiting MBA productivity at the time of sampling.

In Gordon Inlet, the channel (Sites GO6 and GO7) was net photosynthetic; whereas the basin (Sites GO8 and GO9) was net respiratory. The weather on the day of sampling and its affect on the productivity of MBA is likely the dominant influence in this case, where the channel was sampled on a very sunny, calm day, and the basin was sampled on a very stormy, dark, and windy day. Light availability at the sediment surface in the basin was not only reduced because of overcast conditions but also because of the action of strong winds creating waves and resuspending sediments into the water column. As a result, total suspended matter (TSM) at the time of sampling in the basin was

between 76 and 134 mg/l, as compared to 46 mg/l in the channel (Table 3-1). In addition to light limitation, it is likely that wind-driven waves regularly disturb and partly remove the MBA layer in the basin, whereas the channel is within an incised valley, bound in places by high vertical cliffs, and therefore is relatively sheltered from the prevailing winds. Indeed, thick (~0.5 cm) microbial mats were observed at the channel sites. During the day, large pieces of microbial mat would rise to the water surface, carried by the bubbles of oxygen produced by the photosynthesising MBA.

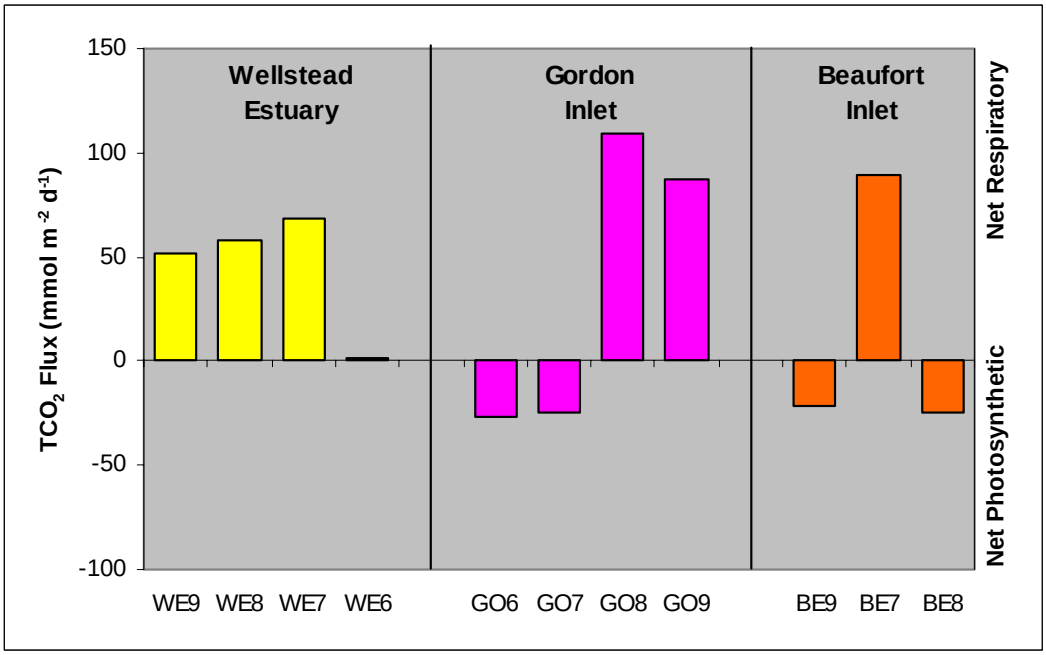


Figure 4-1. Net daily TCO_2 fluxes at sites in Wellstead Estuary, Gordon Inlet, and Beaufort Inlet. A positive TCO_2 flux indicates that, over a period of 24-hours (12-hours of daylight and 12-hours of darkness), a site is net respiratory; whereas a negative TCO_2 flux indicates that over 24-hours, a site is net photosynthetic. Sites within each estuary are arranged left to right from most upstream to most downstream.

Similarly to Gordon Inlet, sediments in Wellstead Estuary and Beaufort Inlet were more respiration dominated at sites where TSM values in the water column were high. While the sediments at sites with lower TSM values were more photosynthesis dominated. In Wellstead Estuary, sites WE9, WE8, and WE7 were net respiratory (Figure 4-1) and had higher TSM values (77, 54, and 56 mg/l respectively; Table 3-1), compared to site WE6, which had a net daily TCO_2 release close to zero and TSM levels of 39 mg/l. Entrance status at the time of the survey (open), and the inflow of marine water was possibly influencing TSM values and also other factors affecting MBA production (e.g. nutrients) in Wellstead Estuary, as several water column parameters were found to increase or decrease with proximity to the entrance (NH_4^+ and salinity increased, and SiO_4^{4-} and TSM decreased). In Beaufort Inlet, photosynthesis dominated in the channel (BE9) and basin (BE8), and respiration dominated at site (BE7) at the channel/basin entrance (Figure 4-1). Correspondingly, TSM values were higher at site BE7 (50 mg/l), compared to sites BE9 (25 mg/l) and BE8 (18 mg/l). Stronger winds at site BE7 during sampling compared to when sampling BE9 and BE8 are likely the cause of higher TSM. Notably, BE9 and BE7 were sampled on the same day, however, BE9 is located within the channel, and is more sheltered from the wind than BE7. BE8 was sampled under

comparatively still conditions. In addition, BE7 is about 0.5 m deeper than sites BE9 and BE8, further reducing the amount of light reaching the sediment surface.

Importantly for water quality in the estuaries, the uptake of nutrients by MBA during photosynthesis was observed at sites with high MBA productivity and represents a potentially important control on nutrient levels. For example, NH_4^+ benthic fluxes in Wellstead Estuary were much higher at sites WE9, WE8, and WE7, compared to site WE6 (Figure 3-4), which had higher rates of photosynthesis compared to respiration (Figure 4-1). Also in Beaufort Inlet, PO_4^{3-} fluxes were greater at site BE7 (Figure 3-7) compared to the more photosynthesis (MBA) dominated sites BE9 and BE8 (Figure 4-1).

4B. NUTRIENT AND CHL-A POOL SIZES

Nutrient pool sizes provide a measure for the mass of nutrients within the whole aquatic system and allow comparisons between different compartments, such as nutrient pool sizes in the surface sediment compared to the water column. Calculations using the water volume and the average measured water column nutrient concentrations gave the mass in tonnes of NH_4^+-bound N, PO_4^{3-}-bound P, and SiO_4^{4-} in the water column of each waterway (Figure 4-2). Also, the mass of each dissolved nutrient in the top 20 cm of sediment (where a depth of 20 cm was estimated as the limit of the most active zone of organic matter degradation) was calculated from each porewater profile (Appendix 6) based on the measured nutrient concentration in each depth layer and the porosity. The average depth-integrated nutrient mass was then multiplied by the sediment surface area of the main basin. In addition to the dissolved inorganic nutrient pool sizes, we calculated Chl-a pool sizes (in mg m^{-2}) in the water column and at the sediment surface (top 0.25 cm) to determine whether MBA or phytoplankton dominate estuarine productivity. Note that these nutrient and Chl-a pool sizes are only for the main basin of each estuary; channel sites were not included in the calculation, except for the separate calculation of Chl-a pool size in the channel of Wellstead Estuary.

The nutrient pool size of surface sediments (top 20 cm) in all estuaries was always larger than the overlying water column pool size (about 1.5 m height) (Figure 4-2), illustrating the large difference in nutrient concentrations between sediments and the water column. Porewater PO_4^{3-} and NH_4^+ concentrations may reach up to 200 and 2000 µM, respectively, while PO_4^{3-} and NH_4^+ concentrations in the water column are below 1 and 20 µM, respectively (Table 3-1).

Benthic and pelagic Chl-a pool sizes differed significantly between the three estuaries at the time of sampling (Figure 4-2). Wellstead Estuary was by far dominated by MBA, with benthic Chl-a almost 10 times higher than water column Chl-a. In contrast, Beaufort Inlet did not reveal any significant quantities of Chl-a at the sediment surface, but Chl-a concentrations in the water column were very high. Gordon Inlet takes an intermediate position with slightly higher levels of benthic Chl-a as compared to water column Chl-a. The lack of high Chl-a concentrations in surface sediments of the main basin of Beaufort Inlet is surprising, given the shallow water depth (1 to 1.5 m) and high water clarity (e.g. light attenuation coefficients of ~1.5 m^{-1}). This observation, however, can be explained by strong winds prevailing during sediment sampling. Because of the shallow water depths, the sediment surface, including the layer of MBA, has likely become suspended by wind-driven waves. This leads to a depletion of significant Chl-a concentrations at the sediment surface, and to an enrichment of water column Chl-a.

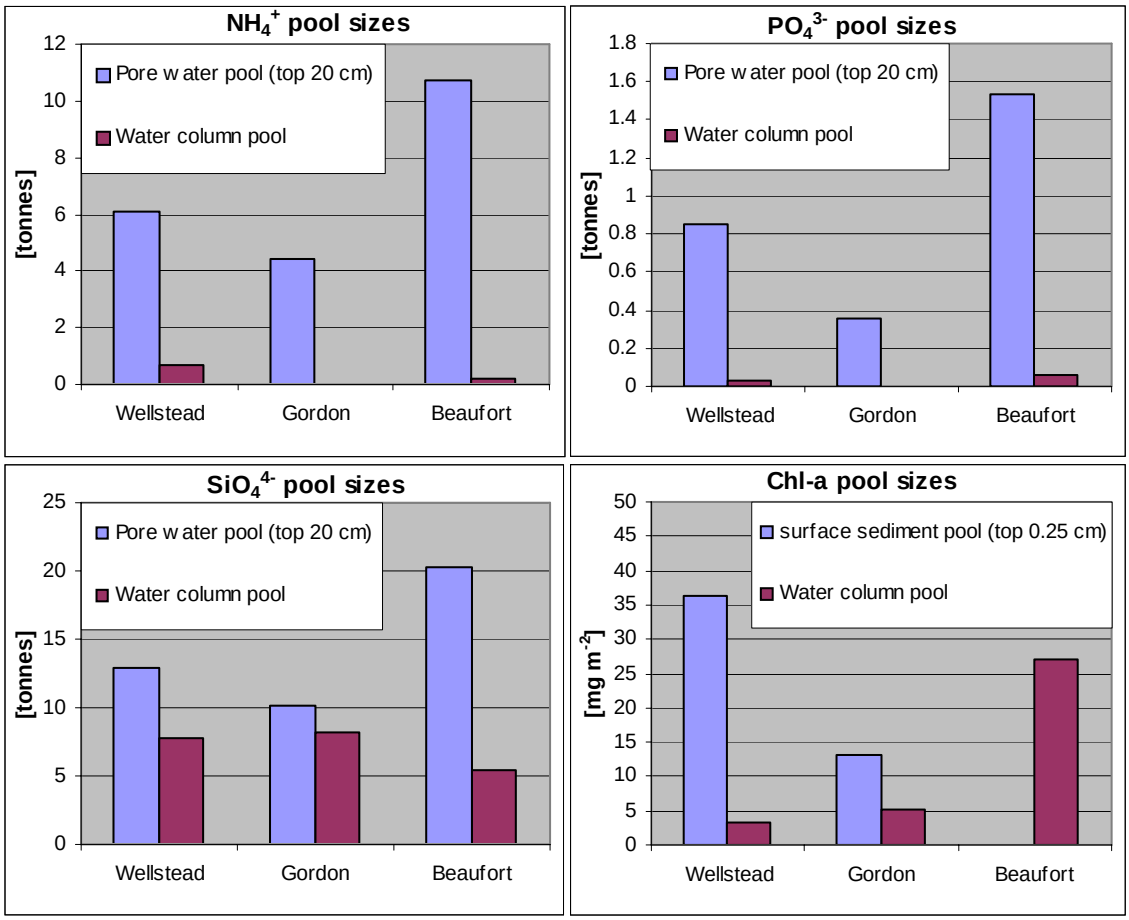


Figure 4-2. Nutrient and Chl-a pool sizes in the surface sediments (nutrients: top 20 cm, Chl-a: top 0.25 cm) and water column of Wellstead Estuary, Gordon Inlet, and Beaufort Inlet. The calculations for these plots only included basin sites from each estuary, channel sites were not included.

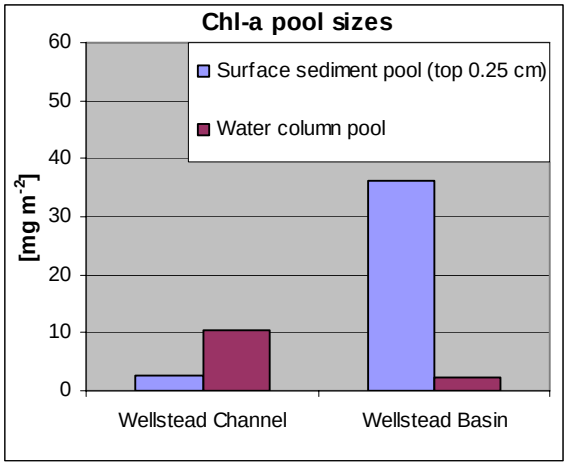


Figure 4-3. Chl-a pool sizes in the surface sediments (top 0.25 cm) and water column of the channel and basin of Wellstead Estuary.

The Chl-a pool sizes of the channel site in Wellstead Estuary (WE9) contrasted significantly to those of the main basin (Figure 4-3). The surface sediment Chl-a pool size was much smaller, and the water column Chl-a pool size was much larger in the channel than in the main basin. This indicates MBA were less abundant in the channel than in the basin at the time of core sampling. As discussed in the previous section *4A. Major Factors Influencing Benthic Fluxes*, high TSM levels can reduce the light available to MBA. TSM values in the channel were particularly high (77 mg/l) compared to the basin (40-56 mg/l; Table 3-1). Consequently, the 'filtering' effect of MBA on benthic fluxes is much reduced in the channel, resulting in high PO_4^{4-} fluxes (Figure 3-7), and also as a consequence, elevated water column P levels (Table 3-1). Combined with large NH_4^+ fluxes and water column N, this is likely leading to phytoplankton growth in the channel; evidenced by the larger water column Chl-a pool size compared to that of the main basin.

4C. ORGANIC MATTER SOURCE

The type of organic matter in the water column and in surface sediments is important for overall water quality because it determines the capacity of nutrient uptake during primary production and the nature of nutrient release during organic matter breakdown. This study used multiple approaches to derive information on the source and type of organic matter in Wellstead Estuary, Gordon Inlet, and Beaufort Inlet. These were to:

1. Analyse the stoichiometry of benthic fluxes, particularly the ratio of TCO_2 : Si benthic fluxes
2. Determine the stable isotopic composition of C and N of the bulk organic matter in sediments
3. Determine the functional lipids (biomarkers) and pigments in surface waters and sediments
4. Identify the phytoplankton present by microscopy and pigment analysis (only at Beaufort)
5. Compare the abundance of Chl-a in the water column and surface sediments

Generally in all three estuaries, the results indicated that most of the labile and non-labile organic material in surface sediments originated from primary productivity (plant growth) occurring within the estuary, with very little contribution from catchment-derived sources. As discussed in the previous section *4A. Nutrient and Chl-a Pool Sizes*, the dominant type of primary productivity within each estuary at the time of the survey differed, where benthic primary production was dominant in Wellstead Estuary and Gordon Inlet, and water column primary production was dominant in Beaufort Inlet. This section discusses more specifically, the types of aquatic plants growing in each estuary, and how the different sources of organic matter are contributing to organic matter breakdown processes and nutrient release.

Silicate (SiO_4^{4-}) is released during the breakdown of diatoms. Diatoms are a type of microalgae that have a cell wall, known as a frustule, which is composed of silica. Benthic flux results showed a release of SiO_4^{4-} from the sediments at all sites, in all estuaries (Figure 3-8), indicating diatoms are contributing to the organic matter degrading in the sediments. However, there are also other sources of labile organic matter driving benthic respiration. A benthic flux ratio of $106TCO_2 : 17SiO_4^{4-}$ is expected when diatoms comprise 100% of the organic matter degrading in the sediment (Brzezinski 1985). The SiO_4^{4-} fluxes of most sites are considerably below that required for this ratio (Figure 4-4), indicating that a significant proportion of the TCO_2 flux is not associated with the breakdown of diatoms. Other sources of organic matter include non-diatomaceous microalgae (phytoplankton and MBA) and macrophytes (seagrasses, and macroalgae). The ratio of $TCO_2 : SiO_4^{4-}$ benthic fluxes is extremely variable in Wellstead Estuary and Gordon Inlet (Figure 4-4); indicating the amount of diatomaceous organic material in the sediments relative to other types of organic matter varies significantly throughout these estuaries. The proportion of diatomaceous material is more consistent in Beaufort Inlet.

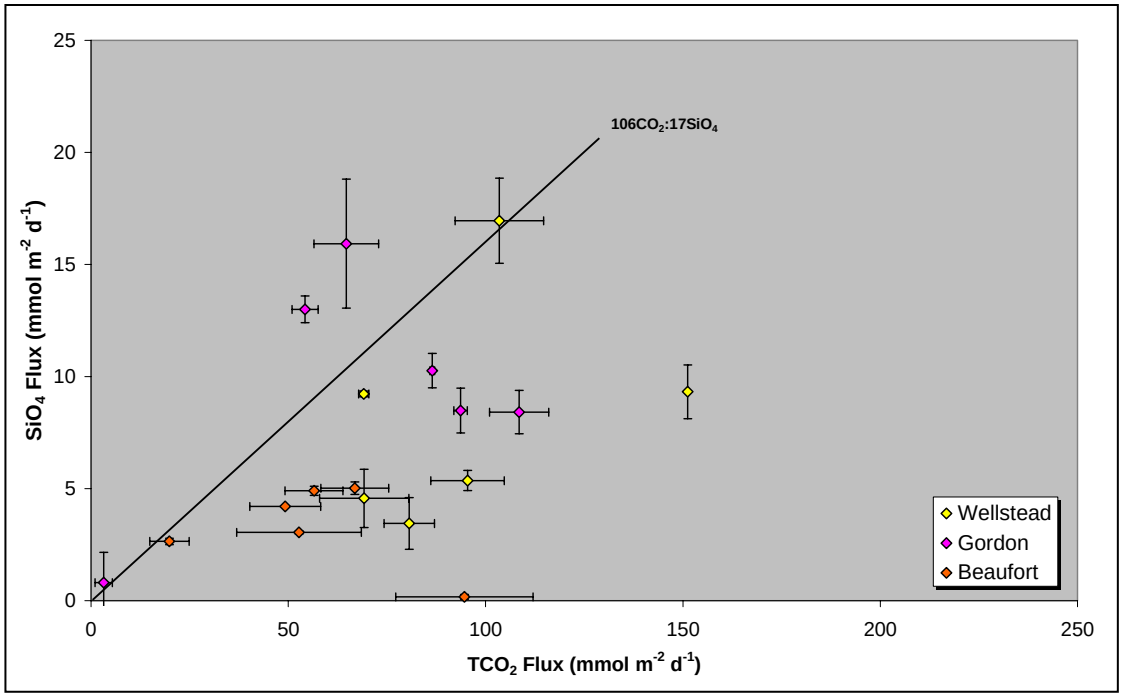


Figure 4-4. SiO_4^{4-} versus TCO_2 benthic fluxes for all sites in Wellstead Estuary, Gordon Inlet, and Beaufort Inlet (dark chambers only). The $106CO_2 : 17SiO_4$ line represents the ratio of $TCO_2 : SiO_4^{4-}$ fluxes expected for the degradation of diatoms. Ratio from Brzezinski (1985).

4C1. Wellstead Estuary

The stable isotopic and lipid composition of organic matter in the sediment of Wellstead Estuary indicates that the biomass was formed within the estuary, and that terrestrial organic matter only constitutes a small proportion. In addition, primary productivity within the estuary is considered predominantly benthic (WRC 2004). Macrophytes are ubiquitous throughout the main basin and the macrophyte density tends to increase moving from upper to lower estuary. The flowering macrophyte *Ruppia megacarpa* and the filamentous algae *Cladophora sp.* are most common. Very high concentrations of Chl-a have also been found at the sediment surface, giving evidence for abundant MBA. The results of this study confirm these observations where, in the main basin, based on Chl-a pool sizes (see previous section *4B. Nutrient and Chl-a Pool Sizes*), the abundance of MBA in the surface sediments was almost 10 times higher than microalgae in the water column. Field observations also found abundant macrophytes in sediments and scums of floating algae were common, particularly along the shoreline (Figure 4-5).

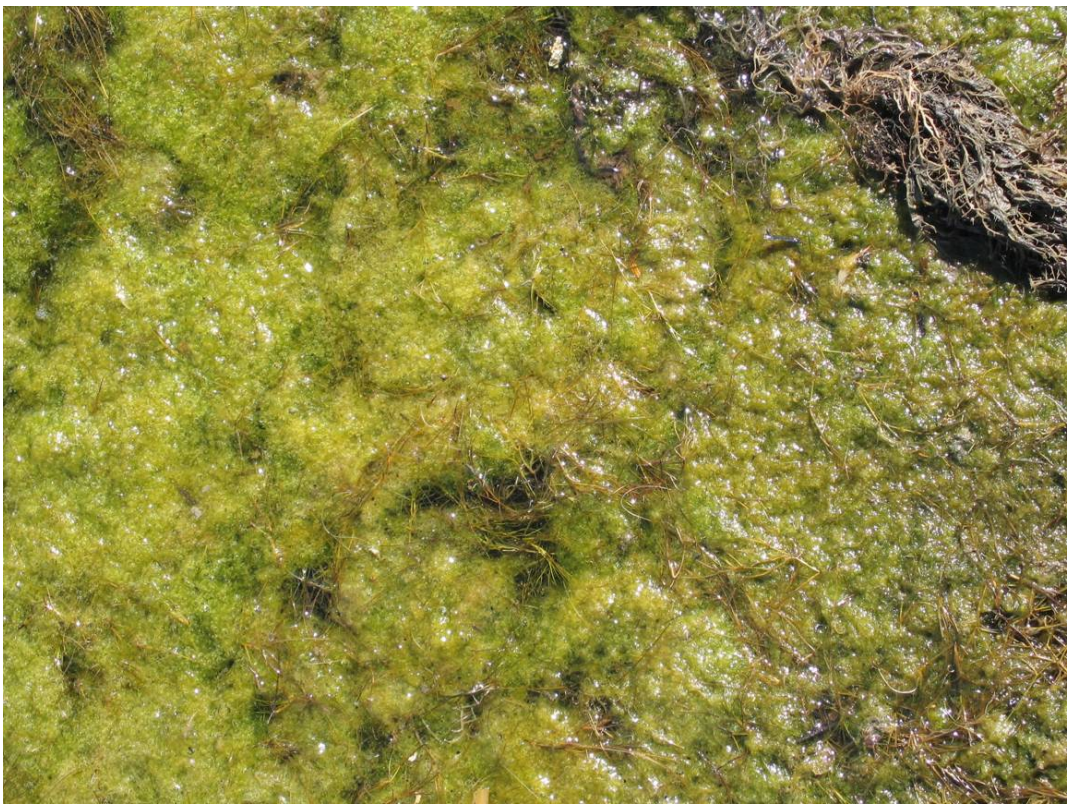


Figure 4-5. Mat ('scum') of macroalgae comprising Ruppia megacarpa and a filamentous algae, likely Cladophora Sp. on the shoreline of Wellstead Estuary.

The lipid distribution of the sampled filamentous algae, tentatively identified as *Cladophora Sp*., revealed a characteristic combination of sterols, which can be used as a 'fingerprint' to detect areas where these algae previously occurred. Interestingly, the sterol pattern in surface sediments at site WE6 (lower main basin) was identical to the filamentous algae sample, but the surface sediments at the other sites did not show this pattern. From the lipid distribution of the filamentous algae, it is also concluded that epiphytic diatoms are associated with the macrophytes. Diatoms however, do not appear to be abundant in the water column, as the phytoplankton community in Wellstead Estuary has never been diatom-dominated, according to monitoring data from July 1999 to May 2003. In fact, diatoms were not even recorded as a minor group in the period October 2002 to May 2003 (WRC 2004). They are however, part of the MBA community, according to the lipid analysis of surface sediments at site WE6. Overall, diatoms only comprise a component of the labile biomass in sediments because SiO_4^{4-} benthic fluxes are typically below (4 out of 6 chambers) that required for the ratio of $106TCO_2$: $17SiO_4^{4-}$ expected for the degradation of diatoms (Figure 4-4). Macrophytes (i.e. *Ruppia* and *Cladophora*) most likely contribute significant amounts of labile organic matter to the bulk organic matter in sediments, and importantly, this has implications for benthic fluxes, since the filamentous macroalgae sample had a molar C : N ratio of 10, compared to a Redfield ratio of 6.6 for phytoplankton (including diatoms). The higher C : N ratio of macrophytes compared to that of phytoplankton would mean less N is released in relation to C during organic matter broken down.

4C2. Gordon Inlet

Similarly to Wellstead Estuary, the stable isotopic and lipid composition of organic matter in the sediments of Gordon Inlet reveals the biomass was formed within the estuary and that terrestrial organic matter constitutes only a very small proportion. Based on Chl-a pool sizes, benthic primary production also exceeds water column primary production, but not to the same degree as found in Wellstead Estuary. The importance of benthic primary production is also evident from the observed abundance of macrophytes.

A piece of microbial mat collected from surface waters between the channel sites GO6 and GO7, was originally formed at the sediment surface; as evidenced by the layer of black mud on its base. Oxygen bubbles found within the mat had formed during photosynthesis, causing the mat to become buoyant and float to the water surface. The distribution of lipids found in the microbial mat suggests a diverse algal community, which includes cyanobacteria. Organic matter in the surface sediments of the main basin (sites GO8 and GO9) reveal the same lipid pattern, even though the microbial mat was mainly observed in the channel. We suspect persistent easterly winds may drive the floating mats growing in the basin, westward into the channel. The widespread presence of such highly productive microalgal mats at the sediment surface could potentially reduce benthic nutrient fluxes quite significantly.

Benthic TCO_2 : SiO_4^{4-} flux ratios derived under dark conditions show a large range, from 4.3 to 13 (Figure 4-4), suggesting diatoms have a highly variable contribution to the labile fraction of organic matter in sediments. Since the microbial mat appears to be highly diverse in its algal composition, and macrophytes may contribute variable proportions to the bulk organic matter in sediments, we suspect that the labile fraction of biomass in the sediment is particularly diverse, despite being collectively formed within the estuary.

4C3. Beaufort Inlet

Beaufort Inlet is similar to Wellstead Estuary and Gordon Inlet, in that functional lipids in the surface sediments only contained minor amounts of compounds derived from terrestrial organic matter, suggesting that the bulk organic matter in the sediments is principally derived from biomass which grew within the estuary. In contrast to Wellstead Estuary and Gordon Inlet however, the Chl-a pool size analysis indicated a dominance of phytoplankton as compared to MBA. Also, the stable isotopic composition of phytoplankton and bulk organic matter in surface sediments is indistinguishable, and suggests a formation of biomass under brackish conditions (as opposed to marine conditions in Wellstead Estuary and Gordon Inlet), based on $\delta^{13}C$ values close to -26. Brackish conditions were indeed prevailing in Beaufort Estuary at the time of the survey, i.e. salinity was close to 18.5 at all sites (Table 3-1).

Detailed organic geochemical studies, in combination with microscopic identification of phytoplankton groups, were carried out along a channel transect from site BE6 to BE12 (Figure 2-3). A strong dominance of euglenophytes was determined by microscopic identification and by independent pigment analysis. Both analyses estimated up to 90% of euglenophytes, followed by up to 25% of cryptophytes. Pigment abundance reached a maximum at site BE10, but it remains unclear whether the local 8 m deep depression at site BE10 serves as a particular source of nutrients for primary production. The dominance of euglenophytes is highly intriguing because their occurrence is very rare and typically associated with highly eutrophic conditions (see http://www.life.umd.edu/labs/delwiche/PSlife/lectures/Euglenophyta.html). Furthermore, “euglenoids can utilize soluble organic compounds for growth, if they are available, and thus their

presence may be an indication of organic pollution" (Jeffrey and Vesk 1997). Molar DIN : DIP ratios in Beaufort Inlet are below 10, indicating a deficiency of inorganic nitrogen available for primary production relative to inorganic phosphorous. Under these conditions, euglenophytes may become dominant, as they have the unique ability to assimilate dissolved *organic* nutrients, which is a mechanism for overcoming deficiencies in available *inorganic* N species.

The dominance of euglenophytes in surface waters allows us to determine a chemical 'fingerprint' for euglenophytes based on the distribution of functional lipids. Lipid distribution in samples from the surface water at sites BE6 and BE10 were very similar and largely dominated by polyunsaturated fatty acids (PUFAs). The sterol distribution was very simple, which is an indication for a single major species being present. In contrast to the surface water samples, samples from the surface sediments did not show a dominance of PUFAs and there was a high diversity of sterols. A similar discrepancy between surface water and surface sediment samples was found for the pigment distribution. While surface water samples were largely dominated by Chl-b (as opposed to Chl-a), surface sediments show a much larger diversity of pigments and Chl-b represents only a very small proportion of all pigments. Systematic differences in the quality of organic matter found in surface water and surface sediments suggest a decoupling of water column and sediment organic matter sources, more specifically, the biomass associated with euglenophytes appears to decompose in the water column and, at least, its most labile fraction does not settle to the sediment. This inference is supported by the characteristic dominance of PUFAs found in euglenophytes, which are known to rapidly decompose.

According to the pigment distribution in surface sediments, diatoms and smaller proportions of chlorophytes, euglenophytes, and cryptophytes form the MBA community, but since the absolute pigment concentrations are low, benthic primary production must be low. SiO_4^{4-} benthic fluxes typically fall short of that required for the ratio of $106TCO_2 : 17SiO_4^{4-}$ expected for the decomposition of diatoms (5 out of 6 chambers; Figure 4-4), indicating macroalgae and non-diatomaceous microalgae contribute to the labile organic matter fraction, in addition to diatoms.

4D. NITROGEN RELEASE FROM SEDIMENTS

Nitrogen (N) is commonly considered the key nutrient controlling primary production in estuarine environments (Howarth and Marino 2006). It can exist in many different forms in the water column and sediment porewaters of estuaries (e.g. NH_4^+, N_2, NO_2^-, NO_3^-, DON) and is transformed from one form to another by different chemical and biological processes. The type of N present, and N-transformation processes occurring, can affect water quality. Ammonia (NH_4^+) is the first product of organic matter breakdown and NO_X (oxidised nitrogen: NO_2^- + NO_3^-) is subsequently produced via the process of nitrification. Both N species are readily used by plants for growth, and therefore assimilated back into organic matter. Denitrification is a further process of organic matter breakdown whereby NO_3^- is converted into N_2 gas. The N_2 gas is subsequently lost to the atmosphere, reducing the pool of N available for plant growth. Therefore, denitrification is a process by which an estuary can rid itself of some N and thereby reduce the likelihood of the accumulation of nutrients within the system and eutrophication. In the absence of abundant NH_4^+ and NO_X however, some micro-organisms have the ability to convert N_2 gas into forms that can be used for biological growth. This process is called biological nitrogen fixation, and can counteract the benefits of denitrification. For further background information about nitrogen cycling, denitrification, and nitrogen fixation see Section 1C. *The Importance of Sediment-Water Interactions*.

In order to determine the important processes involved in N cycling occurring in the sediments of Wellstead Estuary, Gordon Inlet, and Beafort Inlet, this study compared the total net daily (24-hour) release or uptake of NH_4^+, NO_X, and N_2 from the sediments (Figure 4-6). These net daily fluxes were calculated as half the average flux measured in dark chambers (i.e. the flux over 12-hours of night), plus half the flux measured in light chambers (i.e. the flux over 12-hours of day), since there were equal hours of day and night during the sampling period. The plot of net daily NH_4^+, NO_X, and N_2 fluxes (Figure 4-6) shows that at the time of the survey, the fluxes, and as such, the nature of N-cycling processes occurring in the sediments, differed significantly between sites and between the three estuaries.

Photosynthesising MBA appeared to strongly influence N fluxes. Sites where MBA productivity was particularly high at the time of sampling (indicated by net photosynthesis in Figure 4-1) are marked with a green symbol in Figure 4-6. Some sites had a high abundance of MBA in surface sediments, indicated by high Chl-a concentrations, however, reduced light availability at the time of sampling limited MBA productivity, for example sites GO8 and GO9 in Gordon Inlet and sites WE7 and WE8 in Wellstead Inlet (Figure 4-1). Site BE9 in Beaufort Inlet was net photosynthetic regarding TCO_2 fluxes (Figure 4-1), however this site had O_2 uptake under light conditions (Figure 3-2) and relatively low surface sediment Chl-a concentrations, indicating MBA productivity was not particularly high.

As mentioned above, biological nitrogen fixation counteracts denitrification and introduces additional N to the system. Sites where the rate of nitrogen fixation exceeds denitrification have a negative N_2 flux, for example, sites WE9, WE6, GO6, GO7, and BE8 in Figure 4-6. Conversely, sites where the rate of denitrification exceeds nitrogen fixation, or nitrogen fixation is not occurring, have a positive N_2 flux (sites WE8, WE7, GO8, GO9, BE9, and BE7 in Figure 4-6). Interestingly, none of the three estuaries were entirely nitrogen fixation or denitrification dominated. All had at least some sites where nitrogen fixation dominated and some sites where denitrification dominated (Table 4-1). Importantly, this indicates that localised conditions at each site, rather than the overall character of each estuary, are largely determining the extent to which denitrification and nitrogen fixation processes are occurring.

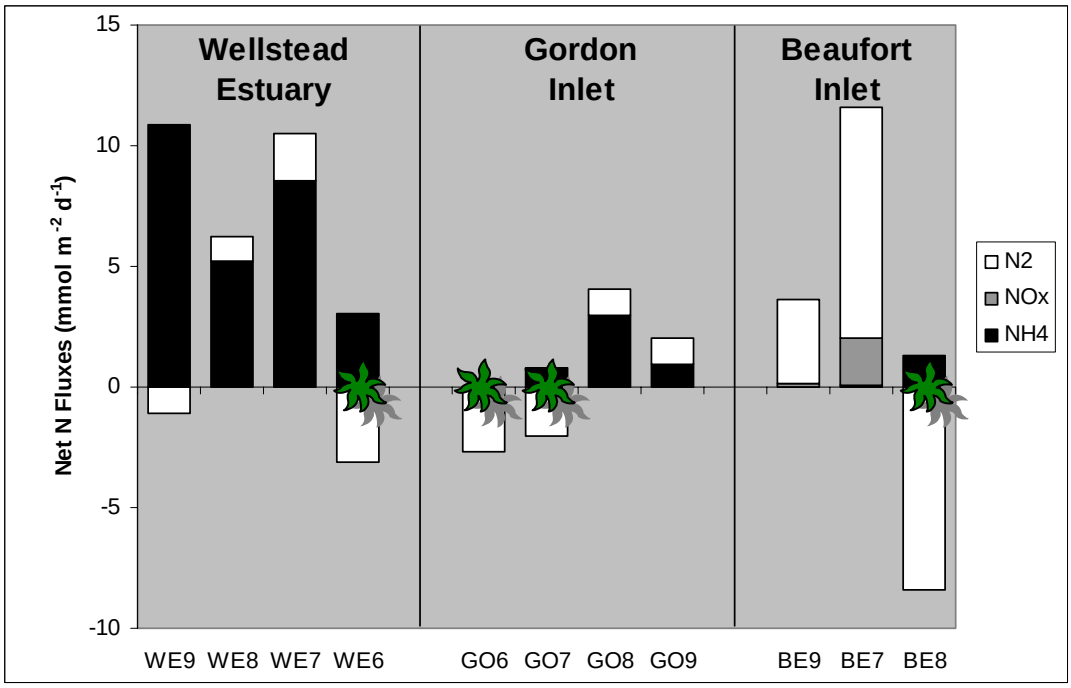


Figure 4-6. Net daily (24-hour) N_2, NO_X, and NH_4^+ fluxes for each site within Wellstead Estuary, Gordon Inlet, and Beaufort Inlet. Sites with high MBA productivity (see section 4A. Major Factors Influencing Benthic Fluxes) are marked with a green symbol. Note that for each site, N species with a positive flux are stacked one on top of the other above the x-axis, whereas N species with a negative flux (usually only N_2, except for site GO6) are stacked one on top of the other below the x-axis. Sites within each estuary are arranged left to right from most upstream to most downstream.

Table 4-1. Dominant process (either N-fixation or denitrification) and denitrification efficiencies for each sampling site in Wellstead Estuary, Gordon Inlet, and Beaufort Inlet. Sites with high MBA productivity (see section 4A. Major Factors Influencing Benthic Fluxes) are marked with a green symbol. Sites within each estuary are in order of most upstream to most downstream. (*) indicates a site where the negative N_2 flux is possibly associated with the formation of oxygen bubbles stripping N_2 from the water column (see the below section 4D1. Wellstead Estuary). Denitrification efficiencies calculated based on total net daily (24-hour) N flux values.

Estuary	Site ID	General Environ.	Dominant Process	Denitrification Efficiency (%)
Wellstead Estuary	WE9	Channel	N-Fixation (*)	--
	WE8	Basin	Denitrification	16
	WE7	Basin	Denitrification	19
	WE6	Basin	N-Fixation	--
Gordon Inlet	GO6	Channel	N-Fixation	--
	GO7	Channel	N-Fixation	--
	GO8	Basin	Denitrification	27
	GO9	Basin	Denitrification	53
Beaufort Inlet	BE9	Channel	Denitrification	96
	BE7	Channel/Basin	Denitrification	82
	BE8	Basin	N-Fixation	--

Denitrification Efficiency

Denitrification efficiency (DE) is an indicator of how well an estuary can cope with excess nitrogen. It is the percentage of total inorganic nitrogen (TIN) released from the sediments (i.e. the sum of the N_2, NO_X, and NH_4^+ fluxes) as N_2 gas (Appendix 4). This is calculated as the N_2 flux divided by the TIN flux (N_2 + NO_X + NH_4^+) x 100. This study used the total net daily (24-hour) flux values (graphed in Figure 4-6) for this calculation. Denitrification efficiencies are only calculated for sites with positive N_2 fluxes.

Comparing all sites where denitrification dominated, the upper estuary sites in Beaufort Inlet had the highest N_2 fluxes and denitrification efficiencies, followed by the basin sites in Gordon Inlet (Figure 4-6; Table 4-1). Wellstead Estuary had very low denitrification efficiencies. The activity of MBA possibly explains this, since MBA preferably assimilate NO_3^-, thereby, reducing the NO_3^- available for denitrification. Indeed, comparing Chl-a pool sizes and Chl-a concentrations in surface sediments indicated that MBA dominates primary production in Wellstead Estuary, whereas phytoplankton are far more productive than MBA in Beaufort Inlet, and Gordon Inlet is somewhere in between. Additionally, Beaufort Inlet had high NO_x fluxes, indicating the absence of any uptake by MBA. These denitrification efficiencies indicate that at the time of the survey, Beaufort Inlet had a higher capacity for removing N from the system than Wellstead Estuary and Gordon Inlet. However, this may vary over time and with varying conditions, for example, in Gordon Inlet it appears that denitrification dominates when MBA productivity is low, and N-fixation dominates under sunny, calm conditions, when MBA productivity is high. These results warn that much of the nitrogen entering Wellstead Estuary, and to a lesser degree Gordon Inlet, is retained within the estuary, remaining available for primary productivity.

The nature of N release from the sediments and denitrification efficiencies are discussed in more detail for each estuary below.

4D1. Wellstead Estuary

Wellstead Estuary had the largest rates of total N release from the sediments compared to Gordon Inlet and Beaufort Inlet, and most of this N is released as NH_4^+ (Figure 4-6). Sites WE7 and WE8, in the middle and upper basin respectively, have evidence for denitrification, with some N released as N_2 gas. However, this is small in comparison to the release of NH_4^+, therefore denitrification efficiencies are very low (Table 4-1). This possibly results from the activity of MBA, as explained above, and means that, at the time of sampling, organic matter breakdown in the sediments was contributing abundant bioavailable N to the overlying water and very little N was being lost from the estuary. In addition, negative N_2 fluxes at two sites (WE9 and WE6), indicate the uptake of N_2 through nitrogen fixation, introducing further bioavailable N to the overall system. MBA is likely fixing N at WE6, however, the occurrence of nitrogen fixation at site WE9, is unusual, since there is a plentiful supply of bioavaliable N. Nitrogen fixation requires significant energy, and nitrogen fixing bacteria will generally only undertake this process if there is insufficient nitrogen available. One possible explaination for the negative N_2 flux could be the formation of oxygen bubbles stripping the N_2 from the water (Evans 2005). Oxygen sondes recorded levels exceeding 140% saturation at site WE9 within the water column during the sampling day, such levels could reasonably result in the formation of bubbles. Oxygen levels at sites WE7, WE8, and WE6 were below 102% during the sampling period.

4D2. Gordon Inlet

In Gordon Inlet, the nature of N release from the sediments differed greatly between the channel (sites GO6 and GO7) and the basin (GO8 and GO9) at the time of sampling (Figure 4-6). In the channel, nitrogen fixation dominated N cycling, with significant N_2 uptake and very little N release. Whereas in the basin, the sediment was releasing significant amounts of N; mostly as bioavailable NH_4^+, but also as N_2 gas, with low to moderate denitrification efficiencies (Table 4-1). These results reflect the effects of MBA on N cycling. The channel was sampled during a still, sunny day, when light availability at the sediment surface, and MBA productivity would have been high. Whereas when sampling in the basin, the weather was overcast and extremely windy, and the water column very turbid; limiting MBA productivity. Therefore, in the channel, N uptake by MBA has reduced NH_4^+ and NO_x release from the sediments. Additionally, with low levels of bioavailable N in the water column, abundant light availability has allowed the activity of nitrogen fixing bacteria. Just the opposite is occurring in the basin, where the suppression of MBA productivity is allowing the release of N to the overlying water. Without the uptake of NO_x by MBA, denitrification can occur in the sediments, releasing N_2. MBA are therefore a major control on N-cycling in Gordon Inlet, and the generally high productivity of MBA during the time of year of the survey is likely the reason for very low nutrient concentrations in the water column (Table 3-1). In general, it seems that bioavailable N in Gordon Inlet is moderated by MBA, and also by a reasonable level of denitrification when MBA productivity is low.

4D3. Beaufort Inlet

The nature of N fluxes in Beaufort Inlet differed to those in Wellstead Estuary and Gordon Inlet (Figure 4-6). Beaufort Inlet was the only estuary with sites having net NO_X release, and also the only estuary with sites having high denitrification efficiencies (sites BE9 and BE7; Table 4-1). MBA productivity was low at these sites, and there was abundant NO_x available for denitrification. With such high NO_x release, it appears that nitrification was producing more NO_X than could be converted to N_2 gas via denitrification. Almost 100% of N released from the sediment was nitrified or denitrified, with very little N released as NH_4^+. Such low rates of bioavailable N release would limit levels of bioavailable N in the water column and be a strong constraint on primary productivity. Indeed, at site BE8 in the main basin, where MBA productivity was high, there were very high rates of N_2 uptake at the sediment surface, indicating the activity of autotrophic nitrogen fixers able to 'fix' N_2 gas in order to overcome deficiencies in dissolved N.

4E. PHOSPHOROUS RELEASE FROM SEDIMENTS

Phosphate (PO_4^{3-}) release from sediments can be a major source of bioavailable phosphorous (P) in the estuary, and the capacity to retain P in sediments can be highly variable (see Section 1C. *The Importance of Sediment-Water Interactions*). Very high retention of P in the sediments was found in a wave-dominated estuary in New South Wales (Haese *et al*. submitted). Where, with very little P release, and comparatively high N release from the sediments, DIN : DIP ratios in the water column were very high, leading to overall P-limitation of primary production. There are two primary control mechanisms for the retention of P in sediments. Firstly, PO_4^{3-} strongly adsorbs to iron(oxy)hydroxide. Consequently, the availability of iron(oxy)hydroxide is critical, and depends on the sediment composition and sedimentation rate, and also on the formation of iron sulfide following sulfide production by sulfate reduction (Haese 2000). Secondly, MBA increase the thickness of the oxic layer in sediments during illumination (daylight) due to photosynthesis, which in turn, enhances iron(oxy)hydroxide formation. Additionally, MBA reduce P release from the sediments during

photosynthesis by assimilating P (Carlton and Wetzel 1988). In this study, the capacity to retain P is assessed by means of PO_4^{3-} benthic fluxes, P : Al ratios in sediments, and PO_4^{3-} porewater profiles.

4E1. Wellstead Estuary

In the main basin of Wellstead Estuary, benthic fluxes of PO_4^{3-} were close to zero (Figure 3-7). Whereas in the channel (site WE9), PO_4^{3-} fluxes were low to moderately high. Site WE9 was also distinct from the basin sites in several other respects. It had the steepest PO_4^{3-} pore water gradient into the top 3 mm of sediment, it also lacked any P/Al enrichment in surface sediments, and lacked a layer of MBA, as indicated from very low Chl-a concentrations at the sediment surface. Overall, sediments of the main basin of Wellstead Estuary retain P very efficiently, which is likely related to the presence of a MBA layer. In contrast, very little P is retained in the sediments of the channel site. N release as NH_4^+ was significant from the sediments of both the main basin and channel, however, the large difference in P release has led to large molar DIN : DIP ratios in the water column of the main basin exceeding 40, whereas the ratio in the channel site was 0.29. This likely explains the differences in water column Chl-a pool sizes, where low P concentrations limit primary productivity in the water column of the main basin, whereas abundant nutrients in the channel allow phytoplankton to flourish.

4E2. Gordon Inlet

Similar to the main basin of Wellstead Estuary, benthic PO_4^{3-} fluxes were hardly detectable throughout Gordon Inlet (Figure 3-7). Given the steep PO_4^{3-} pore water gradient in surface sediments, however, particularly at site GO6 in the channel, one would expect a release of P from sediments. Once again, uptake of P by MBA is likely responsible. Notably, a particularly thick layer of MBA covered surface sediments at site GO6, indicated by very high Chl-a concentrations at the sediment surface. Sediment P/Al ratios also revealed significant enrichment in P in surface sediments. In fact, all sites in Gordon Inlet had distinctive Chl-a and P enrichments in surface sediments. Benthic NH_4^+ fluxes were also very low in Gordon Inlet, likely from uptake of N by MBA. This explains why measurements of nutrient concentrations in the water column were below the detection limit and water column primary productivity (phytoplankton) is low.

4E3. Beaufort Inlet

Beaufort Inlet differs significantly to Wellstead Estuary and Gordon Inlet. Benthic PO_4^{3-} fluxes were generally moderate to very high (Figure 3-7). Sites BE6, BE7, and BE8 have steep PO_4^{3-} pore water gradients in surface sediments, while Chl-a and P enrichments at the sediment surface are lacking. Only the channel site BE9 revealed a minor layer of MBA and a small enrichment in the P : Al ratio in surface sediments. The absence of a significant MBA layer in Beaufort Inlet gives rise to high rates of P release from sediments. Also, since N release is exceptionally low, molar DIN : DIP ratios in the water column of Beaufort Inlet are very low (between 3 and 6.).

5. Key Findings

5A. IMPACTS OF SEDIMENT-WATER INTERACTIONS ON OVERALL WATER QUALITY

5A1. Key Factors Influencing Sediment-Water Interactions and Water Quality in All Three Estuaries

Shallowness and Long Water Residence Times

The shallowness and long water residence times of Wellstead Estuary, Gordon Inlet, and Beaufort Inlet have several consequences for overall water quality in these systems. The small ratio of water volume to sediment surface area results in a strong and immediate coupling between sediment and water column processes and means that dynamic and changeable factors such as wind and microbenthic algae (MBA) production can cause frequent and dramatic changes. Additionally, the same volume of water often remains in contact with the sediments for a long time because freshwater flows are episodic and infrequent, and the estuary mouth closes to the ocean for extended periods. However, the small size and shallowness of these estuaries also means that when mouth openings and large freshwater flows do occur, they rapidly cause significant and widespread changes to geochemical and ecological functioning.

An example of the strong coupling between sediment and water column processes is the ratio of nitrogen (N) to phosphorus (P), where the ratio of N to P being released from the sediments to the overlying water, appears to determine N : P ratios in the water column. In the main basin of Wellstead Estuary, high benthic N : P flux ratios are found along with high water column N : P ratios (>40). Importantly, for the ecology and water quality management of this estuary, this means that P levels are likely the limiting factor for primary production. Conversely, N : P benthic flux ratios and N : P concentration ratios in the water column in Beaufort Inlet are very low (<4). This is likely leading to a deficiency in bioavailable N, and the occurrence of relatively high benthic N-fixation and the pre-dominance of euglenophytes in the water column. Euglenophytes are a type of microalgae with the unique ability to assimilate dissolved *organic* nutrients, which is regarded as a mechanism for overcoming deficiencies in available *inorganic* N species.

Productivity of Microbenthic Algae

In these shallow estuaries, sunlight can penetrate the entire water column and illuminate the estuary bottom, allowing plant growth not only in the water (e.g. of phytoplankton, macrophytes and associated epiphytes) but also on the sediment surface (e.g. seagrasses, macro- and microalgae). As a consequence, aquatic plants strongly influence water quality and nutrient processing within these estuaries. Most notably, microbenthic algae (MBA) affect benthic nutrient and gas fluxes in several ways. When assimilating nutrients into biomass, MBA effectively reduce the delivery of nutrients released from organic matter breakdown in surface sediments to the overlying water. Phosphorus release is additionally reduced because oxygen produced by the photosynthesising MBA causes rapid formation of ironoxyhydroxides, which adsorb phosphorus, retaining it in the sediments. Significantly, MBA are likely to reduce denitrification, since they preferably assimilate NO_3^-, thereby, reducing the NO_3^- available for denitrification. Also, in the absence of sufficient N, some types of MBA can assimilate N from N_2 gas (N-fixation), which effectively introduces additional N to the system. It follows that, factors that influence MBA productivity, will also influence the release of nutrients from the sediments, oxygen concentrations at the sediment surface,

denitrification, and N-fixation rates. Factors that change the availability of light and nutrients required at the sediment surface by MBA include, water depth, shading by overlying macroalgae and seagrasses, and cloud cover. Moderate to strong winds can also form waves strong enough to resuspend surface sediments, which increases turbidity, lowers light levels, and can physically disturb the MBA layer.

Type of Aquatic Plant Growth

As mentioned above, aquatic plants strongly influence water quality in these shallow estuaries. This is because light availability does not generally limit plant growth, either in the water column or on the sediment surface. As such, in all three estuaries, most of the labile and non-labile organic material analysed from surface sediments, was found to originate from primary productivity (plant growth) occurring within the estuary, as opposed to organic material washed in from the catchment. Note that this is the contribution of *organic material* and not necessarily *nutrients*. The input of nutrients from the catchment contributing to primary productivity within the estuaries is potentially high (further discussed in the next section). Therefore, in addition to the influence of MBA on benthic fluxes outlined above, the relative abundance of all different plant types growing in each estuary (e.g. MBA, macrophytes, phytoplankton etc) can influence water quality. For example, macrophytes, such as *Ruppia*, their attached microscopic epiphytes, and associated macroalgae such as *Cladophora sp.* compete with phytoplankton for the available nutrients in the water column. Given abundant nutrients, these macrophytes can grow extensively, filling the entire water column, and creating a large standing stock of organic material. The concern for water quality in this case, is that the macrophytes can then potentially die en-masse following a flood event, bar opening, or during the autumn – winter transition when plants start to die due to light limitation. The sudden load of decaying organic material can lead to anoxia and fish kills. Dense stands of macrophytes can also shade surface sediments, limiting the growth of MBA, and decreasing the nutrient-filtering and sediment oxygenation effects of these benthic plants.

At the time of the survey, benthic (MBA) primary production was dominant in Wellstead Estuary and Gordon Inlet, whereas water column primary production was dominant in Beaufort Inlet. In Wellstead Estuary, macrophytes are often dense and extensive, and they contribute significantly to the labile organic matter degrading in the sediments along with the epiphytic diatoms associated with the macrophytes and the MBA. Macrophytes and MBA also form the bulk of labile organic matter degrading in the sediments of Gordon Inlet and Beaufort Inlet. Interestingly in Beaufort Inlet, phytoplankton make up a significant proportion of the organic matter in the sediments, however it seems the labile proportion of this is broken down in the water column before reaching the sediment.

5A2. Key Features Influencing Sediment-Water Interactions and Water Quality Specific to Each Estuary

The sections below outline the key features influencing sediment-water interactions and water quality in each of the three estuaries. It is important to recognize the context within which these features were measured (i.e. conditions at the time of the survey), given the very changeable nature of these estuaries and their functioning depending on season, rainfall patterns, local weather conditions, entrance status, and freshwater inflows. As such, the characteristics and key processes influencing water quality may differ to those outlined below given a different set of prevailing conditions.

The estuaries were sampled in early autumn (14th March to 4th April 2006). At this time, Wellstead Estuary and Gordon Inlet were open to the ocean, whereas Beaufort Inlet was closed to the ocean. Wellstead Estuary had been open since May 2005, and Gordon Inlet and Beaufort Inlet had opened following a heavy rainfall event in mid January 2006, however Beaufort Inlet quickly closed only a few weeks after this (Geoff Bastyan pers. comm. 28/06/2006). Rainfall in the region is generally higher in winter than in summer, with monthly rainfall averages between 20 and 30mm in summer and between 40 and 50mm in winter. In the two months leading up to the survey, rainfall was substantially above average in January and below average in February. Local weather during the survey was generally dry and sunny. However, there were some overcast days, and the day sites GO8 and GO9 in the basin of Gordon Inlet were sampled, it was rainy with very strong winds. On most sampling days, a strong wind would develop by the afternoon.

Wellstead Estuary

Wellstead Estuary was sampled during a calm, sunny period, and a layer of MBA was well established in the main basin. The biomass of this MBA was significant, and far outweighed that of phytoplankton in the water column. As a consequence, the 'filtering' effect of MBA on benthic nutrient release resulted in none of the three main basin sites having measurable benthic PO_4^{3-} fluxes, whereas the channel site, which lacked an MBA layer, had significant PO_4^{3-} fluxes. All sites had significant NH_4^+ fluxes. Therefore, due to the strong coupling between sediment and water column processes, the ratio of N to P in the water column reflected the fractionation of N and P induced by differences in the magnitude of benthic N and P fluxes. DIN : DIP ratios in the water column of the main basin were very high (> 40), whereas they were very low (0.29) in the channel. As mentioned above, this is likely leading to P limitation of primary production (phytoplankton) in the water column of the main basin. In the channel however, N limitation is more likely. Significantly, this site has plentiful release of NH_4^+ from the sediments, which is possibly leading to abundant phytoplankton in the water column. Indeed, this site had a very large water column Chl-a pool size in comparison to the surface sediments, and also compared to the main basin water column.

Sediments at the two upper basin sites and the channel site were net heterotrophic, i.e. the rate of organic matter breakdown (respiration) was greater than the rate of biomass formation (photosynthesis). Only the lower basin site, near the estuary mouth, had a balance between autotrophy and heterotrophy. The estuary as a whole should be in a near steady-state condition regarding autotrophy and heterotrophy. Therefore, there must be biomass forming somewhere other than right at the sediment surface. Since phytoplankton is not abundant and, based on organic geochemical studies and benthic flux ratio considerations, diatoms do not significantly contribute to primary production, we expect macrophytes and the attached epiphytes are contributing significantly to the basin-wide formation of biomass. The rapidly growing filamentous algae *Cladophora* is likely a key primary producer in the basin. Macrophytes and their epiphytes are particularly

abundant in the lower estuary (near site WE6 and towards the opening to the ocean), which would suggest that the lower basin is net autotrophic and the upper basin and channel are net heterotrophic. Macrophytes are certainly a major source of the organic matter presently decomposing in surface sediments. The composition of this organic matter has a molar C : N ratio of ≥ 10. This results from the contribution of some older, 'pre-decomposed' organic matter already depleted in N, as well as from the input of macrophytes, in particular filamentous macroalgae with a higher C : N ratio than marine phytoplankton (C : N of 6.6).

Wellstead Estuary had very large benthic N fluxes and very low denitrification efficiencies (16-19%). As such, the sediments were releasing abundant bioavailable NH_4^+ and very little N was being lost from the estuary. Likely, the activity of MBA is limiting denitrification. In addition, negative N_2 fluxes and organic geochemical results indicating the presence of cyanobacteria, suggest that MBA are fixing N_2 at sites with lower available NH_4^+ and NO_x. This introduces further bioavailable N to the overall system.

Gordon Inlet

Similarly to Wellstead Estuary, primary productivity in Gordon Inlet was much greater in surface sediments than in the water column, and MBA significantly influenced water quality. Sediment analysis revealed an active MBA layer existing throughout the main basin and channel. Under calm, sunny conditions these MBA were highly productive and most notably, reduced N and P release to the water column, leading to dissolved inorganic N and P concentrations in the water column below detection limit. Cyanobacteria were detected in sampled microbial mats and in surface sediments, and under sunny conditions, negative N_2 fluxes indicated the occurrence of N-fixation. This is likely a mechanism to overcome the depletion in dissolved N. When benthic fluxes were derived in the main basin under overcast, windy conditions, MBA productivity was suppressed, resulting in a greater release of nutrients to the water column and allowing denitrification to occur, with efficiencies between 27-53%.

Beaufort Inlet

Beaufort Inlet differed to Wellstead Estuary and Gordon Inlet in several key respects. Primary productivity was in general much greater in the water column (indicating the dominance of phytoplankton) compared to surface sediments, whereas in Wellstead Estuary and Gordon Inlet, primary productivity was by far much greater in surface sediments (indicating the dominance of MBA) than in the water column. In addition, benthic PO_4^{3-} fluxes were very high and benthic NH_4^+ fluxes very low. This is probably causing the very low molar DIN : DIP ratios in the water column, which were less than 4, and likely leading to N limitation of primary productivity (for reference, the ratio of N : P of marine phytoplankton, the Redfield ratio, is 16). In contrast, just the opposite was the case in the other two estuaries, especially the main basin of Wellstead Estuary, which had very high N fluxes, low P fluxes and water column DIN : DIP ratios greater than 40.

Similarly to Wellstead Estuary and Gordon Inlet, the activity of MBA, or lack of it in some cases, had major consequences for benthic fluxes. In the main basin, MBA were active at the time of sampling, whereas MBA were absent, or less active at upper estuary sites. Without the filtering effect of MBA, benthic N and P fluxes were comparatively higher in the upper estuary sites, compared to the main basin. For the same reason, denitrification efficiencies were extremely high (82-96%), whereas in the main basin, rates of N-fixation were, by far, much greater than denitrification. In this case, N-fixation was likely the response of MBA to the deficiency in bioavailable N.

Whilst at the sediment surface, MBA appear to compensate for the deficiency in bioavailable N through N-fixation, in the water column, euglenophytes, a group capable of assimilating dissolved organic N (DON) in lieu of DIN, dominated the phytoplankton community. Organic geochemical studies revealed that despite the dominance of euglenophytes (up to 90% of the phytoplankton community), the sediment does not receive significant biomass sourced from euglenophytes. This suggests that dead phytoplankton is largely decomposing in the water column.

5B. CONSIDERATIONS FOR MANAGEMENT AND WATER QUALITY MONITORING

Wave-dominated estuaries such as Wellstead Estuary, Gordon Inlet, and Beaufort Inlet have restricted water exchange with the ocean and efficiently trap nutrients coming from the catchment. Therefore, processes which control the cycling of nutrients within the estuary are very important in determining water quality. The shallowness of these estuaries also means that the ratio of water volume to sediment surface area is very small, and thus, processes occurring in the sediments have a significant influence on the water column. Denitrification is a bacterial process of organic matter breakdown occurring in the sediments that releases the nutrient nitrogen (N) as non-bioavailable N_2 gas. This process is often the only way N is lost from wave-dominated estuaries. This study found high rates of denitrification in Beaufort Inlet, moderate rates in Gordon Inlet, and very low rates in Wellstead Estuary. Therefore, reducing N loads from the catchment of particularly Wellstead Estuary, and limiting any increase in N loads from the catchment of Gordon Inlet, would be effective targets for preventing excessive plant growth and subsequent water quality decline.

Phosphorous (P) is often trapped in estuarine sediments by the adsorption to ironoxides. In Wellstead Estuary and Gordon Inlet, the presence of actively photosynthesising micro benthic algae (MBA) appeared to enhance the efficiency of this process, whereby the oxygen produced during photosynthesis, increases the volume of oxygenated sediment. In addition, the uptake of both N and P by MBA for growth, further reduced the release of these nutrients to the overlying water. This resulted in lower levels of N, and especially P, available to plants in the overlying water column, and has led to a dominance of benthic primary productivity over water column primary productivity. In Beaufort Inlet, MBA was much less dominant, especially in the upper estuary, which had very high rates of P release from sediments, suggesting that the capacity to retain P in sediments is very low and any reduction in the P load would improve the nutrient status of this estuary.

The overall role of MBA as a positive or negative influence on the water quality status of these estuaries is difficult to determine. The uptake of nutrients by MBA is important for limiting macrophyte and phytoplankton growth, however there is also evidence to suggest that MBA are reducing denitrification efficiencies and fixing N_2, which is possibly leading to an overall build-up of N in the system. This is especially a risk during long periods of restricted water exchange with the ocean with a gradual increase of nutrients in the estuary due to nutrients from the catchment. Under these conditions, an estuary dominated by MBA, may switch to a system dominated by macroalgae. Shading by macroalgae may then inhibit MBA growth at the sediment surface.

The abundance of macrophytes in Wellstead Estuary, and their potential to grow rapidly, is of concern. The biomass of macrophytes varies widely over time, with huge increases forming dense and extensive beds, which can fill the entire water column. This is then followed by rapid collapse and dieback when conditions change, for example following a storm event, bar opening, or during the autumn – winter transition when plants start to die due to light limitation. This creates a huge oxygen demand when the dead organic material starts to decay in the sediments. In the past, this has been associated with broad scale deoxygenation and fish kills, such as the fish kills that occurred in

Wellstead Estuary when most of the macroalgae died after the bar opened in May 2005 and December 2001. The degrading organic material, under anoxic conditions, would also contribute significant nutrients to the water column.

Therefore, in regards to developing *resource condition targets*, we recommend monitoring the abundance of macroalgae in Wellstead Estuary, particularly during the main growth period, and assess the risk of large-scale algal mass decay by accounting for weather conditions, water levels, and bar status. The daily variation in water column dissolved oxygen levels is a possible means for estimating plant biomass in the system, where the larger the difference between day and night time concentrations, the greater the plant biomass.

Dense stands of macrophytes are also sometimes present in Beaufort Inlet and Gordon Inlet. The relative isolation of Gordon Inlet has prevented much observation of any concerning boom and bust cycles of macrophyte growth, however, problems similar to those of Wellstead Estuary could possibly occur in the future. Therefore, we also recommend monitoring macrophyte abundance in Gordon Inlet, however, at present, it seems that bioavailable N in Gordon Inlet is moderated by MBA, and also by a reasonable level of denitrification when MBA productivity is low. Presently in Beaufort Inlet, the more common occurrence of phytoplankton blooms seems of greater concern, and frequent monitoring of water column Chl-a concentrations in relation to seasonal and local weather conditions may be more relevant. Additionally, the pre-dominance of euglenophyta is often an indicator for eutrophic conditions and possibly for organic pollution. Since Beaufort Inlet is dominated by euglenophyta, its waters should be tested for organic pollution and its source identified

Importantly for designing future monitoring programs, this study found water column properties, and benthic nutrient and gas fluxes were highly controlled by weather conditions, therefore, the interpretation of any environmental data from these shallow estuaries must consider weather conditions at the time of sampling. The day-to-day differences in wind strength and direction, and cloud cover have immediate effects on water column and flux properties, making it difficult to derive long-term temporal trends using typical indicators such as Chl-a and nutrient concentrations in the water column. Therefore, it is important to consider the context within which monitoring and investigative data is collected. In addition, individual observations, e.g. single measurements, may not be representative of the long-term status of the system.

6. References

ANZECC (2000). *Australian and New Zealand Guidelines for Fresh and Marine Water Quality. Volume 1, The Guidelines*. Australian and New Zealand Environment and Conservation Council and the Agriculture and Resource Management Council of Australia and New Zealand, Environment Australia. Commonwealth Government, Canberra.

Arar E.J., and Collins G.B. (1997). *Method 445.0, In-Vitro Determination of Chlorophyll a and Pheophytin a in marine and freshwater algae by fluorescence*. National Exposure Laboratory, Office of Research and Development, US Environmental Protection Agency, Ohio.

Berelson, W., Heggie, D., Longmore, A., Kilgore, T., Nicholson, G., and Skyring, G. (1998). Benthic nutrient cycling in Port Phillip Bay, Australia. *Estuarine, Coastal and Shelf Science*, **46**, 917-34.

Boon, J.J., Hines, H., Burlingame, A.L., Klok, J., Rijpstra, W.I.C., De Leeuw, J.W., Edmunds, K.E., and Eglinton, G. (1983). Organic geochemical studies of Solar Lake laminated cyanobacterial mats. In: Bjoroy M. et al. (Ed.), *Advances in Organic Geochemistry*, Wiley, Chichester, pp. 239-248.

Boudou, J.P., Trichet, J., Robinson, N., and Brassell, S.C. (1986). Lipid composition of a Recent Polynesian microbial mat sequence. *Organic Geochemistry*, **10**, 705-709.

Brearley, A. (2005). *Ernest Hodgkin's Swanland: estuaries and coastal lagoons of southwestern Australia*. Ernest Hodgkin Trust for Estuary Education and Research and National Trust of Australia (WA). University of Western Australia Press, Crawley, Western Australia.

Brzezinski, M.M. (1985). The Si:C:N ratio of marine diatoms: Interspecific variability and the effect of some environmental variables. *Journal of Phycology*, **21(3)**, 347-357.

Calvo, E., Pelejero, C., Logan, G.A., and De Dekker, P. (2004). Dust-induced changes in phytoplankton composition in the Tasman Sea during the last four glacial cycles. *Palaeoceanography*, **19**, 2020.

Carlton, R.G., and Wetzel, R.G. (1988). Phosphorous flux from lake sediments: Effects of epipelic algal oxygen production. *Limnology and Oceanography*. **33**, 562-570.

Cloern, J.E. (1999). The relative importance of light and nutrient limitation of phytoplankton growth: a simple index of coastal ecosystem sensitivity to nutrient enrichment. *Aquatic Ecology*, **33**, 3-16.

Cloern, J.E., Canuel, E. A., and Harris, D. (2002). Stable carbon and nitrogen isotope composition of aquatic and terrestrial plants of the San Francisco Bay estuarine system. *Limnology and Oceanography*. **47**, 713-729.

Eglinton, G., and Hamilton, R.J. (1967). Leaf epicutilar waxes. *Science*, **156**, 1322-1324.

Evans, J.L.B. (2005). *The effect of benthic microalgal photosynthetic oxygen production on nitrogen fluxes across the sediment-water interface in a shallow, sub-tropical estuary*. Masters Thesis, University of Maryland, College Park, United States of America.

Eyre, B.D., Rysgaard, S., Dalsgaard, T., and Christensen, P.B. (2002). Comparison of Isotope Pairing and N_2:Ar Methods for Measuring Sediment Denitrification-Assumptions, Modifications, and Implications. *Estuaries*, **25 (6)**, 1077-1087.

Fiksdahl, A., Bjornland, T., and Liaaen-Jensen, S. (1984). Algal carotenoids with novel end groups. *Phytochemistry*, **23**, 649-655.

Forster, S., Glud, R.N., Gundersen, J.K. and Huettel, M. (1999). In situ study of bromide tracer and oxygen flux in coastal sediments. *Estuarine, Coastal and Shelf Sciences*, **49**, 813-827.

Gelin, F., Volkman, J.K., Largeau, C., Derenne, S., Sinninghe Damste, J.S., and De Leeuw, J.W. (1999) Distribution of aliphatic, nonhydrolyzable biopolymers in marine microalgae. *Organic Geochemistry*, **30**, 147-159.

Gelpi, E., Schneider, H., Mann, J., and Oro, J. (1970). Hydrocarbons of geochemical significance in microscopic algae. *Phytochemistry*, **9**, 603-612.

Grimalt, J.O., de Wit, R., Teixidor, P., and Albaiges, J. (1992). Lipid biogeochemistry of Phormidium and Microcoleus mats. *Organic Geochemistry*, **19**, 509-530.

Haese, R.R. (2000). The reactivity of iron. In: *Marine Geochemistry* (H.D. Schulz and M. Zabel eds.). Springer Verlag Berlin Heidelberg New York. 233-261.

Haese, R.R., Murray, E.J., Smith, C.S., Smith, J., and Clementson, L. (Submitted). Diatoms control nutrient cycles in a temperate coastal lagoon (SE Australia).

Hall, P.O.J., and Aller, R. (1992). Rapid, small-volume, flow injection analysis for ΣCO_2 and NH_4^+ in marine and freshwaters. *Limnology and Oceanography*, **37**, 1113-1119.

Harris, P.T., and Heap, A.D. (2003). Environmental management of clastic coastal depositional environments: inferences from an Australian geomorphic database. *Ocean and Coastal Management*, **46**, 457-478.

Hodgkin, E.P., and Clark, R. (1987). Wellstead Estuary, the estuary of the Bremer River, An inventory of information on the estuaries and coastal lagoons of south Western Australia. *Estuarine Studies Series No*. **1**. Environmental Protection Authority, Government of Western Australia, Perth.

Hodgkin, E.P., and Clark, R. (1988). Beaufort Inlet and Gordon Inlet, Estuaries of the Jerramungup Shire, An inventory of information on the estuaries and coastal lagoons of south Western Australia. *Estuarine Studies Series No*. **4**. Environmental Protection Authority, Government of Western Australia, Perth.

Howarth, R.W., Lane, J., and Cole, J.J. (1988). Nitrogen fixation in freshwater, estuarine and marine ecosystems. 1. Rates and importance. *Limnology and Oceanography*, **33**, 669-687.

Howarth, R.W., and Marino, R. (2006). Nitrogen as the limiting nutrient for eutrophication in coastal marine ecosystems: Evolving views over three decades. *Limnology and Oceanography*, **51**, 364 -376.

Jeffrey, S.W., and M. Vesk. (1997). Introduction to marine phytoplankton and their pigment

signatures. In: *Phytoplankton pigments in oceanography* (Eds.: S.W. Jeffrey, R.F.C. Mantoura, and S.W. Wright), U.N. Educ. Sci. Cult. Org. (Paris), 407-428.

Jørgensen, B.B. (1996). Material flux in sediments. In: *Eutrophication in coastal marine ecosystems. Coastal and Estuarine Studies, 52*. Jørgensen, B.B. and Richardson, K. (editors). Pages 115-154.

Kana, T.M., Darkangelo, C., Hunt, M.D., Oldam, J.B., Bennett, G.E., and Cornwell, J.C. (1994). Membrane inlet mass spectrometer for rapid high-precision determination of N_2, O_2 and Ar in environmental samples. *Analytical Chemistry*, **66**, 4166-70.

Koster, J., Volkman, J.K., Rullkotter, J., Scholz-Bottcher, B.M., Rethmeier, J., and Fisher, U. (1999). Mono-, di- and trimethyl-branched alkanes in cultures of the filamentous cynaobacterium *Calothrix scopulorum*. *Organic Geochemistry*, **30**, 1367-1379.

Mehrbach, C., Culberson, C.H., Hawley, J.E., and Pytkowitcz, R.M. (1973). Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure. *Limnology and Oceanography*, **18(6)**, 897-907.

NLWRA (2002). *Australian Catchment, River and Estuary Assessment 2002*. National Land and Water Resources Audit. Commonwealth Government, Canberra. Data and associated reports and information available from the OzEstuaries website: www.ozestuaries.org

Prosser, I.P., Rustomji, P., Young, B., Moran, C., and Hughes, A. (2001). Constructing River Basin Sediment Budgets for the National Land and Water Resources Audit. *Technical Report 15/01*. CSIRO Land and Water, Australian Government, Canberra.

Rohmer, M., Bouvier-Nave, P., and Ourisson, G. (1984). Distribution of hopanoid triterpenes in prokaryotes. *Journal of General Microbiology*, **130**, 1137-1150.

Ryan, D.A., Heap, A.D., Radke, L., and Heggie, D.T. (2003). Conceptual Models of Australia's Estuaries and Coastal Waterways: Applications for Coastal Resource Management. *Geoscience Australia Record, 2003/09*. Geoscience Australia, Australian Government, Canberra.

Schubert, C.J., Villanueva, J., Calvert, S.E., Cowie, G.L., von Rad, U., Schulz, H., Berner, U., and Erlenkeuser, H. (1998). Stable phytoplankton community structure in the Arabian Sea over the past 200,000 years. *Nature*, **394**, 563-566.

Seitzinger, S.P. (1990). Denitrification in aquatic sediments. In: *Denitrification in soil and sediment*. Revsbech, N.P. and Sørensen J. (editors). Plenum Press, New York. pp 301-322.

Summons, R.E., Jahnke, L.L., Hope, J.M., and Logan, G.A. (1999). 2-methylhopanoids as biomarkers for cyanobacterial oxygenic biosynthesis. *Nature*, **400**, 554-557.

Summons, R.E., Jahnke, L.L., Cullings, K.W., and Logan, G.A. (2001). Cyanobacterial biomarkers: triterpenoids plus steroids? *EOS*, Transactions of the AGU.

Sundby, B., Gobeil, C., Silverberg, N., and Mucci, A. (1992). The phosphorus cycle in coastal marine sediments. *Limnology and Oceanography*, **37(6)**, 1129-1145.

Van Heukelem and Thomas (2001), J. Chromatogr.A., 910, 31-49

Versteegh, G.J.M., Bosch, H.J., and De Leeuw, J.W. (1997) Potential palaeoenvirnmental information of C24 to C36 mid-chain diols, keto-ols and mid-chain hydroxy fatty acids; a critical review. *Organic Geochemistry*, **27**, 1-13.

Viso, A.-C., and Marty, J.C. (1993). Fatty acids from 28 marine microalgae. *Phytochemistry*, **34**, 1521-1533.

Volkman, J.K. (1986). A review of sterol markers for marine and terrigenous organic matter. *Organic Geochemistry*, **9**, 83-99.

Volkman, J.K. (2003). Sterols in microorganisms. *Applications in Microbiology and Biotechnology*. **60**, 495-506.

Volkman, J.K. (2005). Sterols and other triterpenoids: source specificity and evolution of biosynthetic pathways. *Organic Geochemistry*, **36**, 139-159.

Volkman, J.K., Barrett, S.M., Blackburn, S.I., Mansour, M.P., Sikes, E.L., and Gelin, F. (1998). Microalgal biomarkers: A review of recent research developments. *Organic Geochemistry*, **29**, 1163-1179.

Volkman, J.K., Barrett, S.M., Dunstan, G.A., and Jeffery, S.W. (1992). C30-C32 alkyl diols and unsaturated alcohols in microalgae of the class Eustigmatophyceae. *Organic Geochemistry*, **18**, 131-138.

Water and Rivers Commission (1999). *Gordon Inlet Sampling Program, Draft Report*, Summary of Water and Rivers Commission Gordon Inlet Data 1997-1999 by Ben Boardman, Water and Rivers Commission, South Coast Regional Office, Government of Western Australian, Albany.

Water and Rivers Commission (2001a). Estuaries of the South Coast, A Pictorial Record of the Estuaries, Embayments and River Mouths of the South Coast of Western Australia. Information CD, Water and Rivers Commission, South Coast Regional Office, Government of Western Australian, Albany.

Water and Rivers Commission (2001b). *Wellstead Inlet Sampling Program, Draft Report*, Summary of Water and Rivers Commission Wellstead Inlet Data 1997-2001 by Ben Boardman, Water and Rivers Commission, South Coast Regional Office, Government of Western Australian, Albany.

Water and Rivers Commission (2004). Situation Paper for the Wellstead Estuary, South Western Australia. *Department of Environment, Water Resource Management Series* No WRM **x**. Government of Western Australia, Perth.

Appendix 1 – Benthic Chamber Operations

Benthic chambers comprised a plexiglass cylinder, which isolated a volume of water (~8.4 L) in contact with 0.066 m^2 of bottom sediment (Figure 2-4). Chambers were left with the lid open to equilibrate with ambient conditions over night before shutting the lid and commencing the incubation. Divers drew samples from manual chambers using 110 mL syringes attached to the end of tubes connected to the inside of each chamber. Ambient water from immediately outside each chamber replaced water taken for sample draws. This entered each chamber via a narrow 20 cm tube that permitted water entry only during sample draws. Samples were corrected for the addition of ambient water before flux calculations were performed.

Sub-samples for:

- NH_4^+, NO_X, SiO_4^{4-}, PO_4^{3-} were filtered immediately after collection through 0.45 μM filters and transported to the NMI laboratory in Perth for analysis usually within 48 hours.
- pH were left unfiltered and analysed immediately at the nearby field laboratory.
- alkalinity were filtered immediately after collection through 0.45 μM filters and analysed by Gran titration within 24 hours of collection at the nearby field laboratory.
- TCO_2 samples to be analysed via the direct method (refer to Appendix 3) were unfiltered and had 30 μL of concentrated $HgCl_2$ solution added to preserve the sample.
- N_2 gas analysis were not filtered and carefully transferred (avoiding the introduction of bubbles) into 10 ml gas tight Quickfit glass vials containing 30 μL of concentrated $HgCl_2$ solution to preserve the sample. The glass vials were stored in a water bath at in-situ temperature (~20 °C) until analysed 3 weeks later at the Geoscience Australia laboratories in Canberra.

Appendix 2 – Core Sample Procedures

Using a pole corer (Figure 2-5), we collected cores using core barrels comprising a PVC tube, 73 mm internal diameter. Once in the sediment, the core barrel was sealed by closing a ball valve at the top. This prevented disturbance of the sediment inside the core barrels during retrieval. In each core barrel, we obtained a sediment depth of around 400 mm and left a 100 mm cap of water to prevent exposure of the sediment to air.

Cores were processed at a nearby field laboratory immediately after collection. We extruded and sliced each core into 1cm intervals. Sediment slices were loaded into centrifuge tubes, which were centrifuged at 11 000 rpm for 5 min to separate the solid phase from the porewaters. The porewaters were removed using a syringe and filtered through 0.45 μm filters. TCO_2 was analysed by means of the direct method (Appendix 3). The remaining sample was analysed for PO_4^{3-}, NH_4^+, NO_X, and SiO_4^{4-} within 48 hours of sample collection at the NMI laboratories in Perth (Appendix 3).

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

Appendix 3 – Chemical Analysis

A3A. DIRECT CARBON DIOXIDE BY DISSOLVED INORGANIC CARBON ANALYSER

Total dissolved inorganic carbon (TCO_2) was analysed without any sample pre-treatment with the dissolve inorganic carbon analyser (DIC) analyser AS-C3 (Apollo SciTech), which includes an infrared-based CO_2 detector (LiCor 7000). Certified sea water was used as a standard (A.G. Dickson, UC San Diego). The precision of the measurements were typically 0.1 %, i.e. differences of 2 µmol/l on a background of 2000 µmol/l were detectable. Benthic chamber samples had a volume of 0.5 ml, whereas the highly concentrated porewater samples had volumes between 0.05 and 0.1 ml. A memory effect was found when samples with large concentration differences were measured one after another, which was accounted for by analysing each sample 3 times and the first two sample results were discarded. Unfortunately, the power supply of the instrument failed during the field survey and this method was not able to be applied on samples from Beaufort Inlet.

A3B. INDIRECT CARBON DIOXIDE BY MEANS OF GRAN TITRATION

In addition to using the DIC analyser explained above, TCO_2 was also determined by means of Gran titration. For this method the alkalinity was determined by Gran titration, whilst the carbonate alkalinity (CA) was estimated by subtracting the alkalinity contribution of $B(OH)_4^-$. Carbon dioxide (TCO_2) was estimated from pH and carbonate alkalinity according to Mehrbach *et al*. (1973) using:

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

Where:
a_h is the activity of the hydrogen ion
K_1 and K_2 are the first and second ionisation constants of carbonic acid (H_2CO_3).

A3C. DISSOLVED INORGANIC NUTRIENTS

Ammonia (NH_4^+), nitrate + nitrite (NO_X), phosphate (PO_4^{3-}), and silicate (SiO_4^{4-}) were determined within 48 hours of sample collection at the NMI laboratories (Cottesloe, WA). A table of limits of reporting and associated measurement uncertainty to a 95 % confidence interval for various levels is shown below (Table 3A).

NH_3-N/NH_4-N (sol): Automated phenate method
Ammonia nitrogen was determined by an automated flow injection analyser with a spectrophotometer that included a flow-through-cell, used at 640 nm (for UV-vis detection). An intensely blue compound indophenol is formed by the reaction of ammonia hypochlorite, and phenol catalysed by sodium nitroprusside. There is no interference from other trivalent forms of nitrogen. Interfering turbidity was removed by filtration through a 0.45 mm cellulose nitrate filter paper. The lowest limit of reporting was 0.01 mg L^{-1}.

NO_x-N: Automated cadmium reduction method
Total oxidised nitrogen was determined by an automated flow injection analyser with a spectrophotometer that included a flow-through-cell, used at 540 nm (for UV-vis detection). Nitrate is reduced quantitatively to nitrite in the presence of cadmium. The sample is passed through a column containing granulated copper-cadmium to reduce the nitrate to nitrite. The nitrite (originally

present plus reduced nitrate) is determined by diazotising with sulphanilamide and coupling with a-naphthylethylenediamine dihydrochloride to form a highly coloured azo dye that is measured colorimetrically at 540 nm. Concentrations of Fe, Cu or other metals above several mg L^{-1} lowers reduction efficiency. Oil and grease will coat cadmium surface. Interfering turbidity was removed by filtration through a 0.45 mm cellulose nitrate filter paper. The lowest limit of reporting was 0.01 mg L^{-1}.

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

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

PO_4-P (sol react): Automated Ascorbic Acid Reduction method

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

Table 3A. Limits of reporting (and associated measurement uncertainty to 95 % confidence intervals) for the methods used for analysis of nutrients by NMI (Cottesloe, WA)..

Analyte	Method Number	Level 1 (LOR)	Level 2	Level 3	Level 4	Level 4 (expressed as %)
Ammonia as NH3-N - High Level	WL119	1 ± 0.4 mg/L	2 ± 0.5 mg/L	5 ± 0.8 mg/L	10 ± 1.6 mg/L	>10 mg/L ± 16%
Ammonia as NH3-N - Low Level	WL239	0.01 ± 0.010 mg/L	0.05 ± 0.012 mg/L	0.20 ± 0.028 mg/L	0.50 ± 0.067 mg/L	>0.50 mg/L ± 13%
Nitrite as NO2-N - High Level	WL119	0.3 ± 0.36 mg/L	3 ± 0.45 mg/L	6 ± 0.69 mg/L	12 ± 1.3 mg/L	>12 mg/L ± 10%
Nitrite as NO2-N - Low Level	WL239	0.01 ± 0.005 mg/L	0.02 ± 0.006 mg/L	0.05 ± 0.007 mg/L	0.20 ± 0.018 mg/L	>0.20 mg/L ± 9%
Nitrate as NO3-N - High Level	WL119	0.2 ± 0.24 mg/L	1 ± 0.26 mg/L	5 ± 0.53 mg/L	10 ± 1.2 mg/L	>10 mg/L ± 11%
Nitrate as NO3-N - Low Level	WL239	0.01 ± 0.007 mg/L	0.05 ± 0.011 mg/L	0.10 ± 0.018 mg/L	0.20 ± 0.035 mg/L	>0.20 mg/L ± 17%
Silica as SiO2	WL239	0.001 ± 0.0038 mg/L	0.020 ± 0.0040 mg/L	0.10 ± 0.065 mg/L	0.40 ± 0.022 mg/L	>0.40 mg/L ± 5%
ortho-Phosphate as PO4-P - High Level	WL119	0.1 ± 0.06 mg/L	0.2 ± 0.07 mg/L	0.5 ± 0.09 mg/L	1.0 ± 0.14 mg/L	>1.0 mg/L ± 14%
ortho-Phosphate as PO4-P - Low Level	WL239	0.005 ± 0.007 mg/L	0.020 ± 0.013 mg/L	0.10 ± 0.018 mg/L	0.50 ± 0.049 mg/L	>0.50 mg/L ± 10%

A3D. DISSOLVED NITROGEN GAS

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

A3G. CHLOROPHYLL A

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

A3H. TOTAL SUSPENDED MATTER

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

A3I. PIGMENTS

Water column

Sample filters were cut into small pieces and covered with 100% acetone (3 mls) in a 10 ml centrifuge tube. The samples were vortexed for about 30 seconds and then sonicated in an ice-water bath for 15 minutes in the dark. The samples were then kept in the dark at 4 °C for approximately 15 hours. After this time 200 µL water was added to the acetone such that the extract mixture was 90:10 acetone:water (vol:vol) and sonicated once more in an ice-water bath for 15 minutes. The extracts were quantitatively transferred to a clean a centrifuge tube and centrifuged to remove the filter paper. The final extract was filtered through a 0.2 µm membrane filter (Whatman, anatope) prior to analysis by HPLC using a Waters - Alliance high performance liquid chromatography system, comprising a 2695XE separations module with column heater and refrigerated autosampler and a 2996 photo-diode array detector. Immediately prior to injection the sample extract was mixed with a buffer solution (90:10 28 mM tetrabutyl ammonium acetate, pH 6.5 : methanol) within the sample loop. After injection pigments were separated using a Zorbax Eclipse XDB-C8 stainless steel 150 mm x 4.6 mm ID column with 3.5 µm particle size (Agilent Technologies) and the gradient elution procedure of Van Heukelem and Thomas, (2001). The flow rate was 1.1 mL min^{-1} and the column temperature was 55°C. The separated pigments were detected at 436 nm and identified against standard spectra using Waters Empower software. Concentrations of chlorophyll a, chlorophyll b and β,β-carotene in sample chromatograms were determined from standards (Sigma) while all other pigment concentrations were determined from standards (DHI, Denmark).

Microphytobenthos

The microphytobenthos (MPB) samples were weighed and quantitatively transferred to 50 ml centrifuge tubes. 100% acetone (8-10 mls) was added to each tube and the tubes were vortexed for about 30 seconds and then sonicated in an ice-water bath for 15 minutes in the dark. The samples were then kept in the dark at 4 °C for approximately 15 hours. After this time the tubes were centrifuged and the supernatant from each tube decanted into a separate 25 ml volumetric flask which were stored in the dark at 4 °C. A second extraction was performed on each MPB sample with a resting time of only 3 hours. The samples were again centrifuged and the supernatant of the second extraction was added to the first. A pre-determined volume of water was added to each flask such that the final extract mixture was 90:10 acetone:water (vol:vol). Each flask was made to the 25 ml mark with 100% acetone and then filtered through a 0.2 µm membrane filter (Whatman, anatope) prior to analysis by HPLC as described above.

A3J. STABLE ISOTOPES

δ15N, δ13C, TN% and TC% in sediments and organic matter were analysed using a Carlo Erba Elemental Analyser attached to a Finnigan MAT 252 Stable Isotope Mass Spectrometer. Approximately 1 mg of ground sample was placed into 8 x 5 mm tin capsules and the capsules crimped and folded into solid pellets. Samples for carbon analysis were additionally acidified in situ using sulphurous acid and dried prior to analysis. Samples are combusted in a furnace and the separation of N_2 gas and CO_2 gas, from other combustion products, undertaken on a gas GC column.

A3L. BIOMARKER ANALYSIS

All samples were freeze-dried before analysis. Sample filters were powdered using solvent-clean mortar and pestle. Core and grab samples were extracted using a Dionex Accelerator Solvent Extractor ASE 200 with dichloromethane at 100°C and under 1000 psi. Filters, microbial mat, floating algae and phytoplankton samples were ultrasonically extracted with dichloromethane (3-4 ×) and the organic extracts recovered by centrifugation were combined. 5% of the total organic extract was derivatized with Bis-trifluroacetimide (BSTFA) before analysis. Aliquots were analyzed 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}.

A3M. X-RAY FLUORESCENCE SPECTROMETRY (XRF) ANALYSIS

Major elements (SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O, P_2O_5 and SO_3) were determined in sediments samples on a Philips PW2404 4kW Sequential Spectrometer using a Rh tube and according to a modified version of Norris and Hutton's (1969) methods. The instrument is 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 is combined with flux material and 0.5 ml of 20% LiNO3 added. The mixture is heated at 400 ºC for 10 minutes then at 1100 ºC for a further 10 minutes during which time a tablet of Ammonium Iodide is added. The resulting melt is poured into moulds, cooled then introduced to the XRF. Table 3B lists the detection limits for each of the major elements.

Table 3B. Detection limits for major elements determined by X-Ray Fluorescence Spectrometry

Analyte	Detection Limit
SiO_2	0.006%
TiO_2	0.002%
Al_2O_3	0.001%
Fe_2O_3	0.002%
MnO	0.001%
MgO	0.004%
CaO	0.002%
Na_2O	0.004%
K_2O	0.002%
P_2O_5	0.001%
SO_3	0.001%

Appendix 4 – Benthic Flux and Denitrification Efficiency Calculations

A4A. BENTHIC FLUXES ACROSS THE SEDIMENT-WATER INTERFACE

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

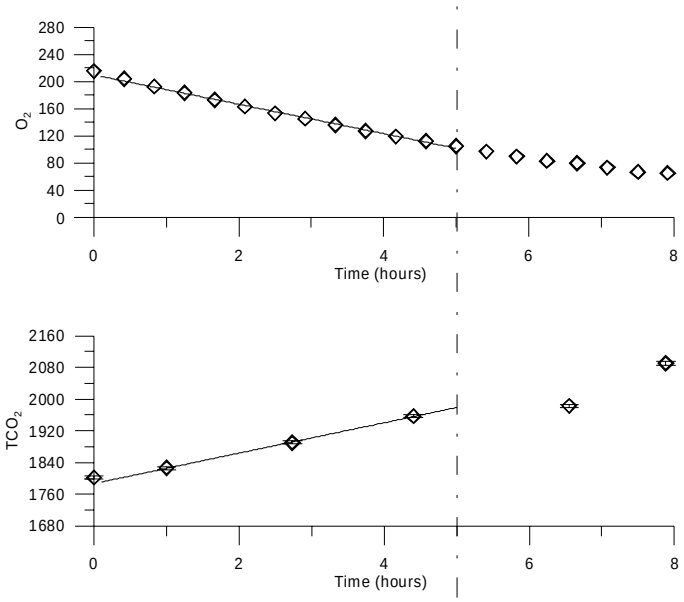


Figure 4A. O_2 and TCO_2 in μM. Fluxes were determined only from data points that fell within the time that O_2 uptake was linear. In this example, O_2 uptake was linear for the first 5 hours; indicating that, during this time, the chamber was not significantly perturbing the nutrient dynamics of the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

A4B. DENITRIFICATION EFFICIENCY

Denitrification efficiency is the percentage of total N (the sum of NH_4^+, NO_X, and N_2) released from the sediment as N_2 gas. We calculated N_2 fluxes by directly measuring the change in N_2 concentrations inside each chamber. The equation used for calculating denitrification efficiencies is:

(1) $$Denitr.eff.[\%] = \frac{J(N_2)}{J(NH_4^+ + NO_X + N_2)} \times 100$$

Where:
$J(N_2)$ is the N_2 flux measured in each chamber
$J(NH_4^+ + NO_X + N_2)$ is the sum of NH_4^+, NO_X and N_2 fluxes measured in each chamber

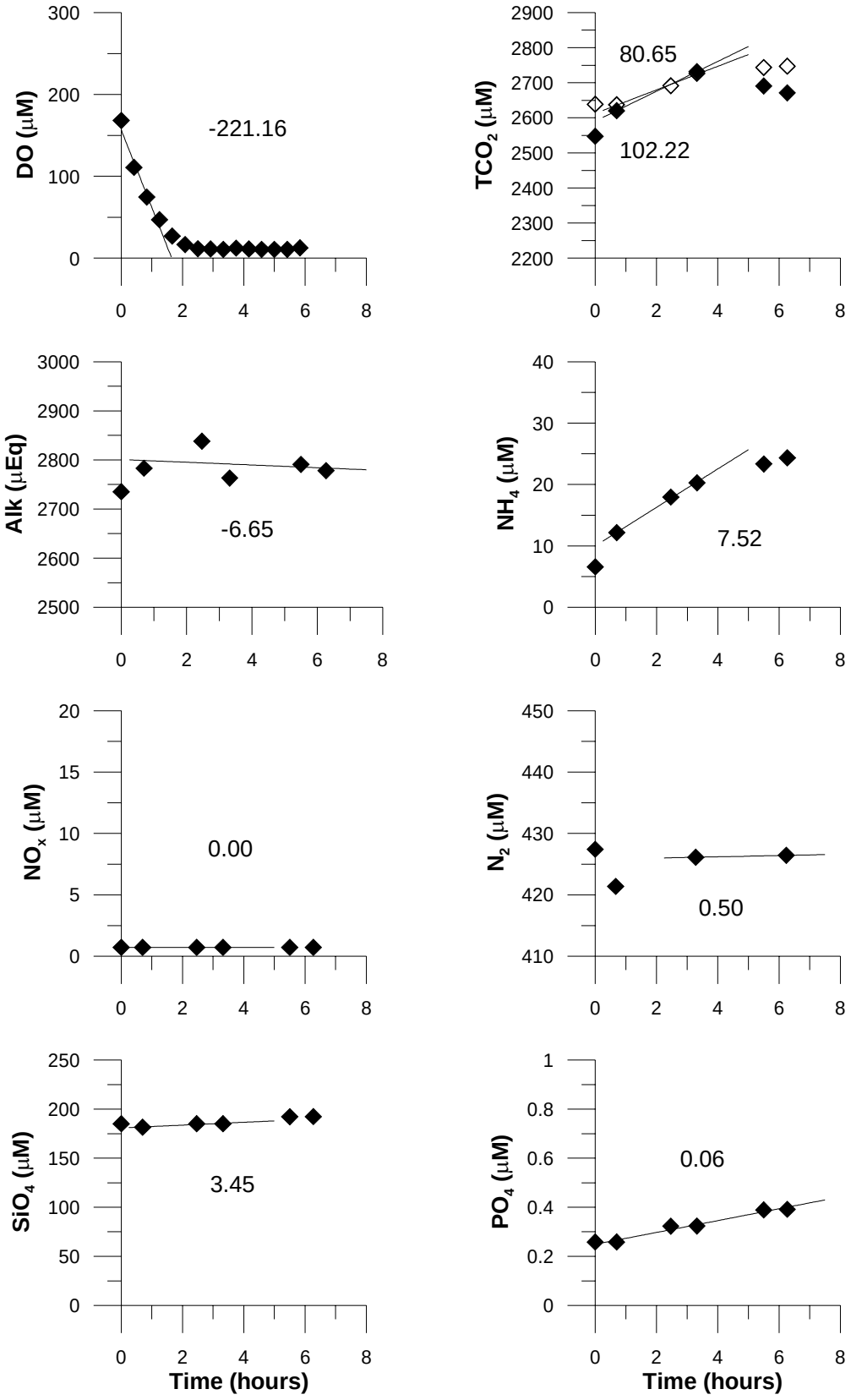
Appendix 5 – Solute vs Time Plots from Benthic Chambers

Notes:

- Table 3-2 in Chapter 3, presents the benthic flux rates measured in each benthic chamber deployment. These rates were calculated based on the plots below using the method outlined in Appendix 4, Section A4A.
- the y-axis scales for each solute are kept constant for all chamber deployments within the one estuary. For example, the scale for TCO_2 ranges between 2200 and 2900 µM for all chamber deployments from Wellstead Estuary and between 1600 and 2400 µM for those in Gordon Inlet.
- the open diamond (◊) on the TCO_2 plots refers data measured using the dissolved inorganic carbon (DIC) analyser (see Appendix 3, Section A3A),
- the closed diamonds (♦) represent data calculated from Alkalinity and pH measurements (see Appendix 3, Section A3B)
- the number in the centre of each plot is the calculated flux in mmol m^{-2} day^{-1},
- the top right corner indicates whether the chamber was light or dark and if a labelled $^{15}NO_3$ or $^{15}N_2$ isotope spike was used,
- the regression lines are drawn through only the data points used to calculate the flux,
- Sites are ordered from most upsteam to most downsteam in each estuary.

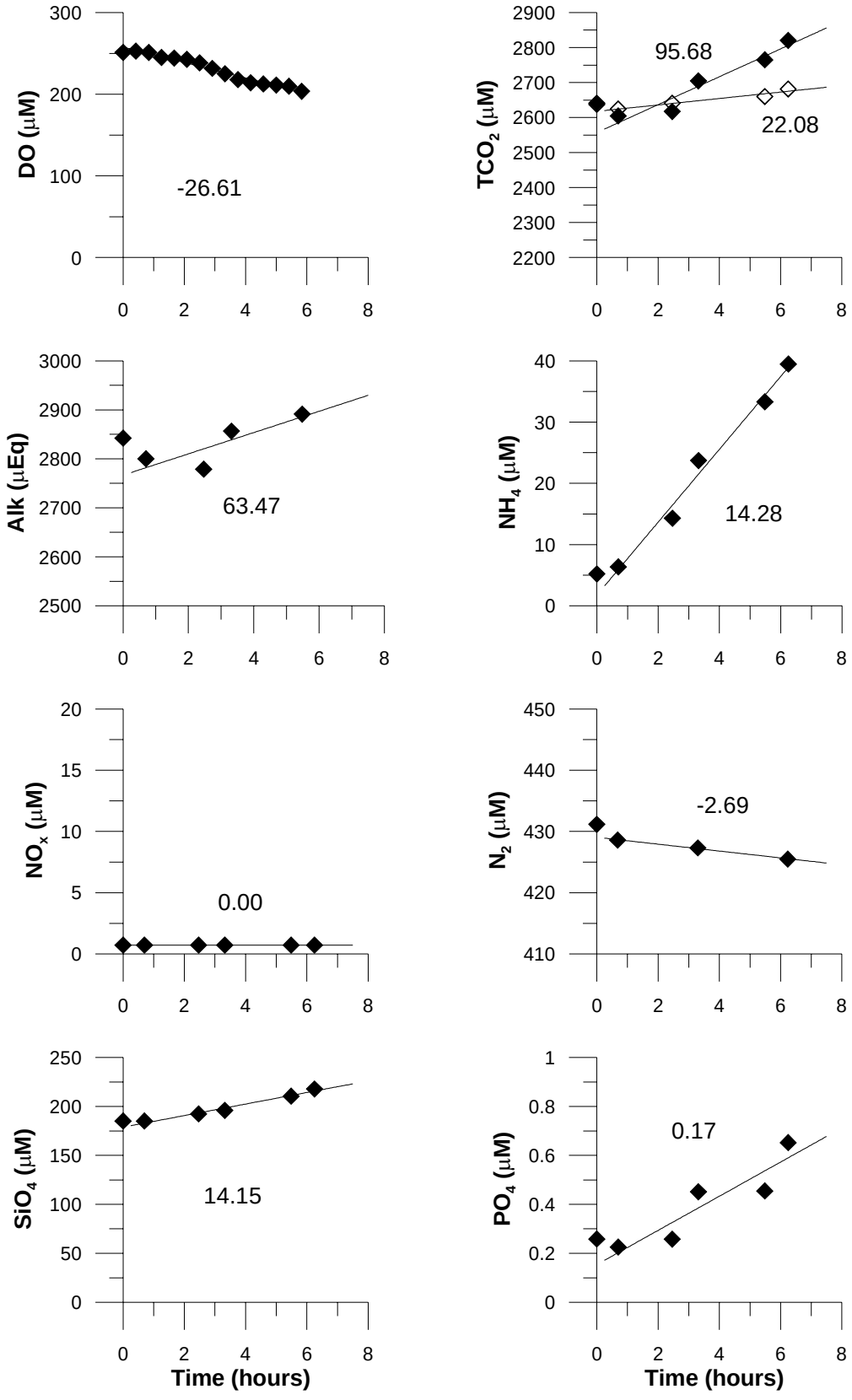
Dark

WE9 - 3


DO (μM)
-221.16
TCO2 (μM)
80.65
102.22
Alk (μEq)
-6.65
NH4 (μM)
7.52
NOx (μM)
0.00
N2 (μM)
0.50
SiO4 (μM)
3.45
PO4 (μM)
0.06
Time (hours)
Time (hours)

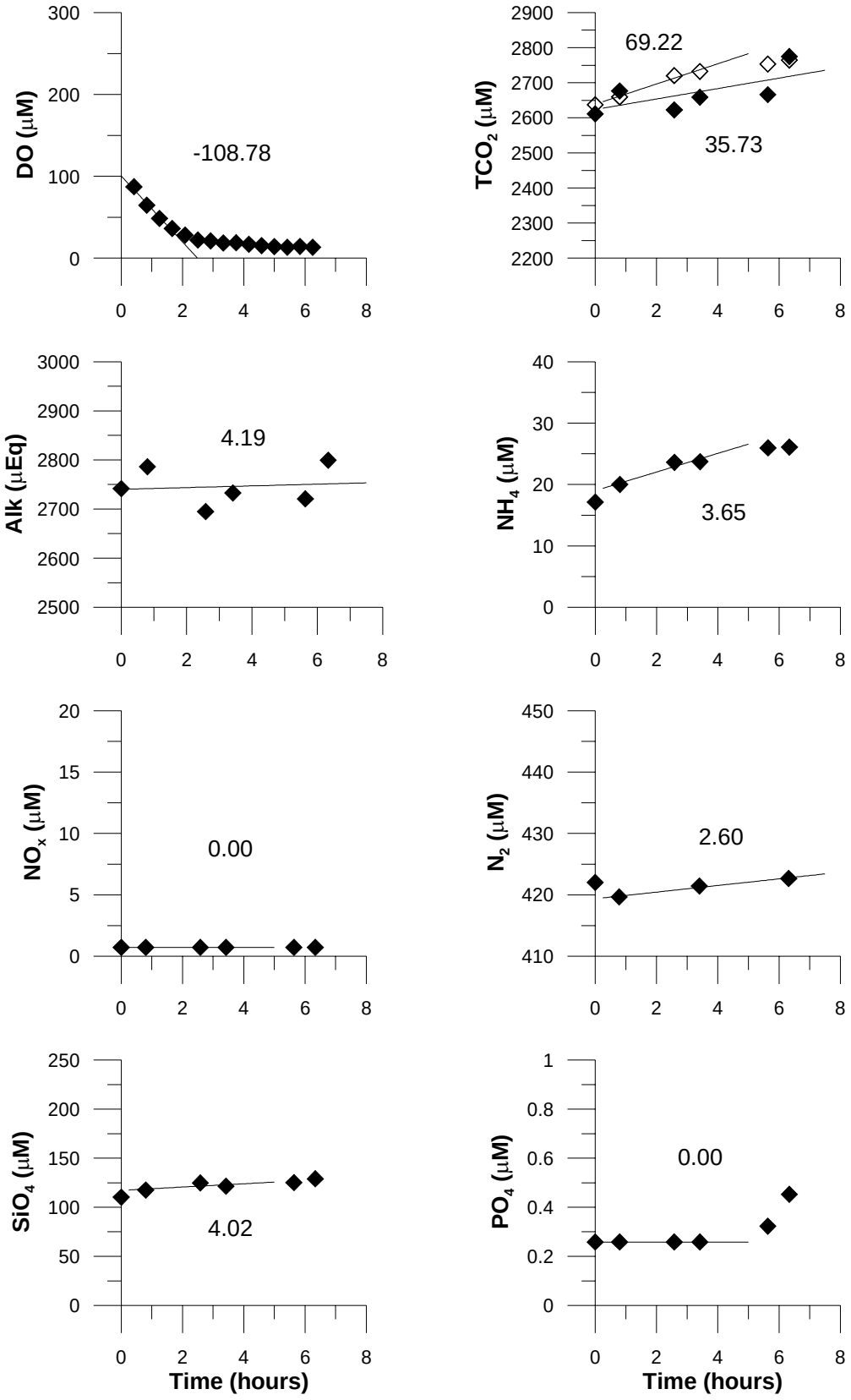
Light

WE9 - 6


DO (μM)
-26.61
TCO2 (μM)
95.68
22.08
Alk (μEq)
63.47
NH4 (μM)
14.28
NOx (μM)
0.00
N2 (μM)
-2.69
SiO4 (μM)
14.15
PO4 (μM)
0.17
Time (hours)
Time (hours)

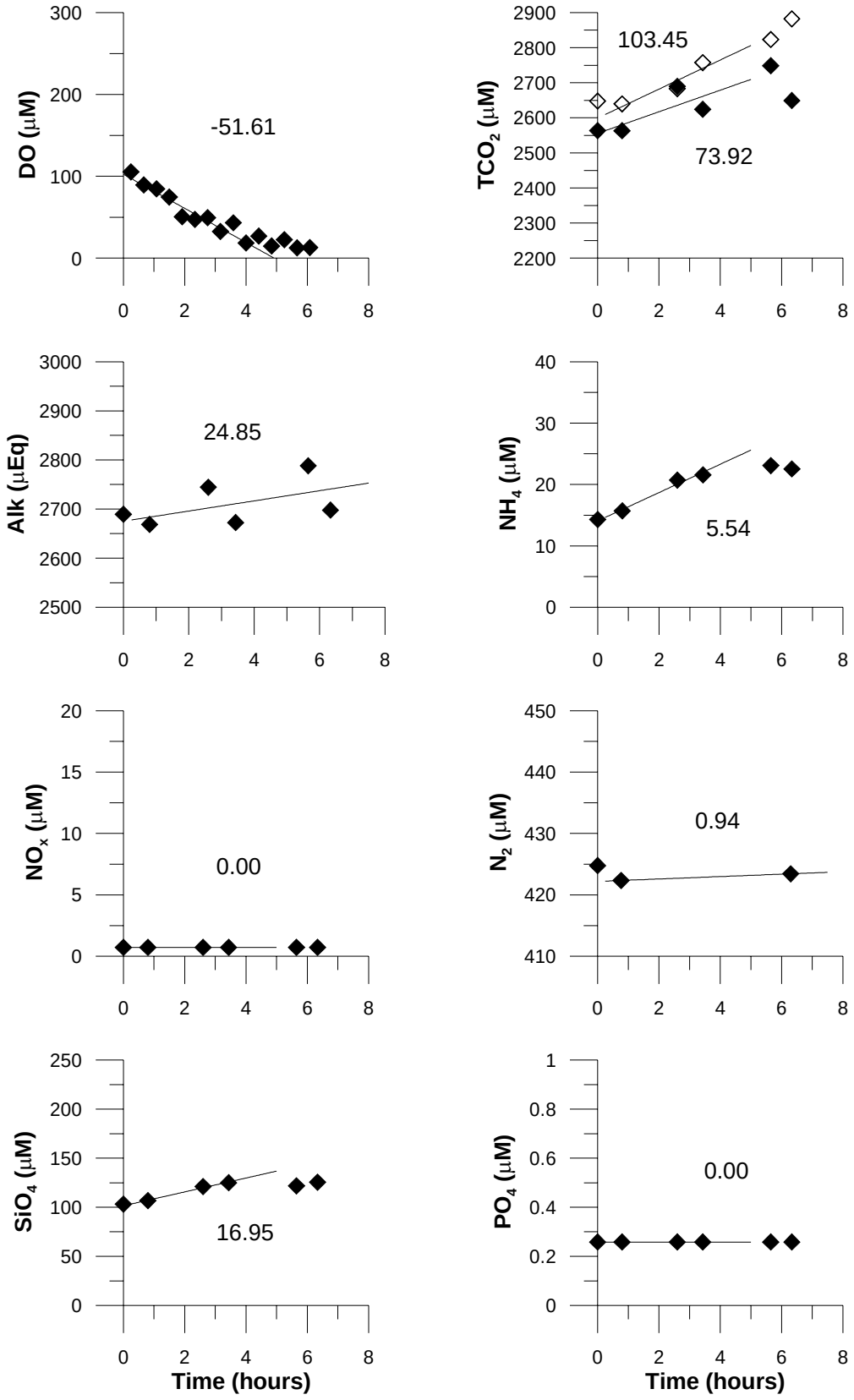
Dark

WE8 - 4


DO (μM)
-108.78
TCO2 (μM)
69.22
35.73
Alk (μEq)
4.19
NH4 (μM)
3.65
NOx (μM)
0.00
N2 (μM)
2.60
SiO4 (μM)
4.02
PO4 (μM)
0.00
Time (hours)
Time (hours)

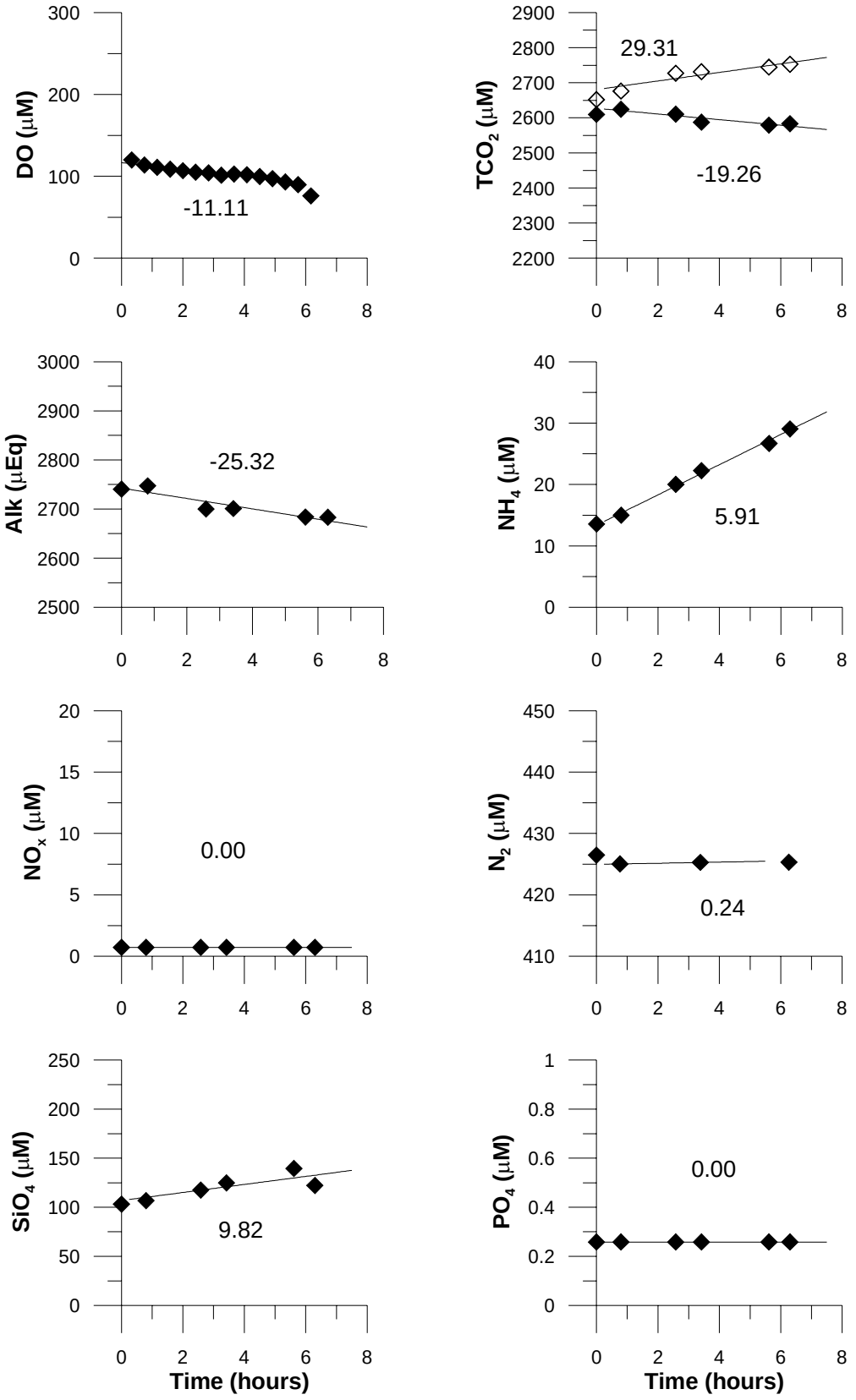
Dark

WE8 - 7


DO (μM)
-51.61
TCO2 (μM)
103.45
73.92
Alk (μEq)
24.85
NH4 (μM)
5.54
NOx (μM)
0.00
N2 (μM)
0.94
SiO4 (μM)
16.95
PO4 (μM)
0.00
Time (hours)
Time (hours)

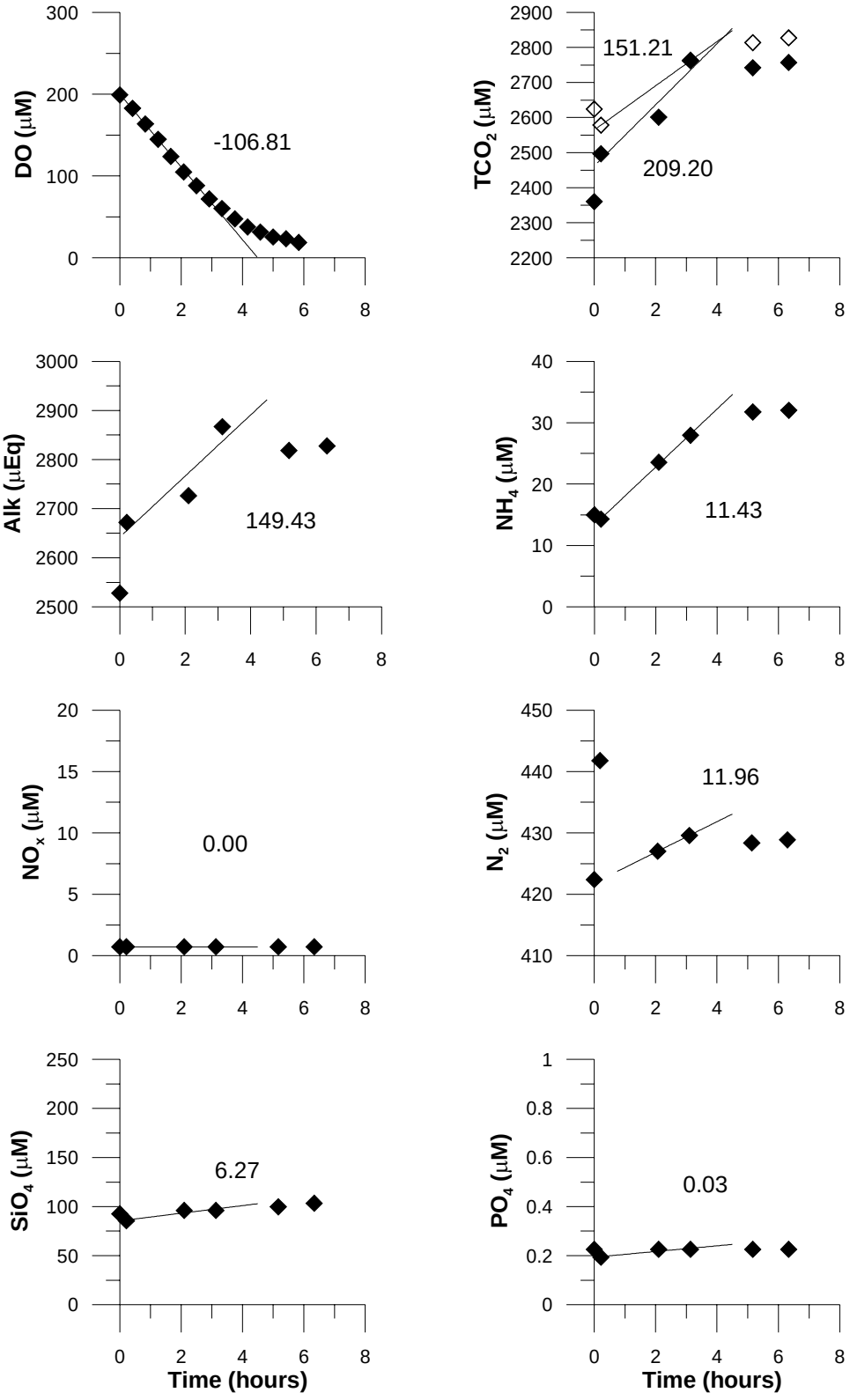
Light

WE8 - 9


DO (μM)
-11.11
TCO2 (μM)
29.31
-19.26
Alk (μEq)
-25.32
NH4 (μM)
5.91
NOx (μM)
0.00
N2 (μM)
0.24
SiO4 (μM)
9.82
PO4 (μM)
0.00
Time (hours)
Time (hours)

Dark
N_2 Spike

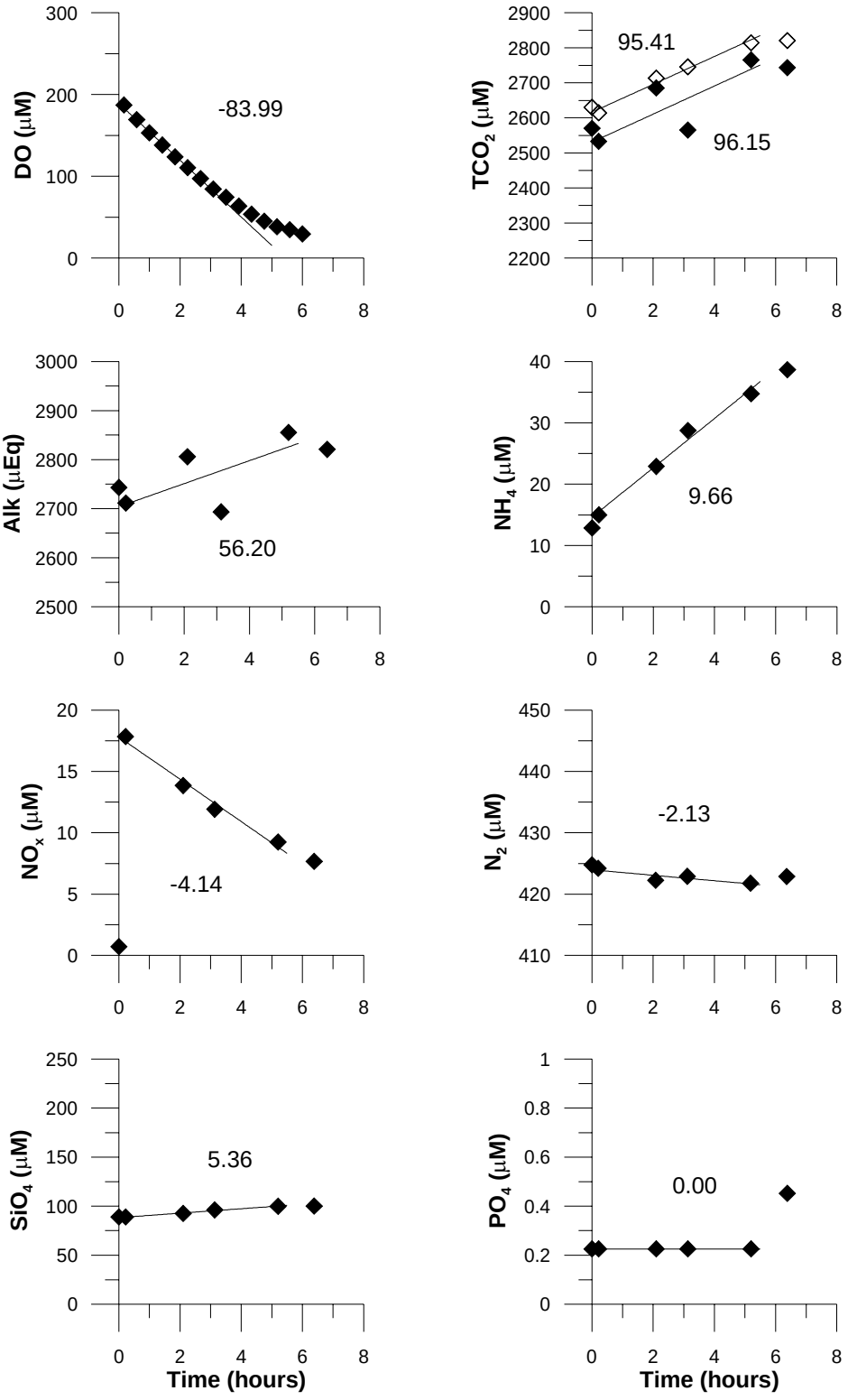
WE7 - 4



Dark

$^{15}NO_3$ Spike

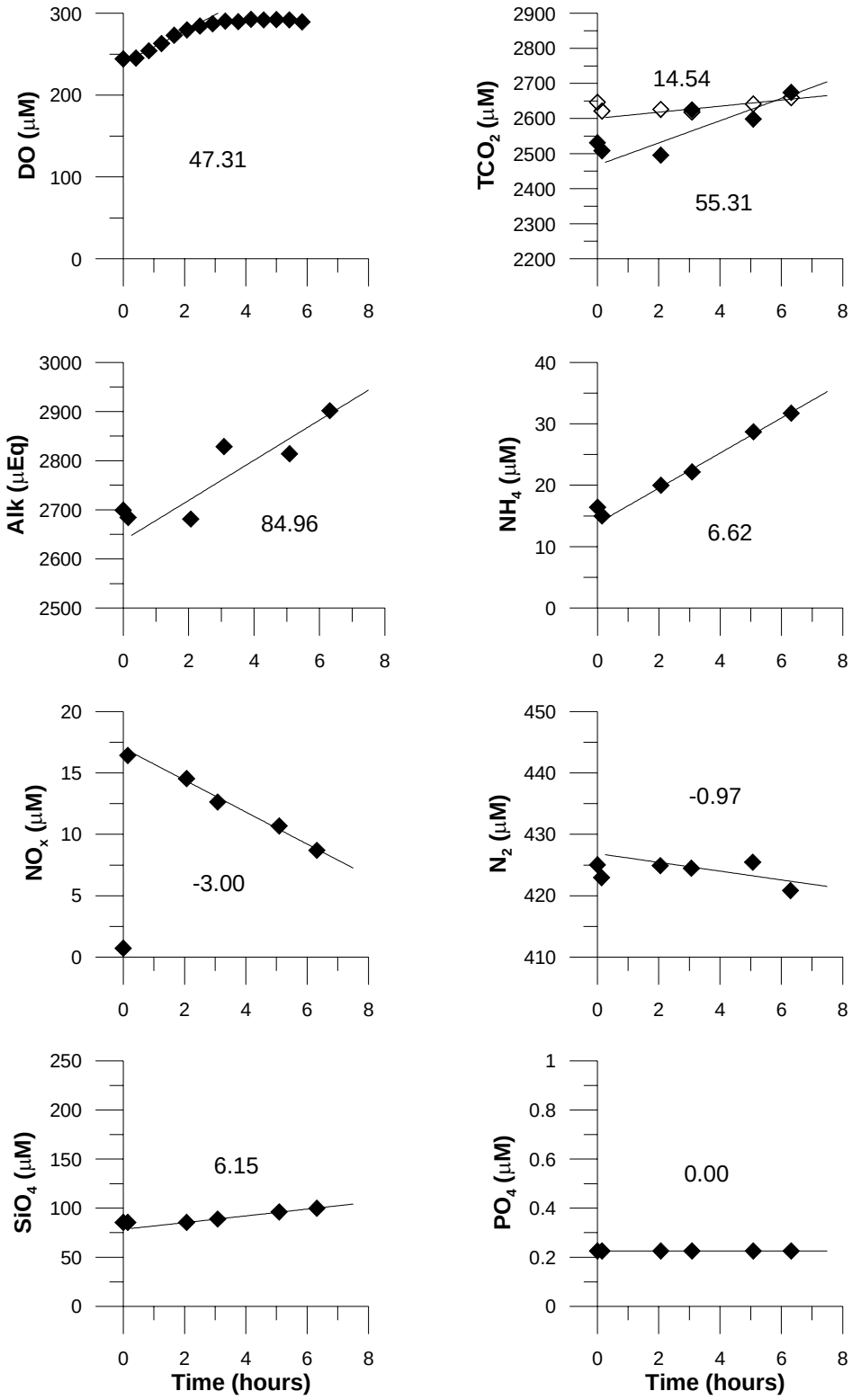
WE7 - 7



Light

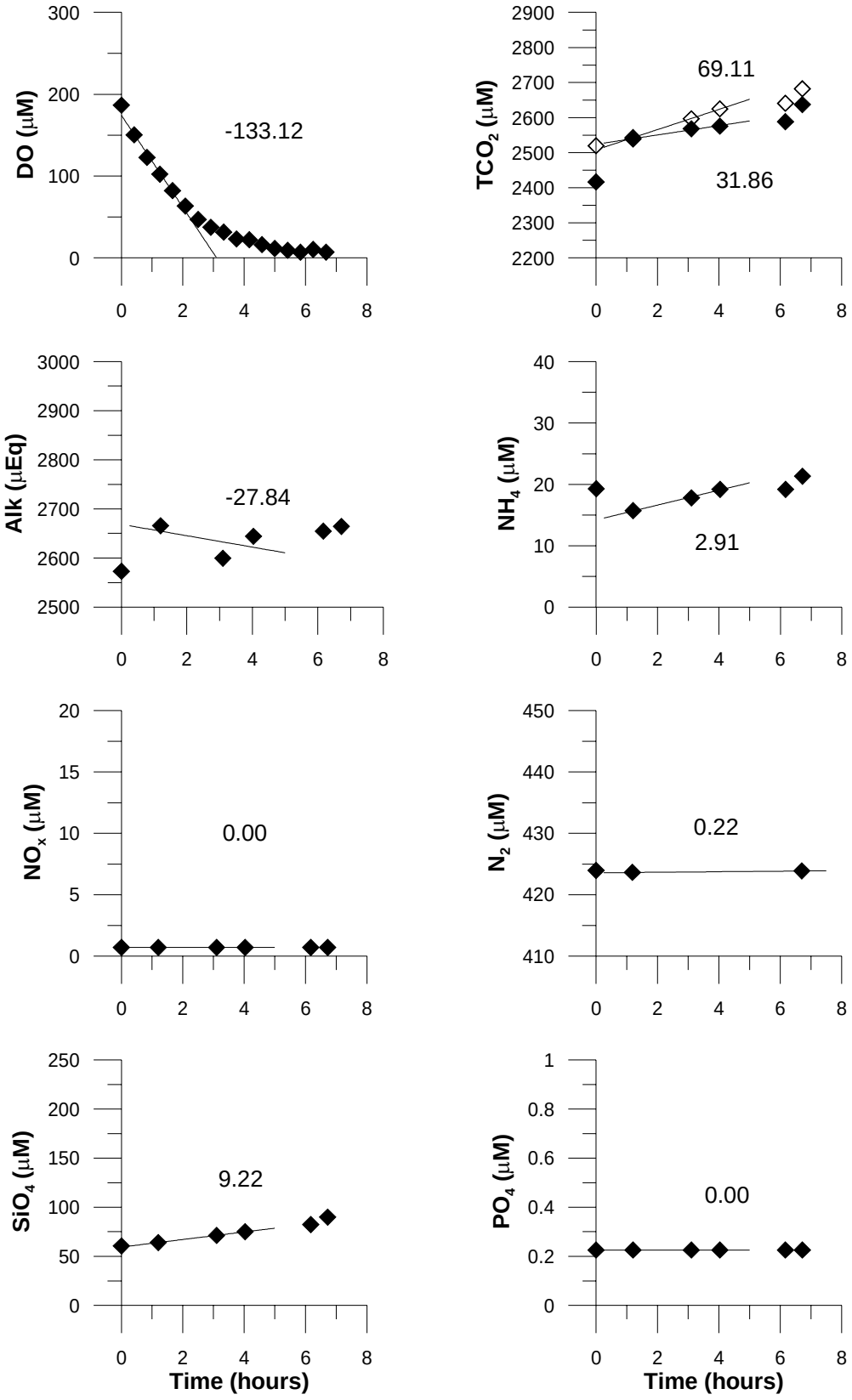
$^{15}NO_3$ Spike

WE7 - 9

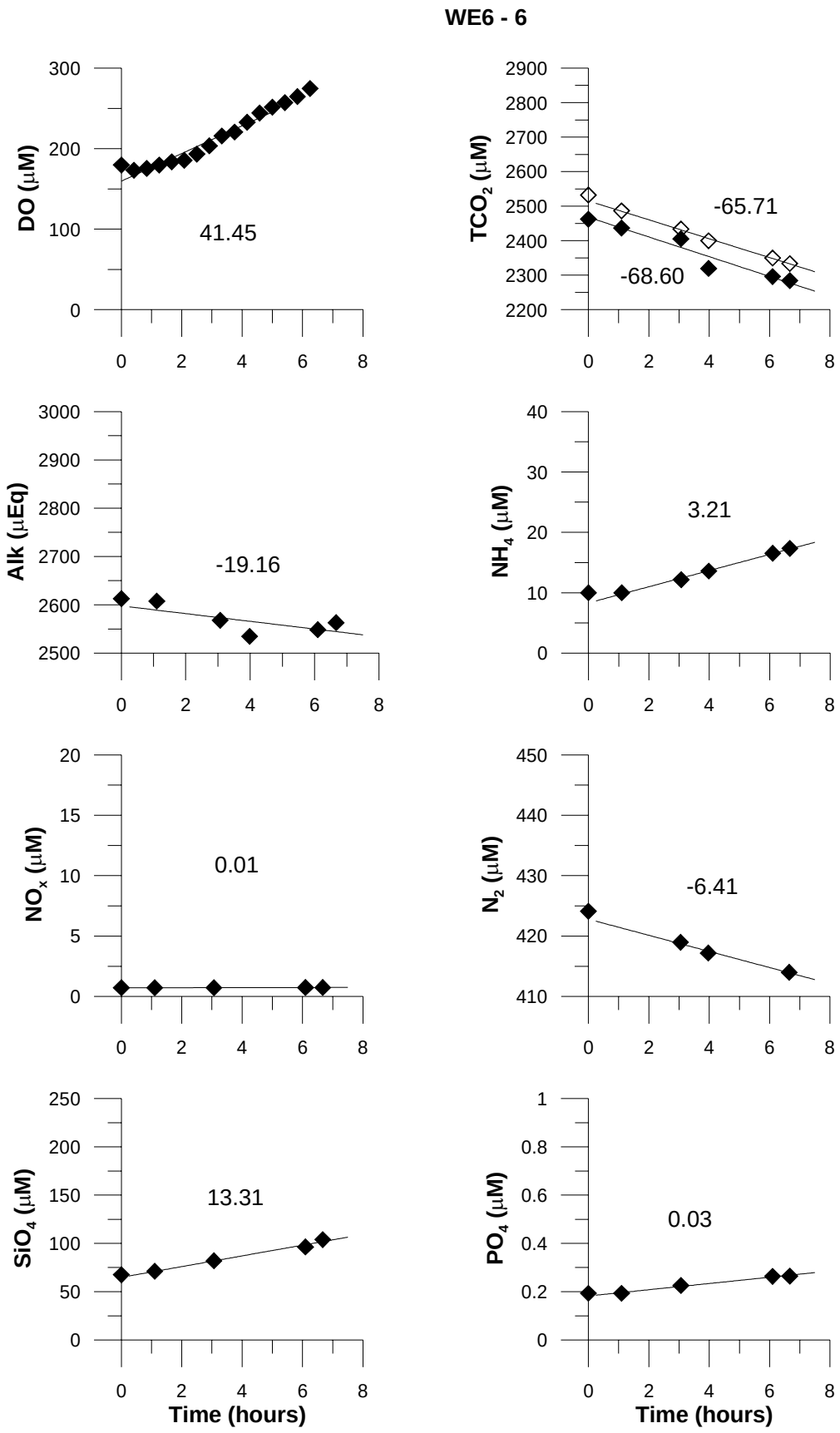


Dark

WE6 - 3

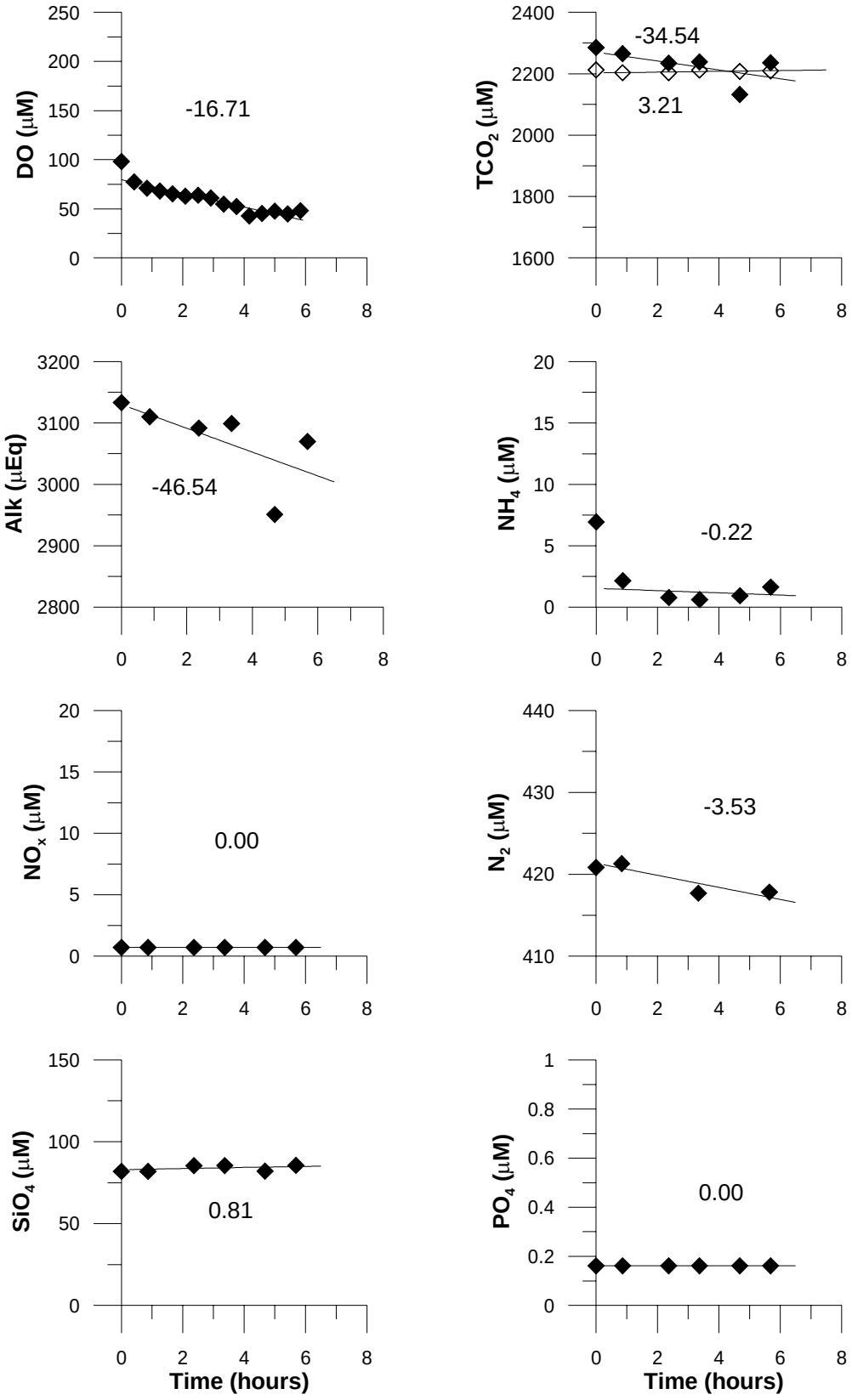

DO (μM)
-133.12
TCO2 (μM)
69.11
31.86
Alk (μEq)
-27.84
NH4 (μM)
2.91
NOx (μM)
0.00
N2 (μM)
0.22
SiO4 (μM)
9.22
PO4 (μM)
0.00
Time (hours)
Time (hours)

Light


WE6 - 6
DO (μM)
41.45
TCO2 (μM)
-65.71
-68.60
Alk (μEq)
-19.16
NH4 (μM)
3.21
NOx (μM)
0.01
N2 (μM)
-6.41
SiO4 (μM)
13.31
PO4 (μM)
0.03
Time (hours)
Time (hours)

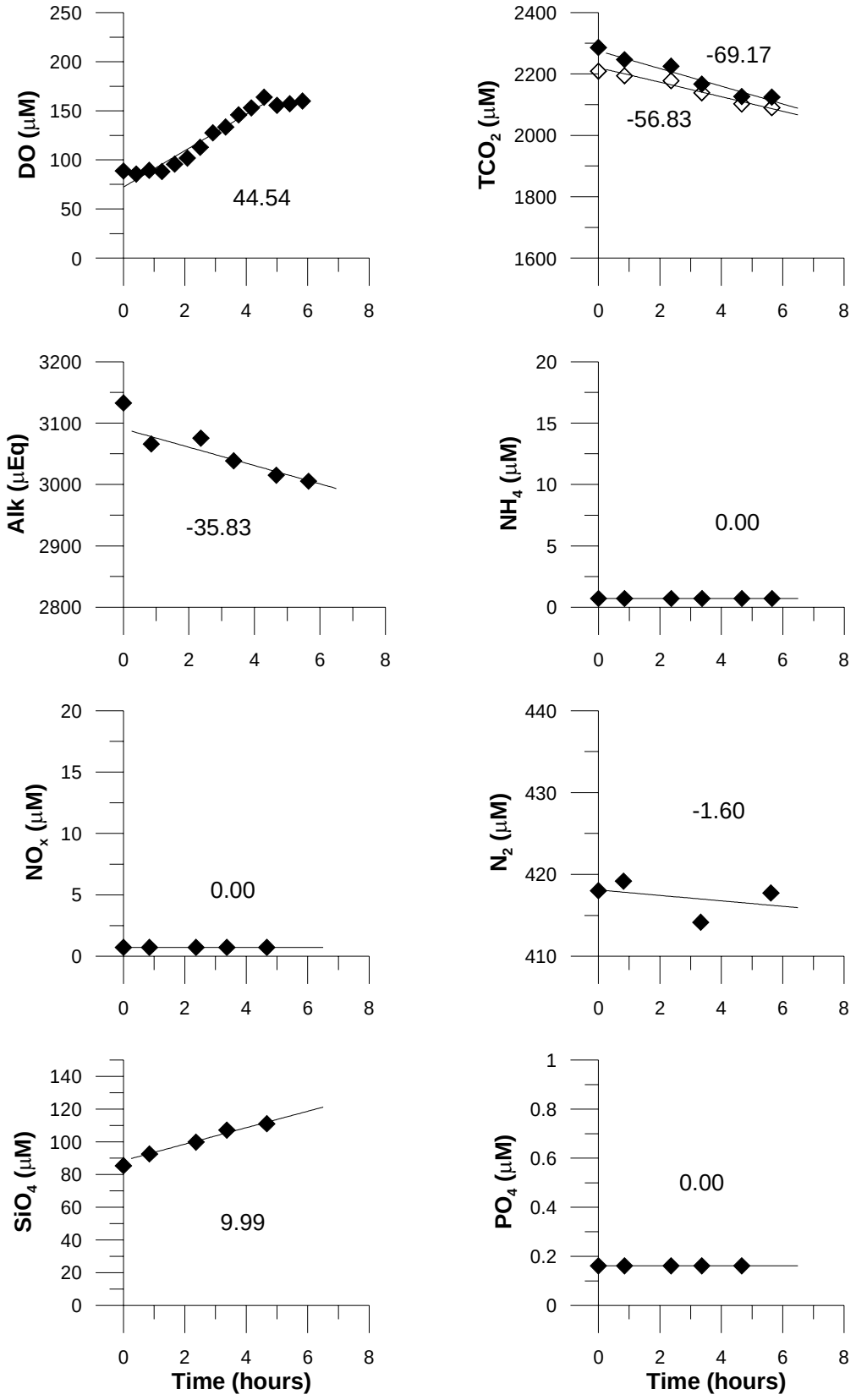
Dark

GO6 - 3


DO (μM)
-16.71
TCO2 (μM)
-34.54
3.21
Alk (μEq)
-46.54
NH4 (μM)
-0.22
NOx (μM)
0.00
N2 (μM)
-3.53
SiO4 (μM)
0.81
PO4 (μM)
0.00
Time (hours)
Time (hours)

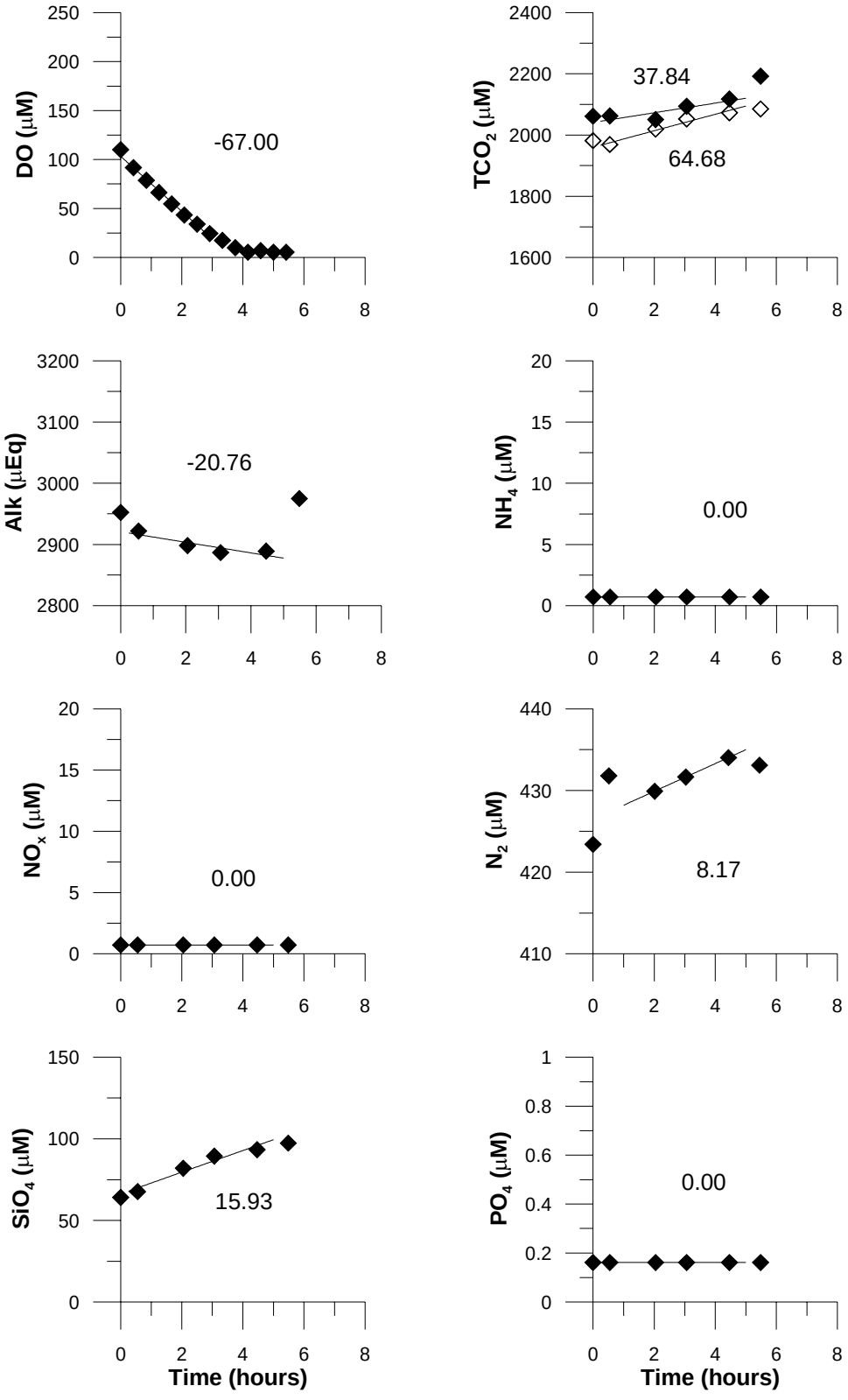
Light

GO6 - 6


DO (μM)
44.54
TCO2 (μM)
-69.17
-56.83
Alk (μEq)
-35.83
NH4 (μM)
0.00
NOx (μM)
0.00
N2 (μM)
-1.60
SiO4 (μM)
9.99
PO4 (μM)
0.00
Time (hours)
Time (hours)

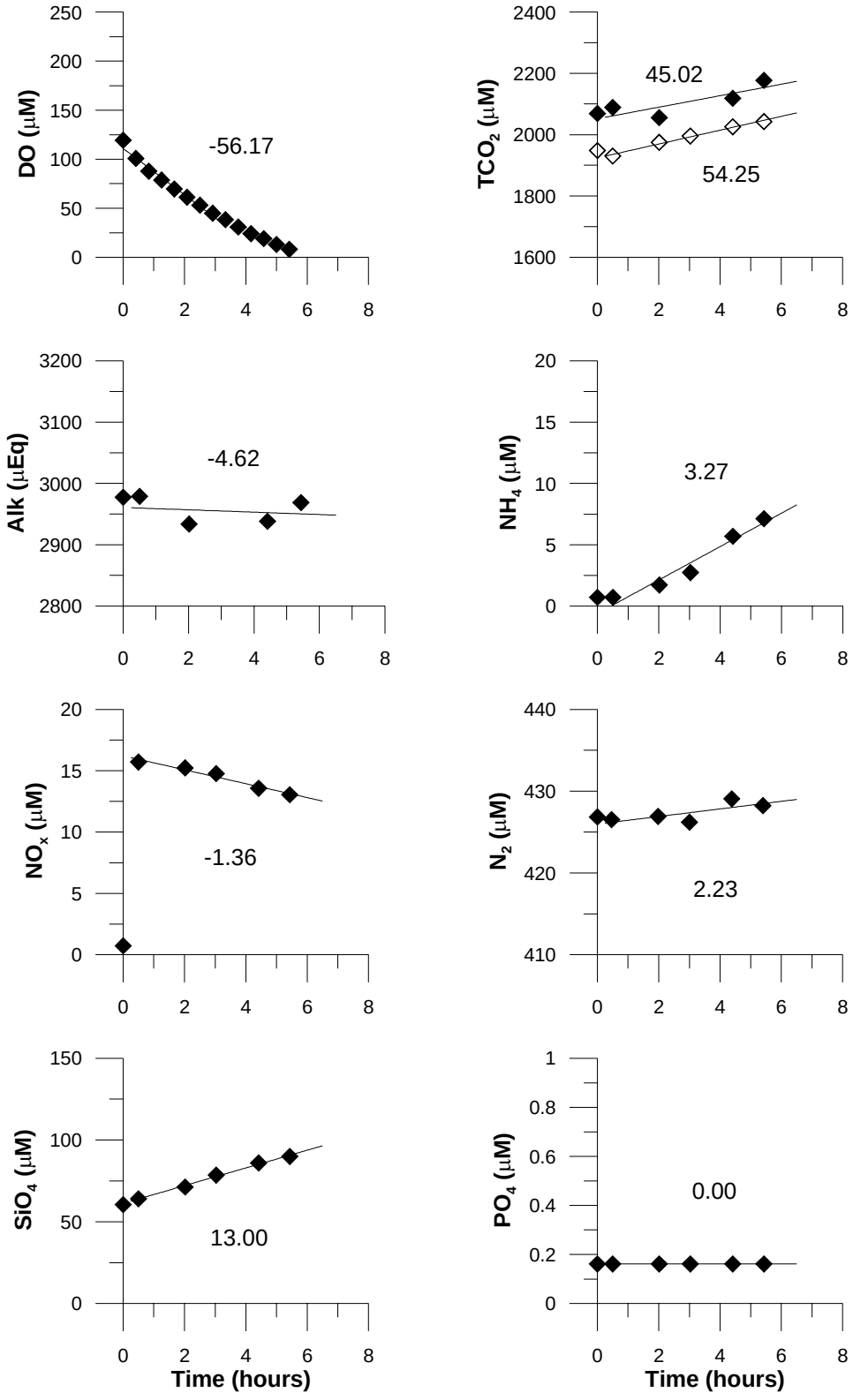
Dark
N_2 Spike

GO7 - 4



Dark
$^{15}NO_3$ Spike

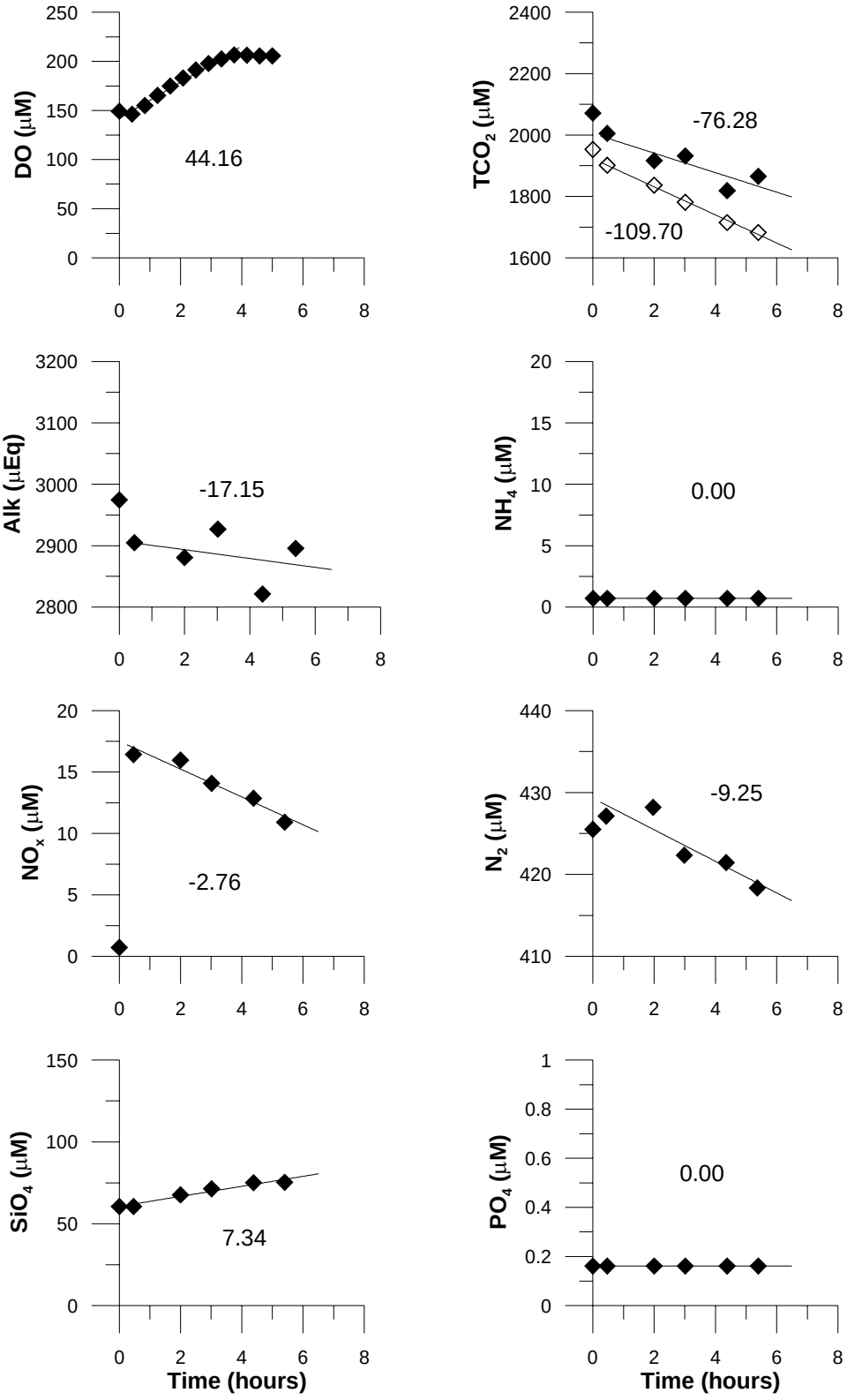
GO7 - 7



Light

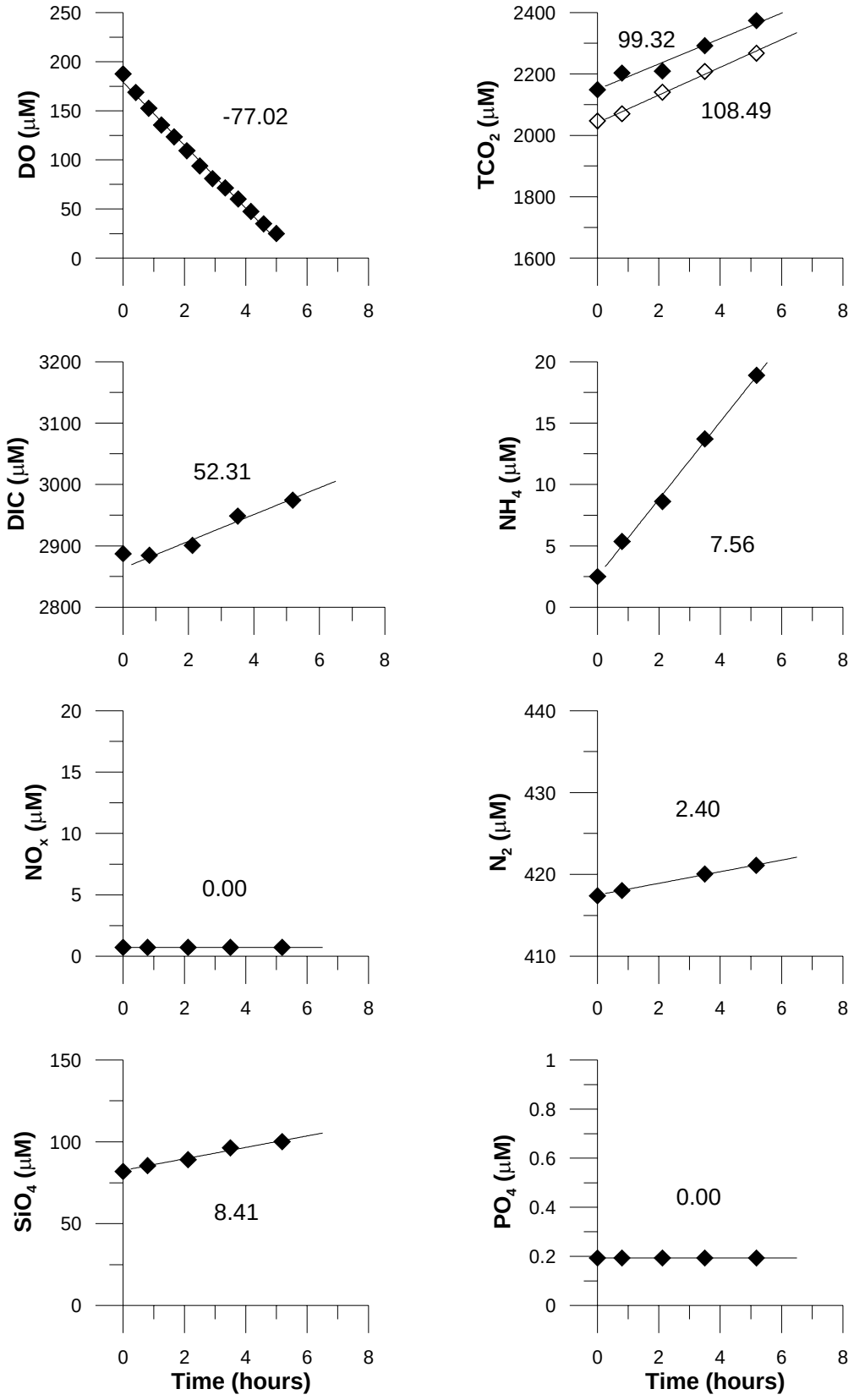
$^{15}NO_3$ Spike

GO7 - 9



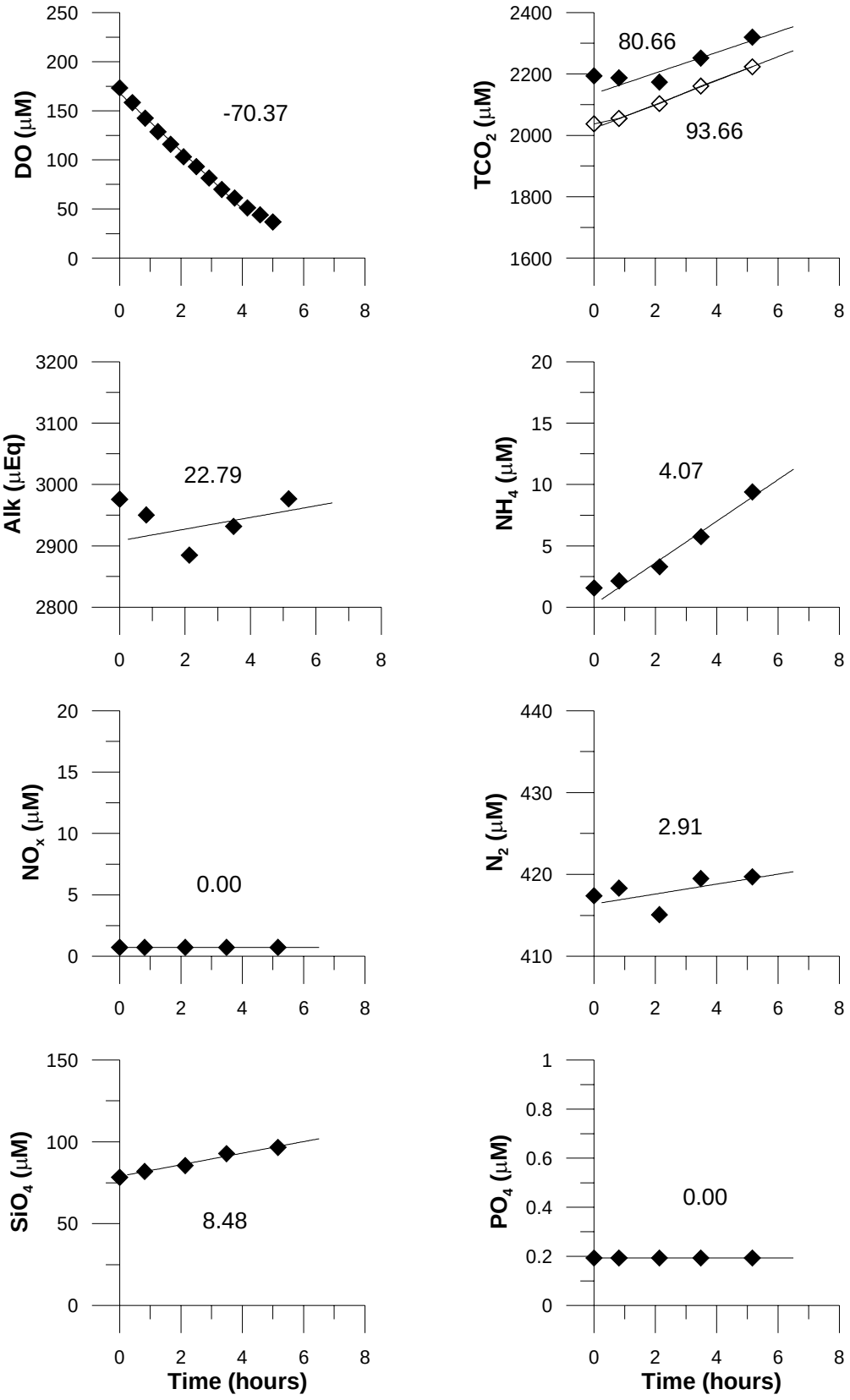
Dark

GO8 - 4


DO (μM)
-77.02
TCO2 (μM)
99.32
108.49
DIC (μM)
52.31
NH4 (μM)
7.56
NOx (μM)
0.00
N2 (μM)
2.40
SiO4 (μM)
8.41
PO4 (μM)
0.00
Time (hours)
Time (hours)

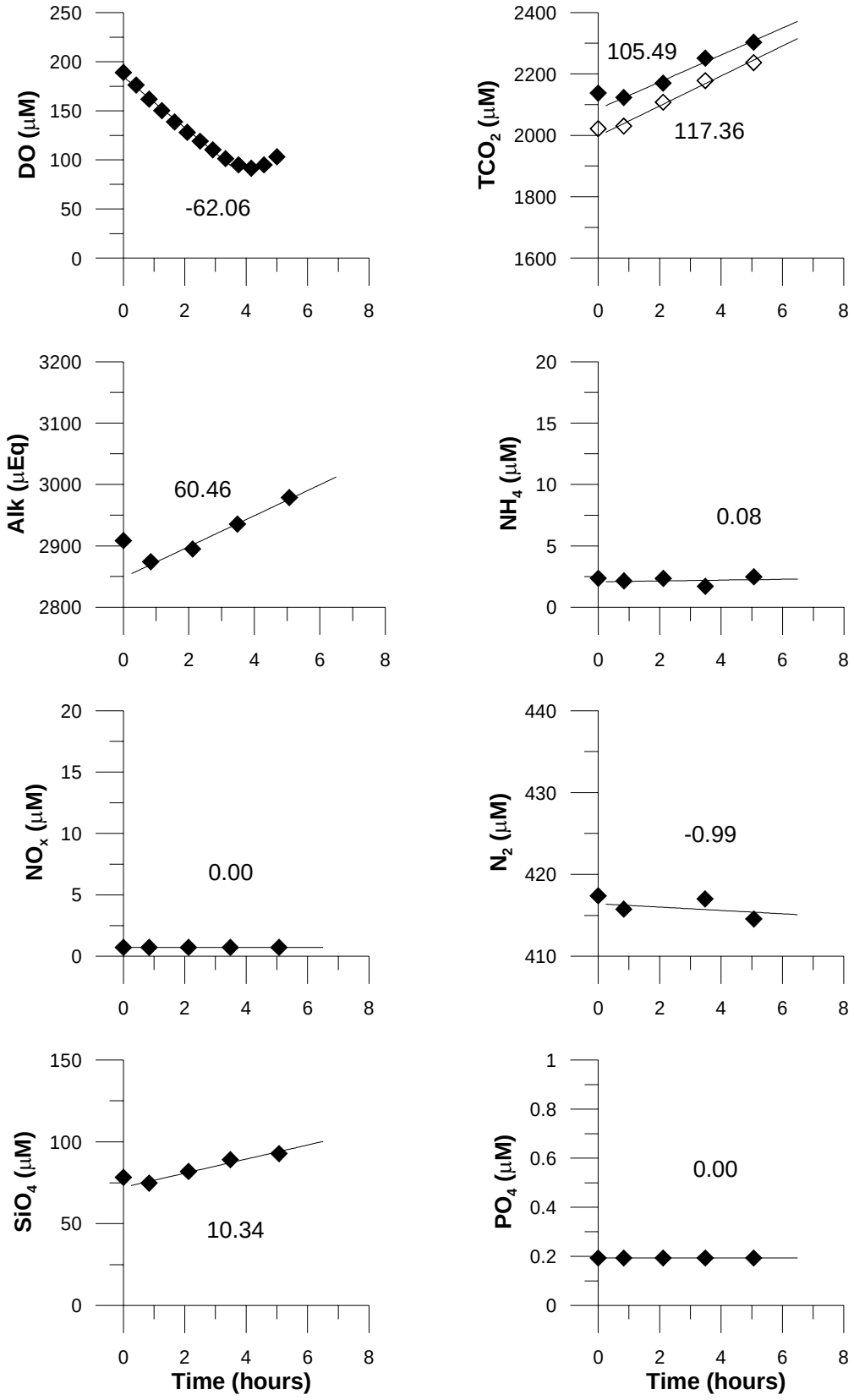
Dark

GO8 - 7


DO (μM)
-70.37
TCO2 (μM)
80.66
93.66
Alk (μEq)
22.79
NH4 (μM)
4.07
NOx (μM)
0.00
N2 (μM)
2.91
SiO4 (μM)
8.48
PO4 (μM)
0.00
Time (hours)
Time (hours)

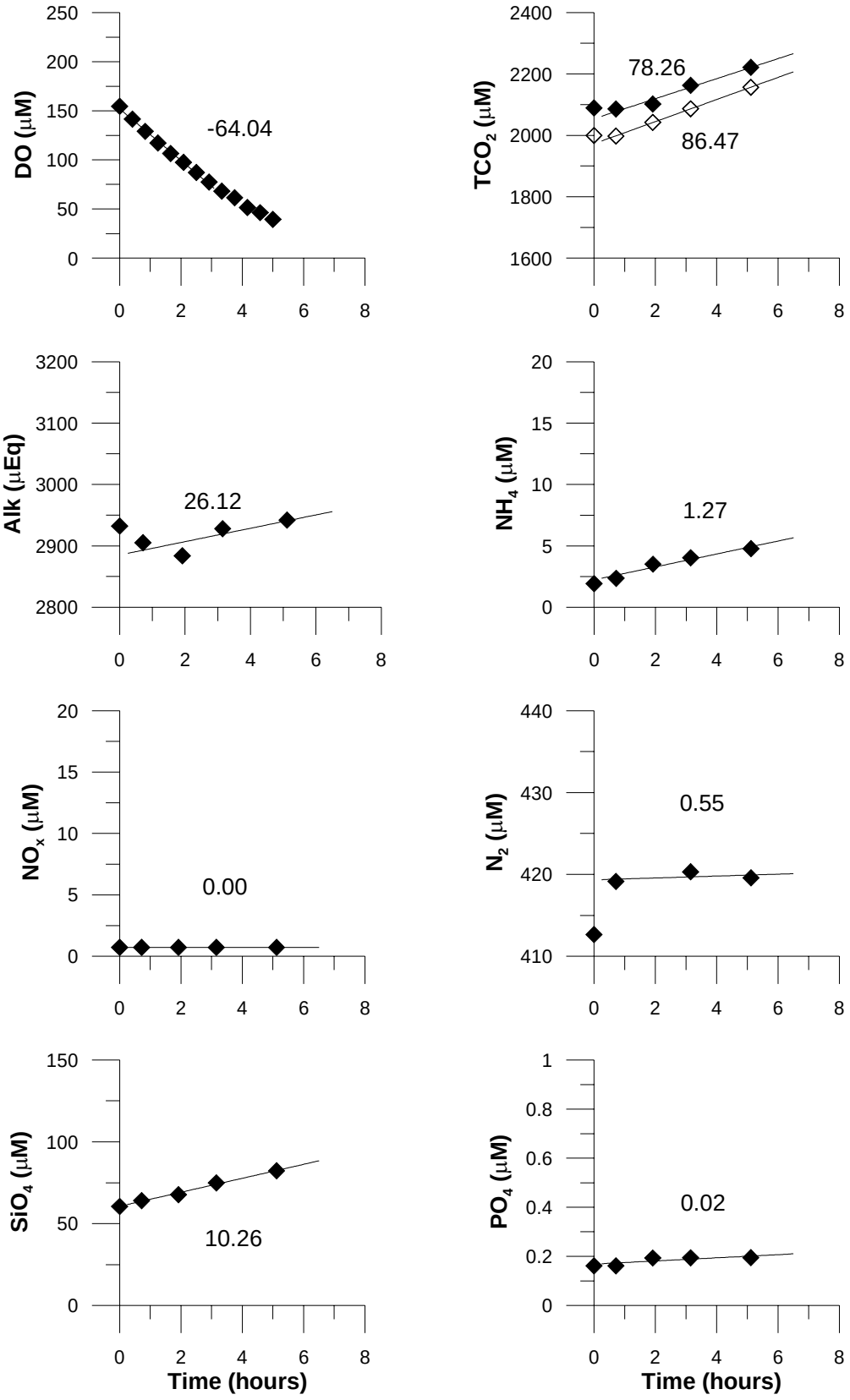
Light

GO8 - 9


DO (μM)
-62.06
TCO2 (μM)
105.49
117.36
Alk (μEq)
60.46
NH4 (μM)
0.08
NOx (μM)
0.00
N2 (μM)
-0.99
SiO4 (μM)
10.34
PO4 (μM)
0.00
Time (hours)
Time (hours)

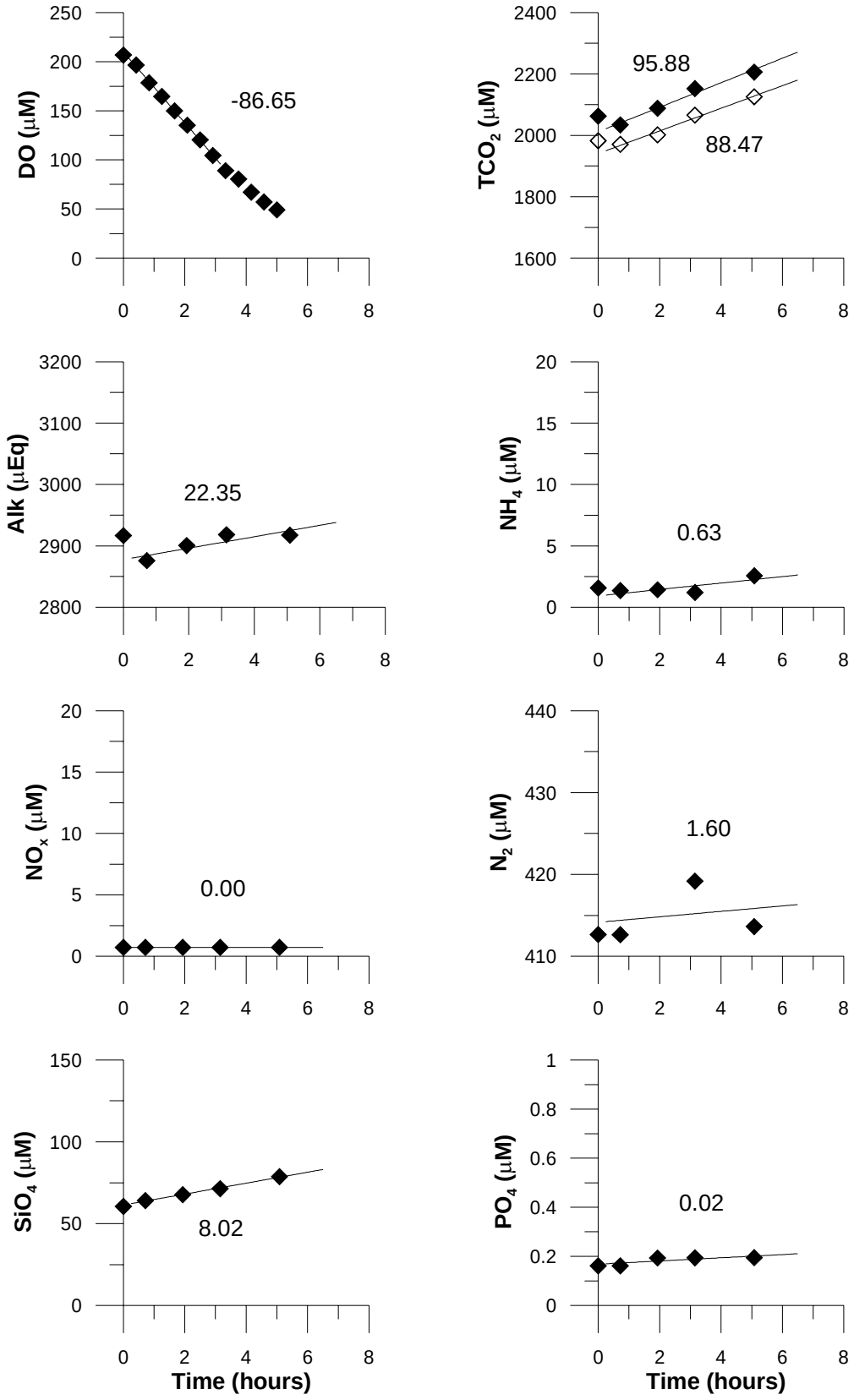
Dark

GO9 - 3


DO (μM)
-64.04
TCO2 (μM)
78.26
86.47
Alk (μEq)
26.12
NH4 (μM)
1.27
NOx (μM)
0.00
N2 (μM)
0.55
SiO4 (μM)
10.26
PO4 (μM)
0.02
Time (hours)
Time (hours)

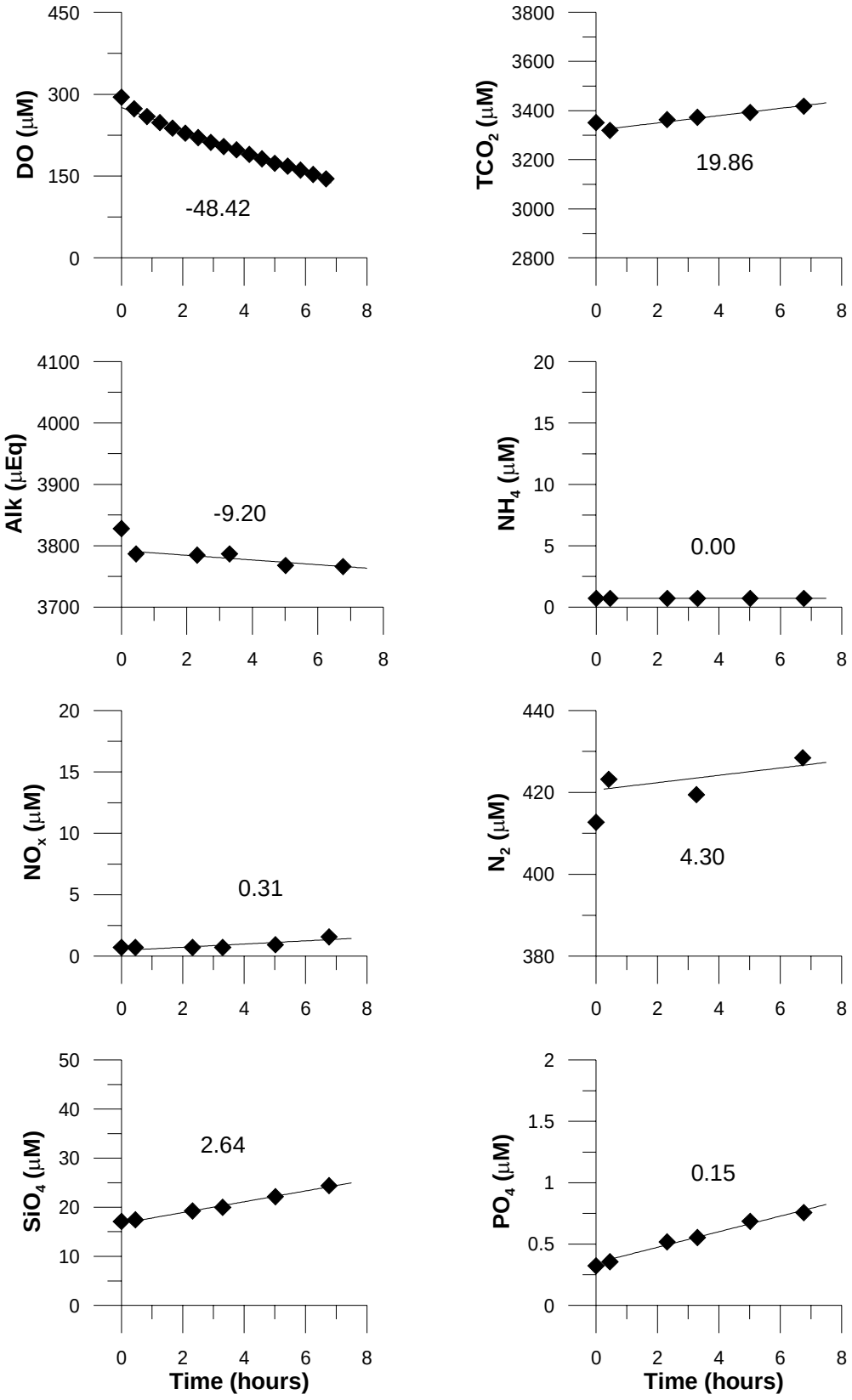
Light

GO9 - 6


DO (μM)
-86.65
TCO2 (μM)
95.88
88.47
Alk (μEq)
22.35
NH4 (μM)
0.63
NOx (μM)
0.00
N2 (μM)
1.60
SiO4 (μM)
8.02
PO4 (μM)
0.02
Time (hours)
Time (hours)

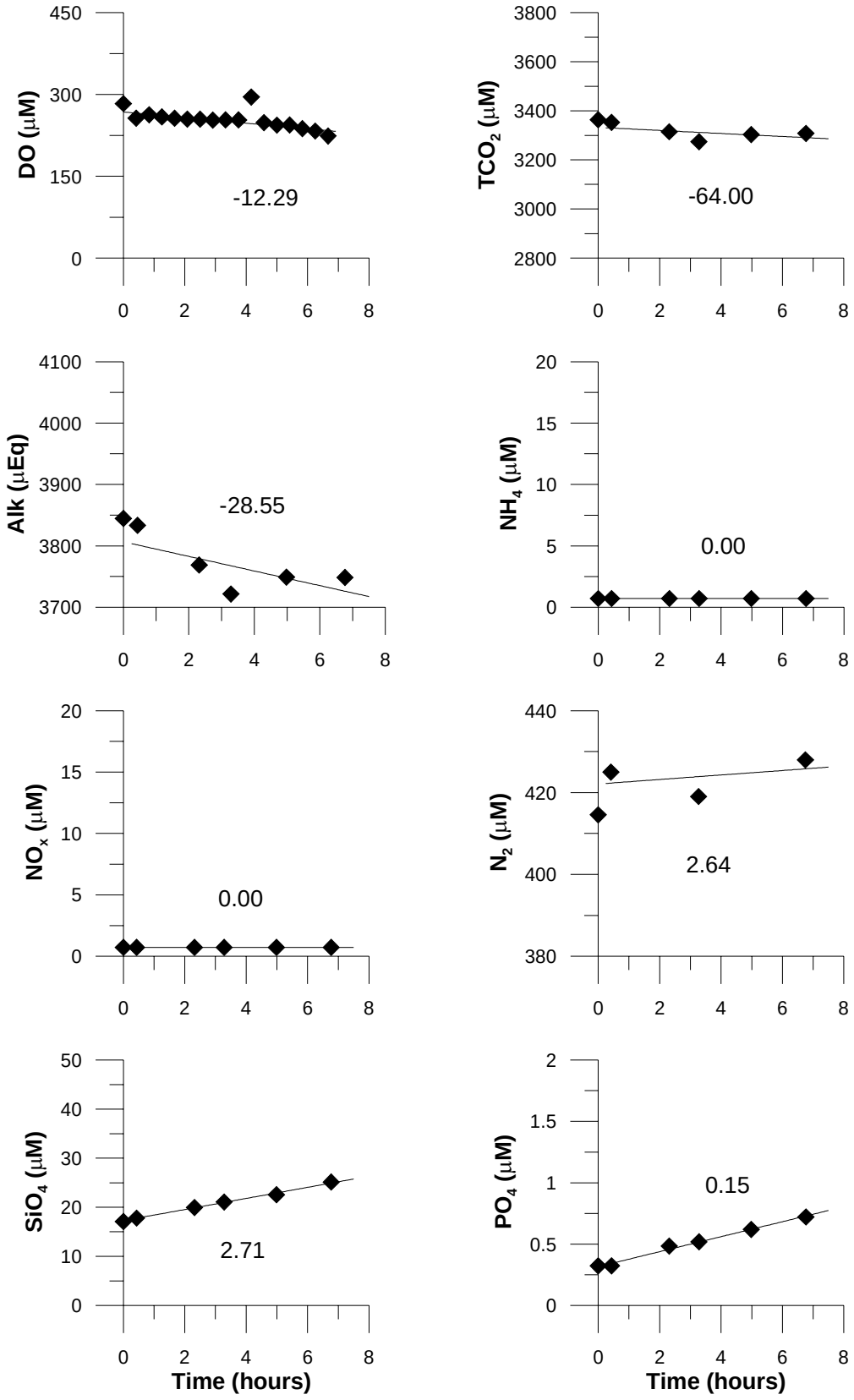
Dark

BE9 - 3


DO (μM)
-48.42
TCO2 (μM)
19.86
Alk (μEq)
-9.20
NH4 (μM)
0.00
NOx (μM)
0.31
N2 (μM)
4.30
SiO4 (μM)
2.64
PO4 (μM)
0.15
Time (hours)
Time (hours)

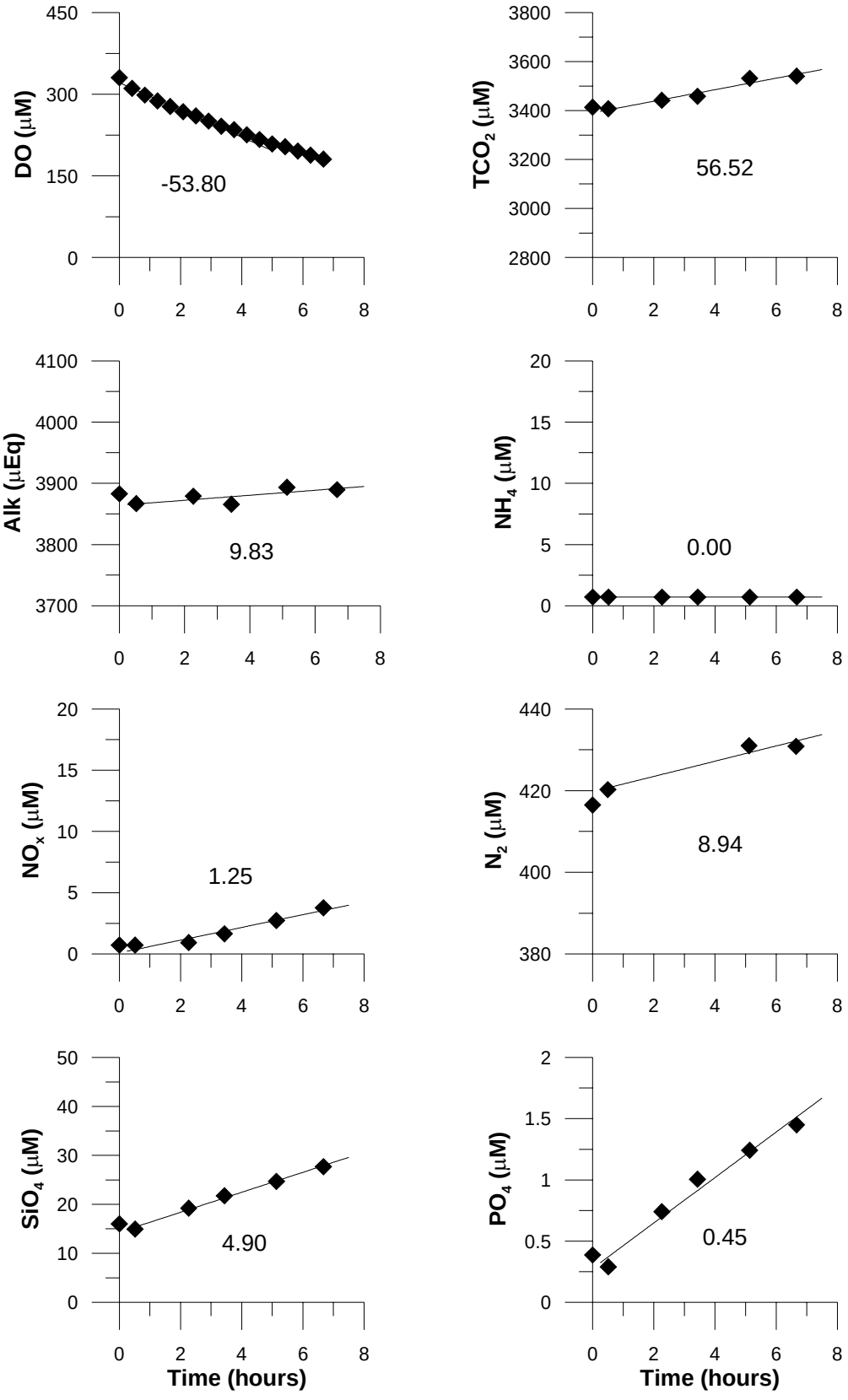
Light

BE9 - 6


DO (μM)
-12.29
TCO2 (μM)
-64.00
Alk (μEq)
-28.55
NH4 (μM)
0.00
NOx (μM)
0.00
N2 (μM)
2.64
SiO4 (μM)
2.71
PO4 (μM)
0.15
Time (hours)
Time (hours)

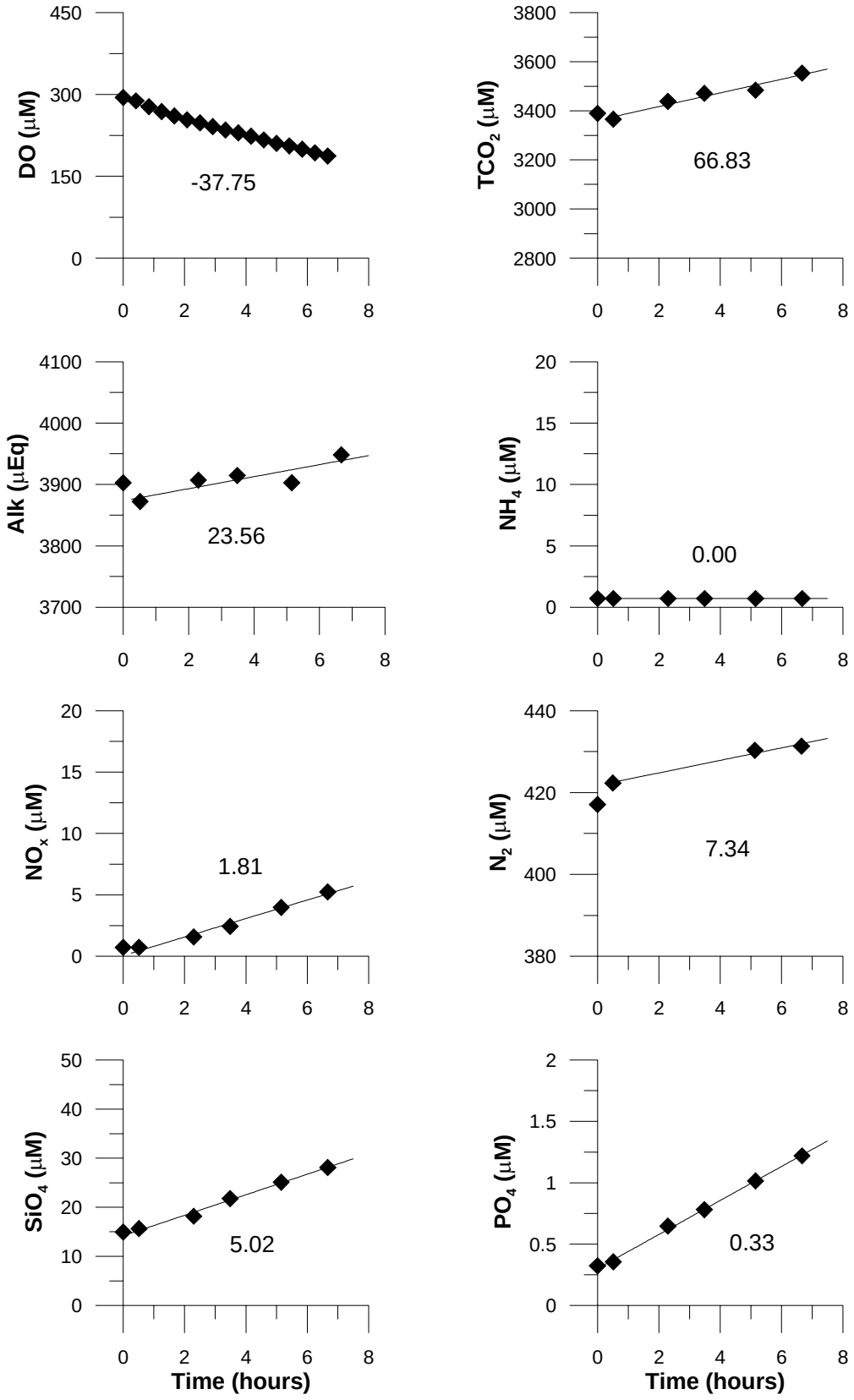
Dark

BE7 - 4


DO (μM)
-53.80
TCO2 (μM)
56.52
Alk (μEq)
9.83
NH4 (μM)
0.00
NOx (μM)
1.25
N2 (μM)
8.94
SiO4 (μM)
4.90
PO4 (μM)
0.45
Time (hours)
Time (hours)

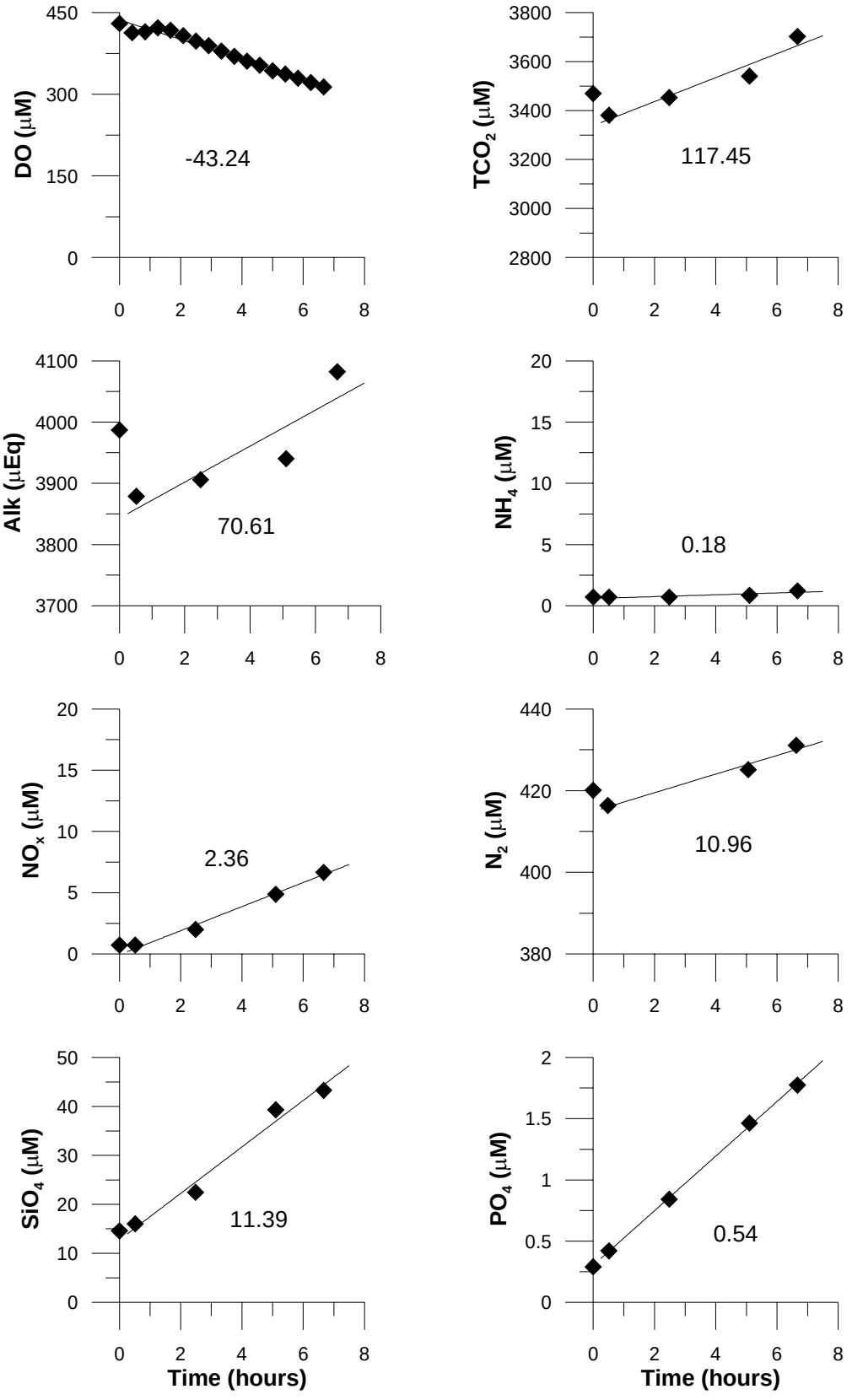
Dark

BE7 - 7


DO (μM)
-37.75
TCO2 (μM)
66.83
Alk (μEq)
23.56
NH4 (μM)
0.00
NOx (μM)
1.81
N2 (μM)
7.34
SiO4 (μM)
5.02
PO4 (μM)
0.33
Time (hours)
Time (hours)

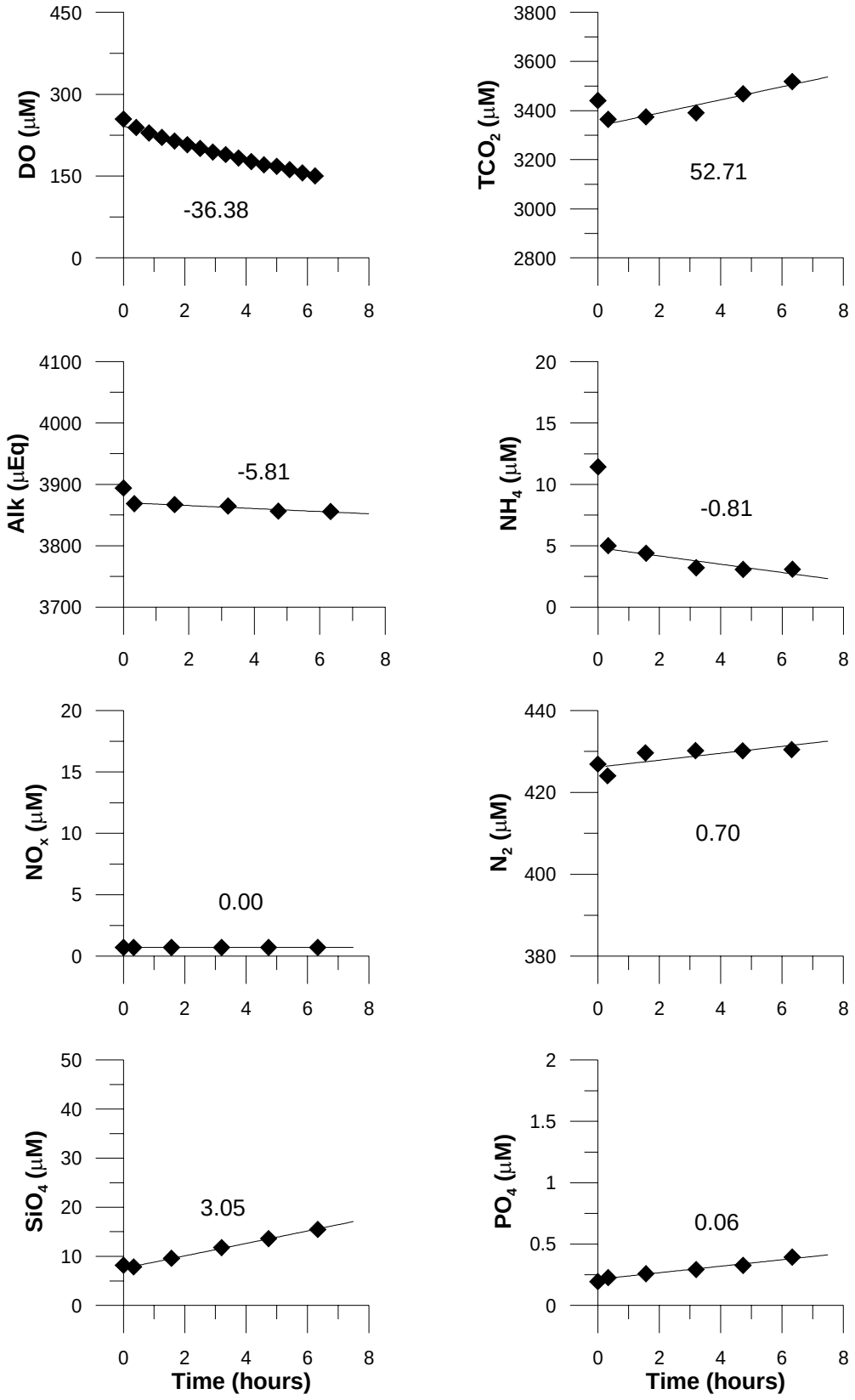
Light

BE7 - 9

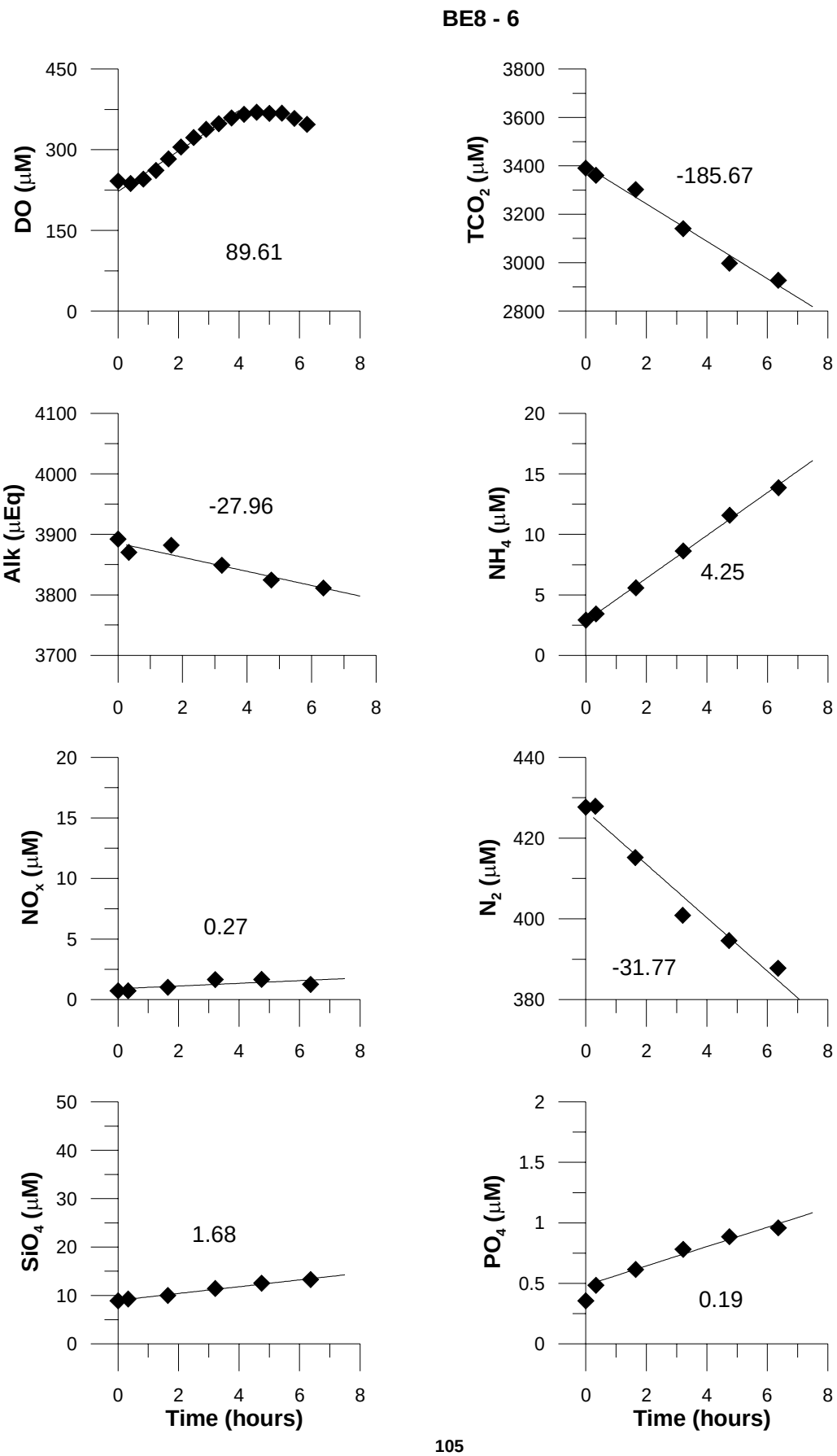

DO (μM)
-43.24
TCO2 (μM)
117.45
Alk (μEq)
70.61
NH4 (μM)
0.18
NOx (μM)
2.36
N2 (μM)
10.96
SiO4 (μM)
11.39
PO4 (μM)
0.54
Time (hours)
Time (hours)

Dark

BE8 - 3


DO (μM)
-36.38
TCO2 (μM)
52.71
Alk (μEq)
-5.81
NH4 (μM)
-0.81
NOx (μM)
0.00
N2 (μM)
0.70
SiO4 (μM)
3.05
PO4 (μM)
0.06
Time (hours)
Time (hours)

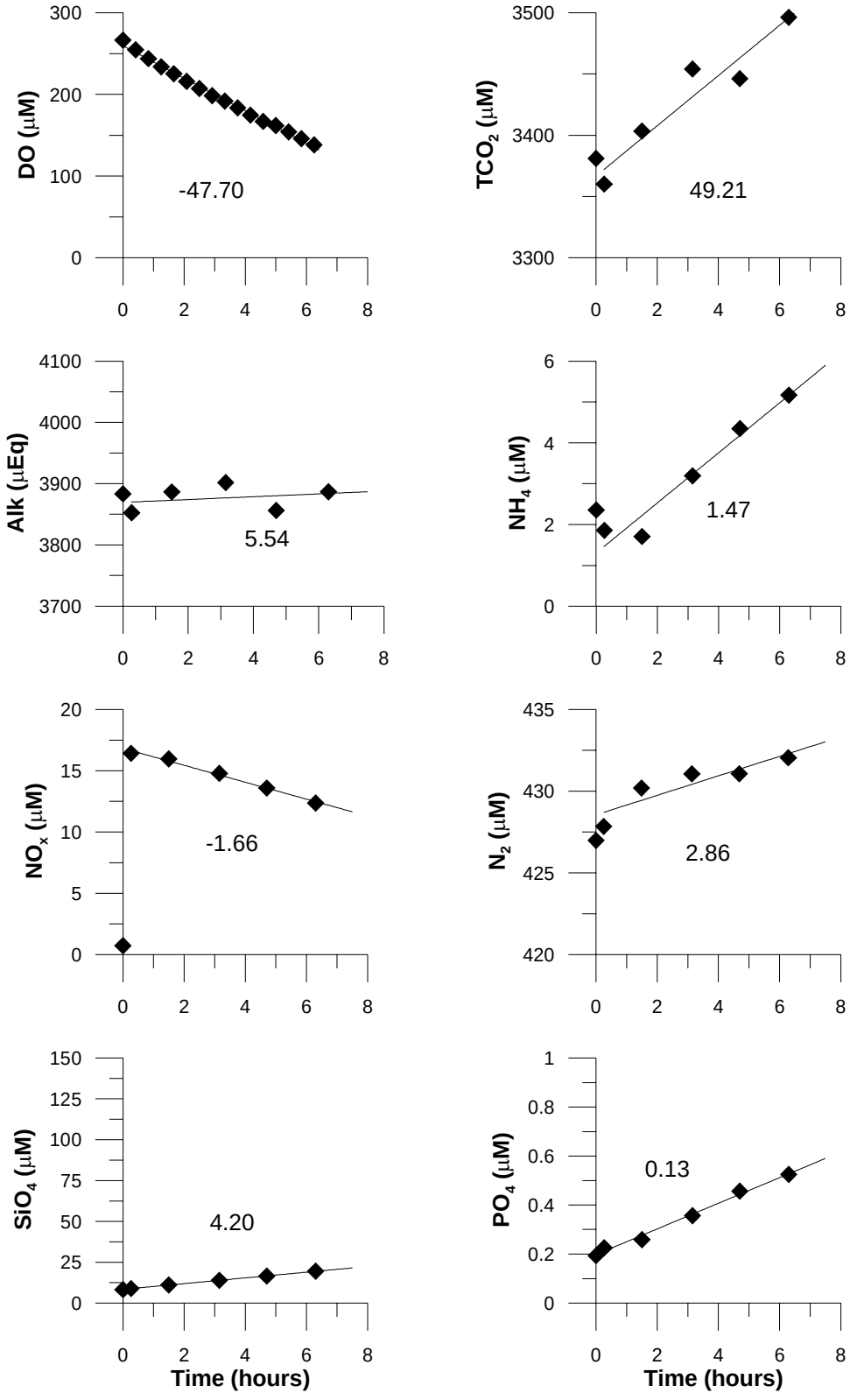
Light


BE8 - 6
DO (μM)
89.61
TCO2 (μM)
-185.67
Alk (μEq)
-27.96
NH4 (μM)
4.25
NOx (μM)
0.27
N2 (μM)
-31.77
SiO4 (μM)
1.68
PO4 (μM)
0.19
Time (hours)
Time (hours)

Dark

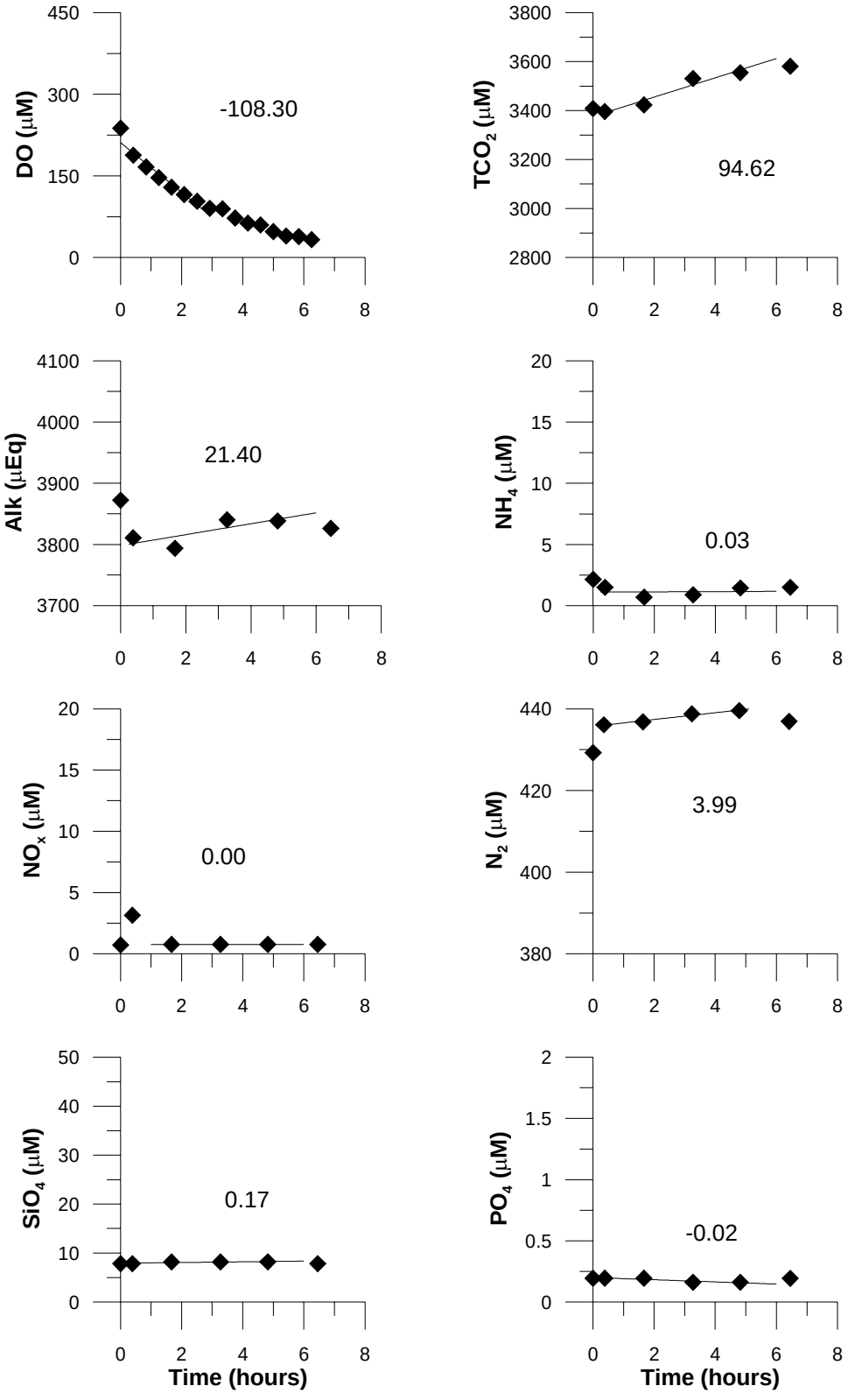
$^{15}NO_3$ Spike

BE8 - 4



Dark
N_2 Spike

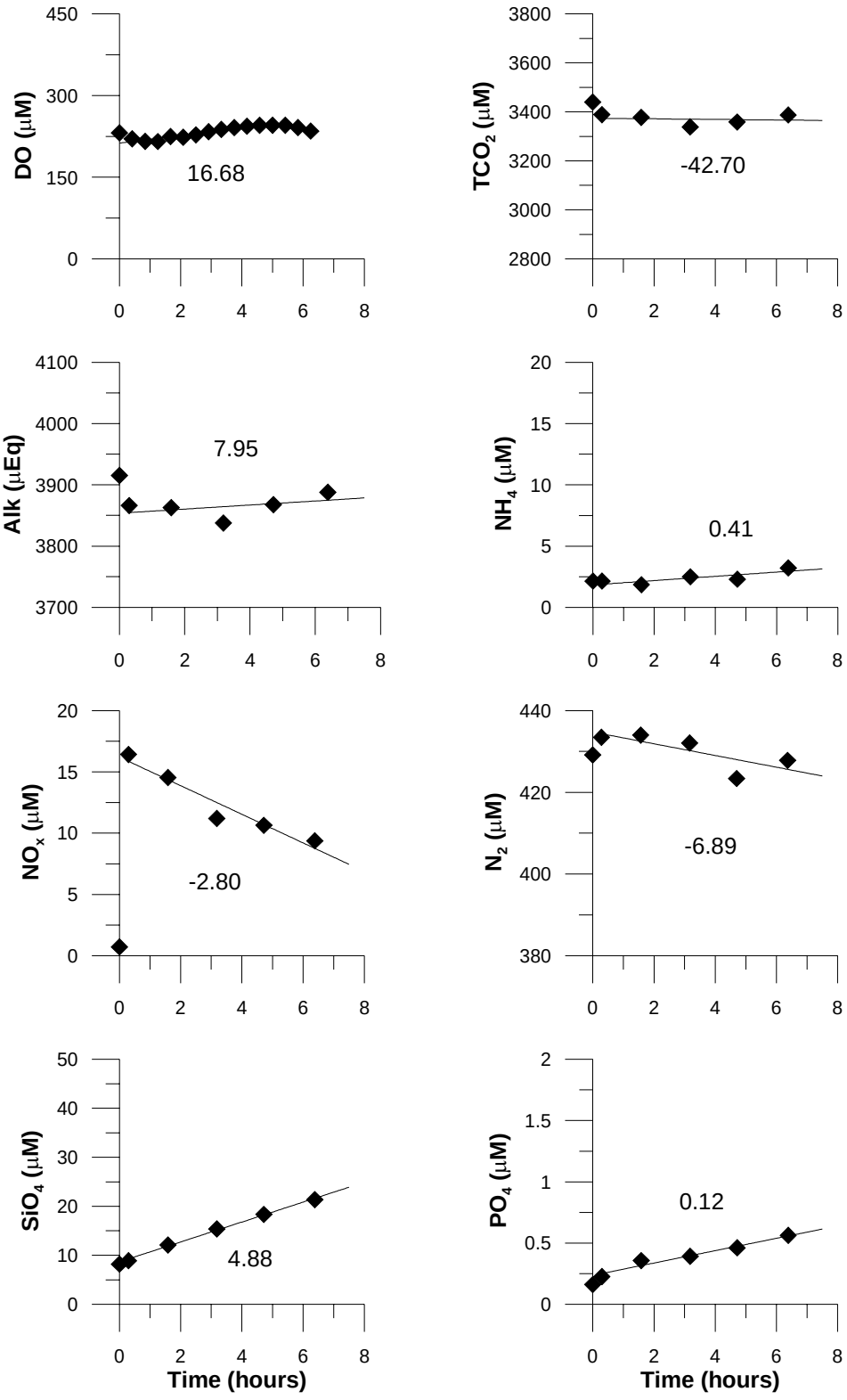
BE8 - 7



Light

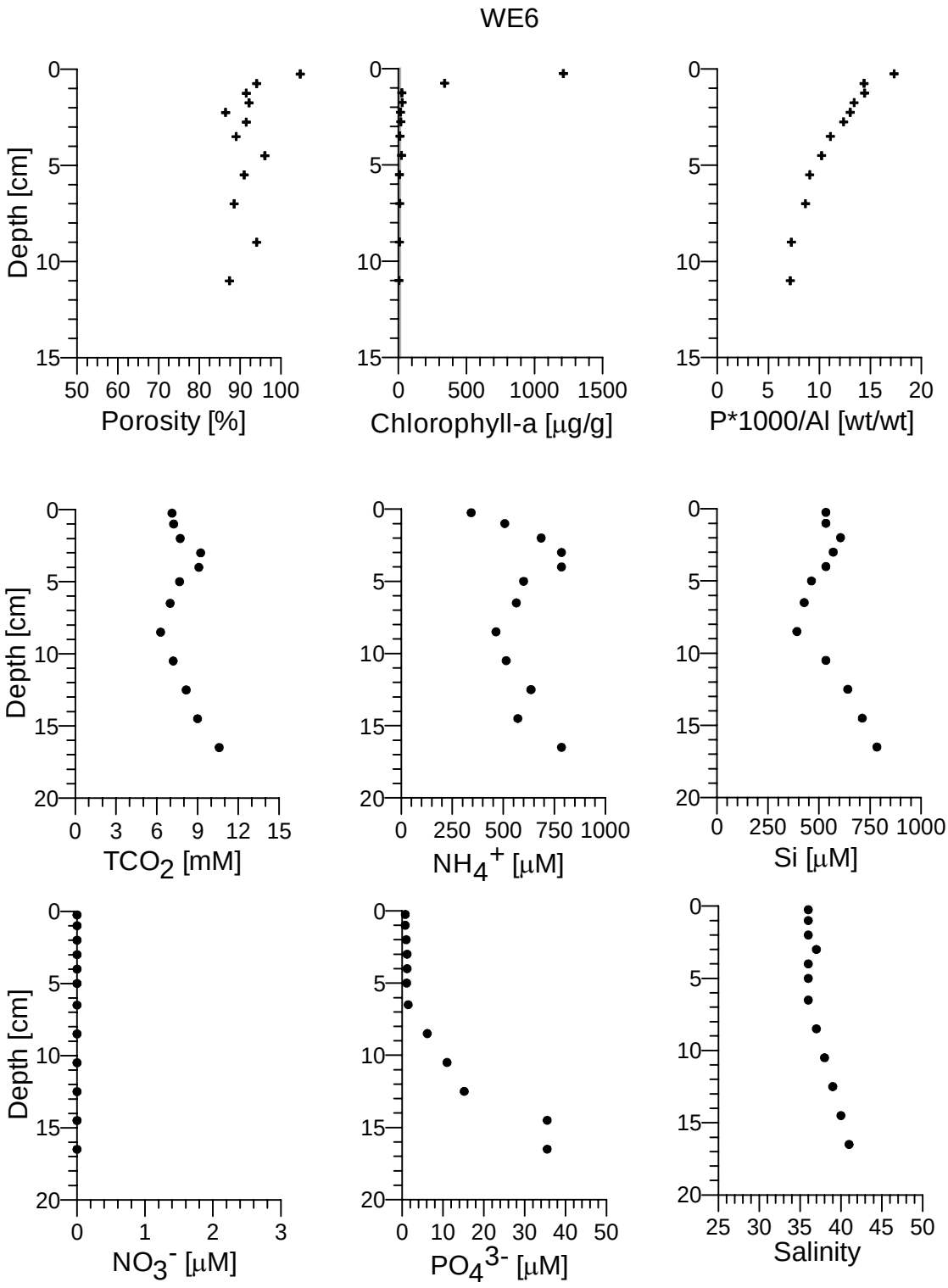
$^{15}NO_3$ Spike

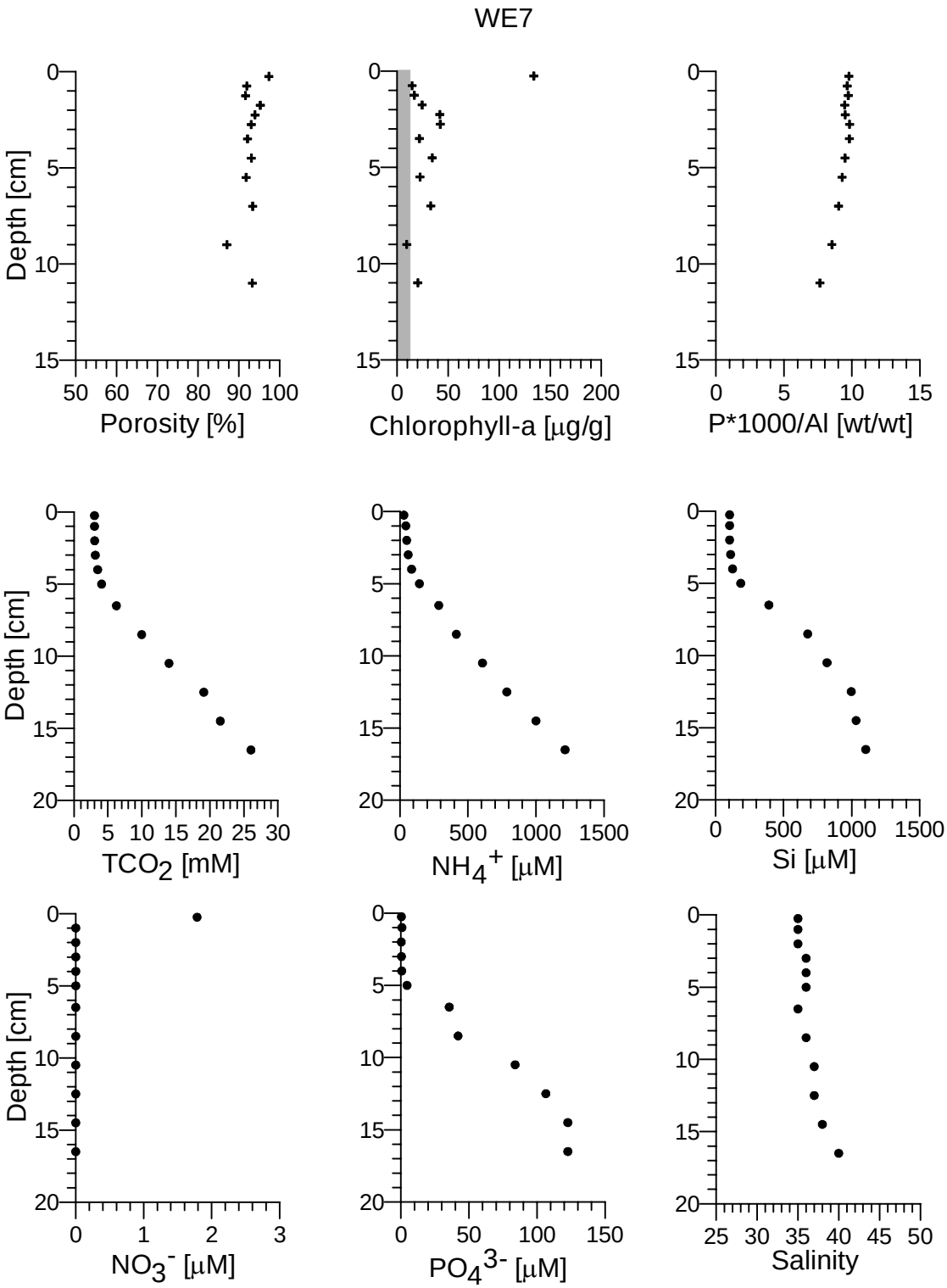
BE8 - 9

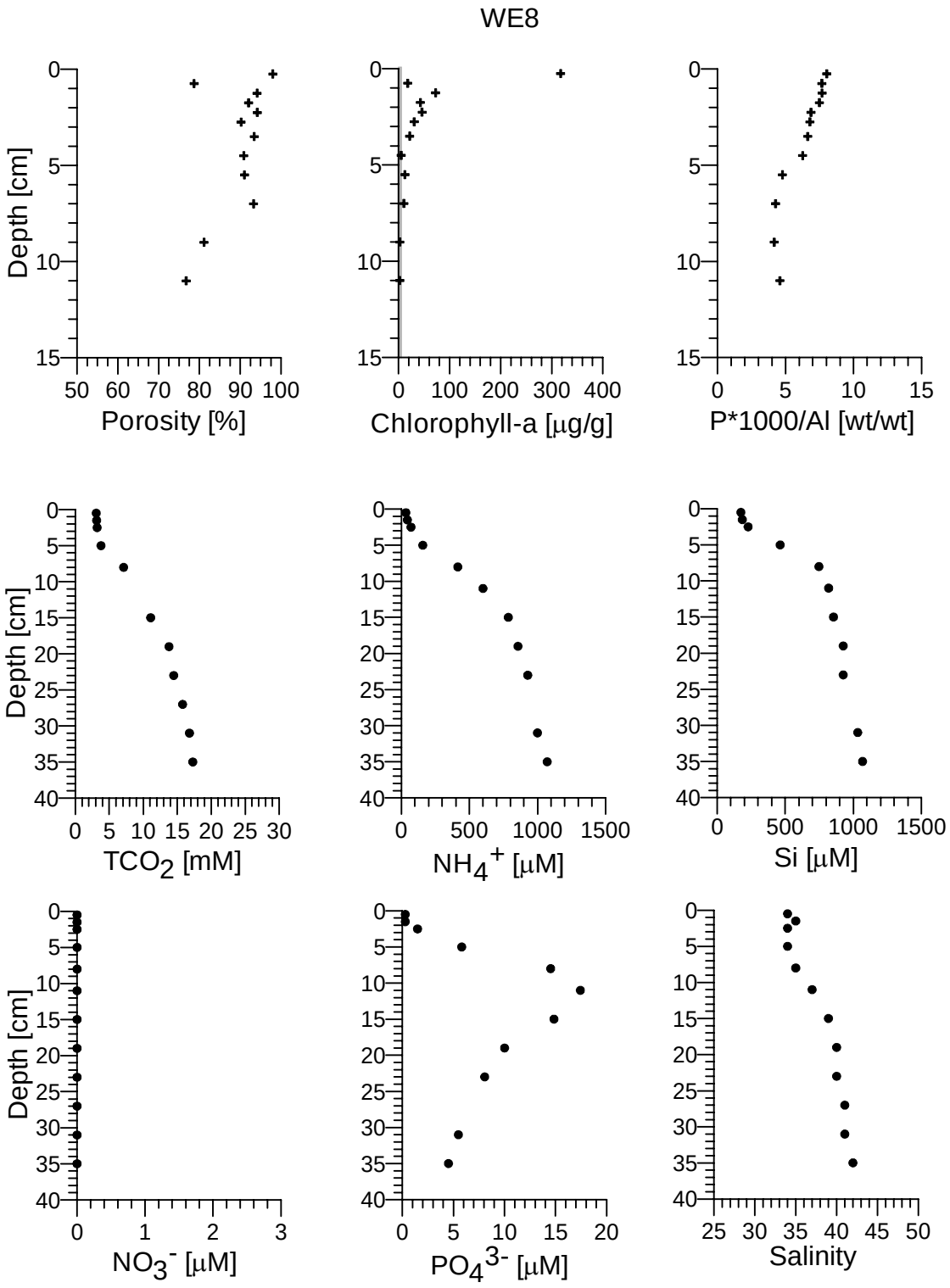


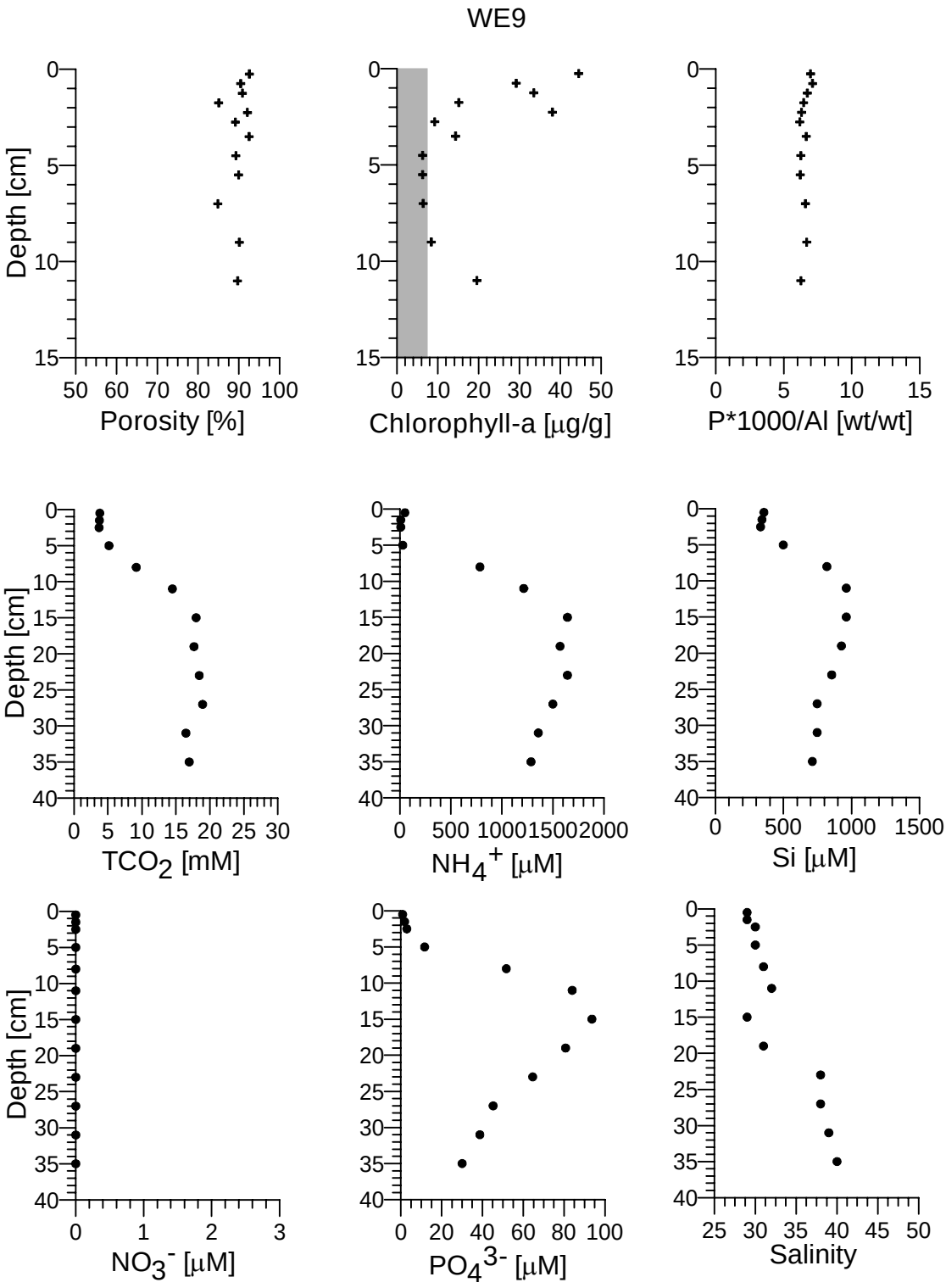
Appendix 6 – Down Core Pore Water and Solid Phase Plots

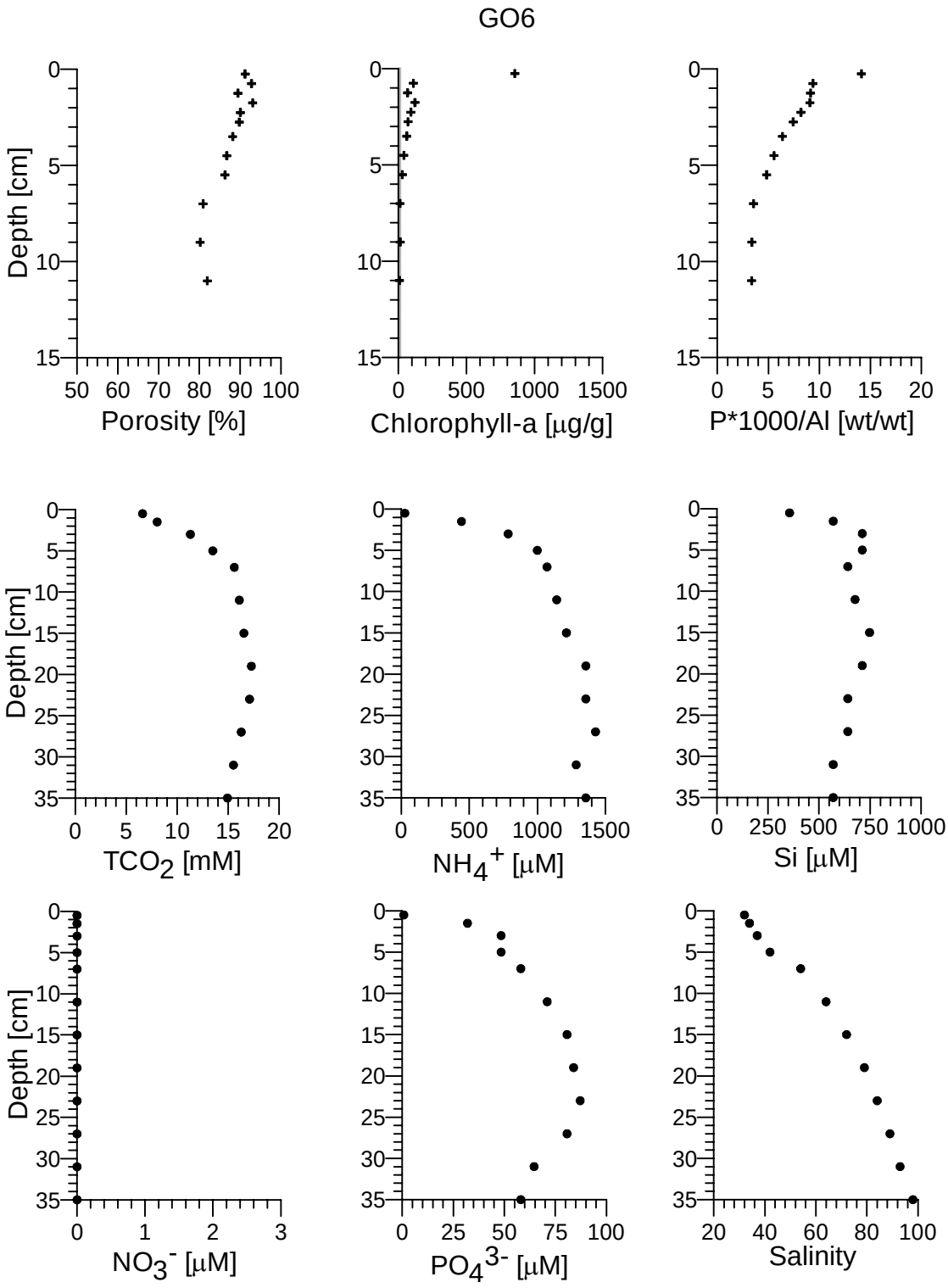
Note that for each parameter, the x-axis scale is not kept constant, and varies between sites. For example, the scale for Chlorophyll-a ranges between 0 and 1500 µg/g for Wellstead Site 6, whereas it ranges between 0 and 200 µg/g for Wellstead Site 7.

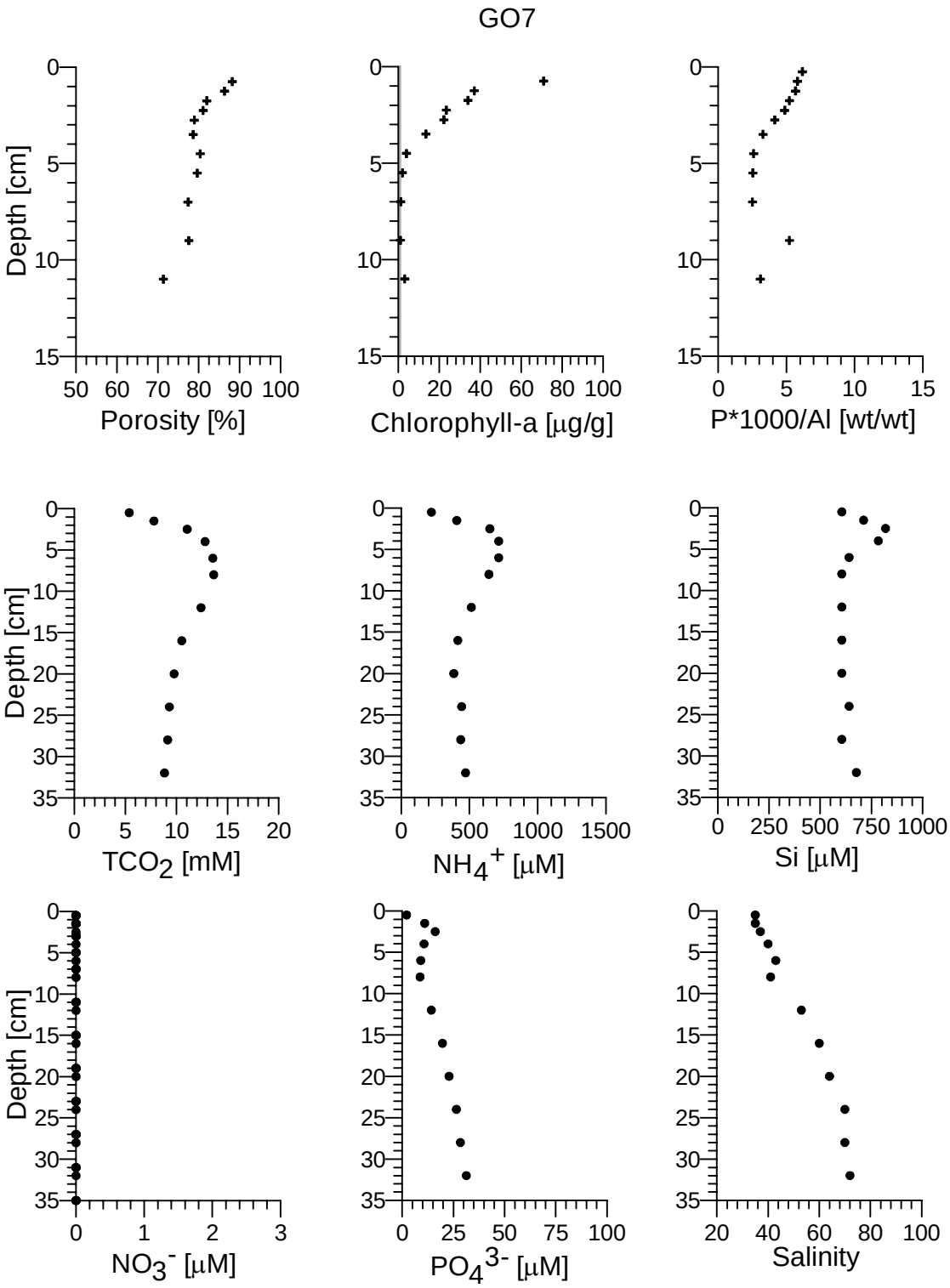

WE6
Depth [cm]
Porosity [%]
Chlorophyll-a [μg/g]
P*1000/Al [wt/wt]
TCO2 [mM]
NH4+ [μM]
Si [μM]
NO3- [μM]
PO43- [μM]
Salinity

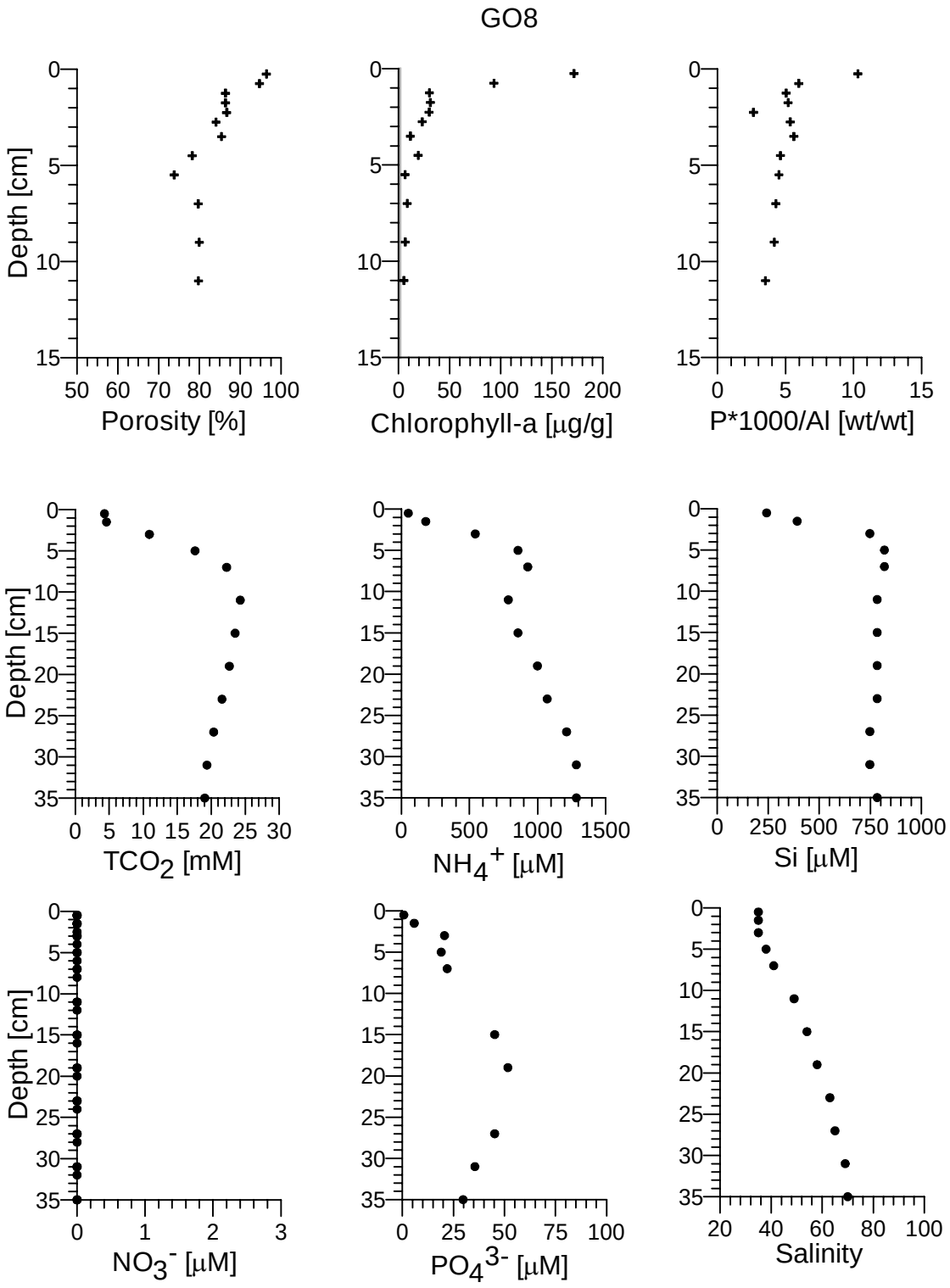

WE7
Depth [cm]
Porosity [%]
Chlorophyll-a [µg/g]
P*1000/Al [wt/wt]
TCO2 [mM]
NH4+ [µM]
Si [µM]
NO3- [µM]
PO43- [µM]
Salinity

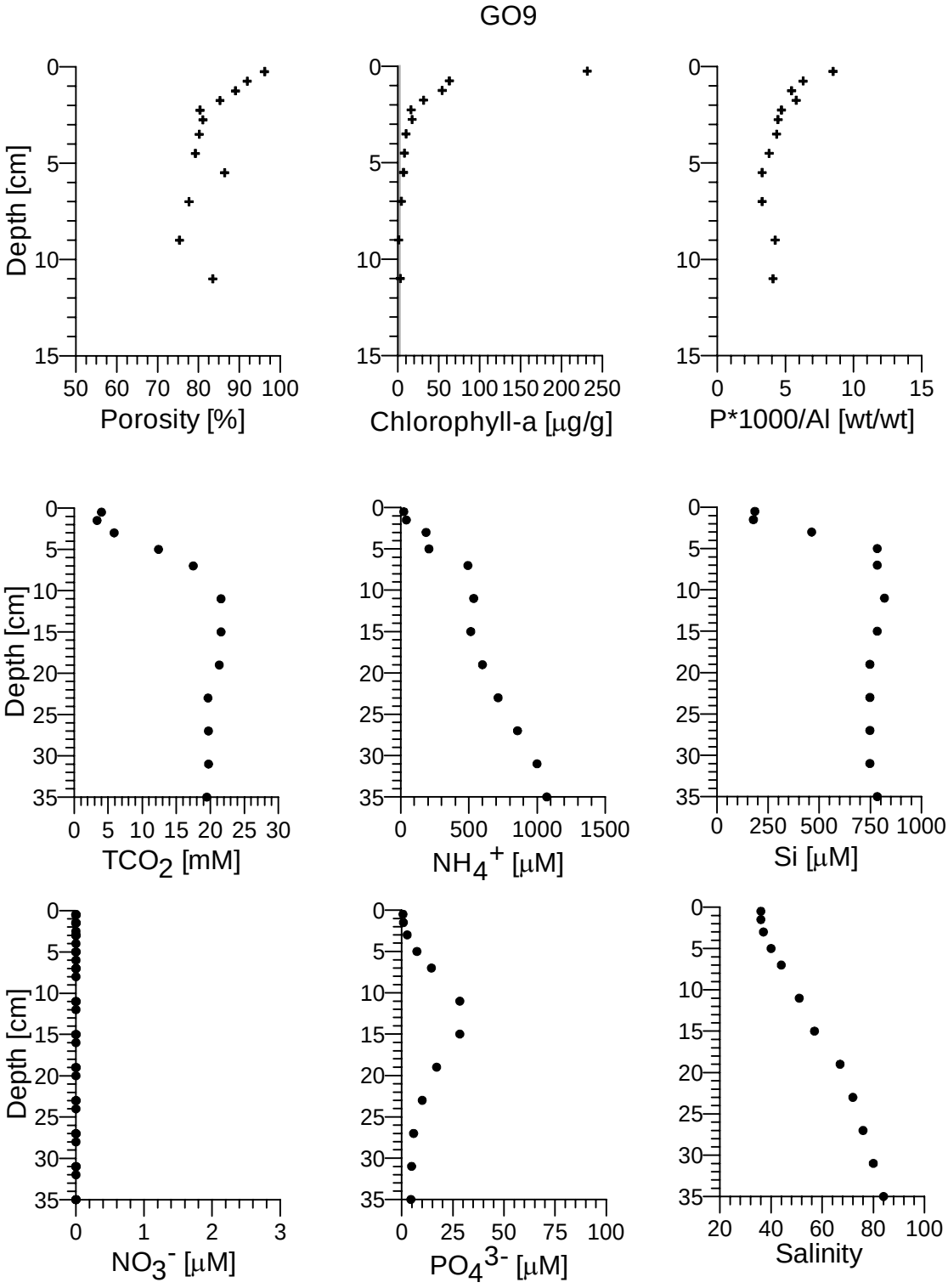

WE8
Depth [cm]
Porosity [%]
Chlorophyll-a [μg/g]
P*1000/Al [wt/wt]
TCO2 [mM]
NH4+ [μM]
Si [μM]
NO3- [μM]
PO43- [μM]
Salinity

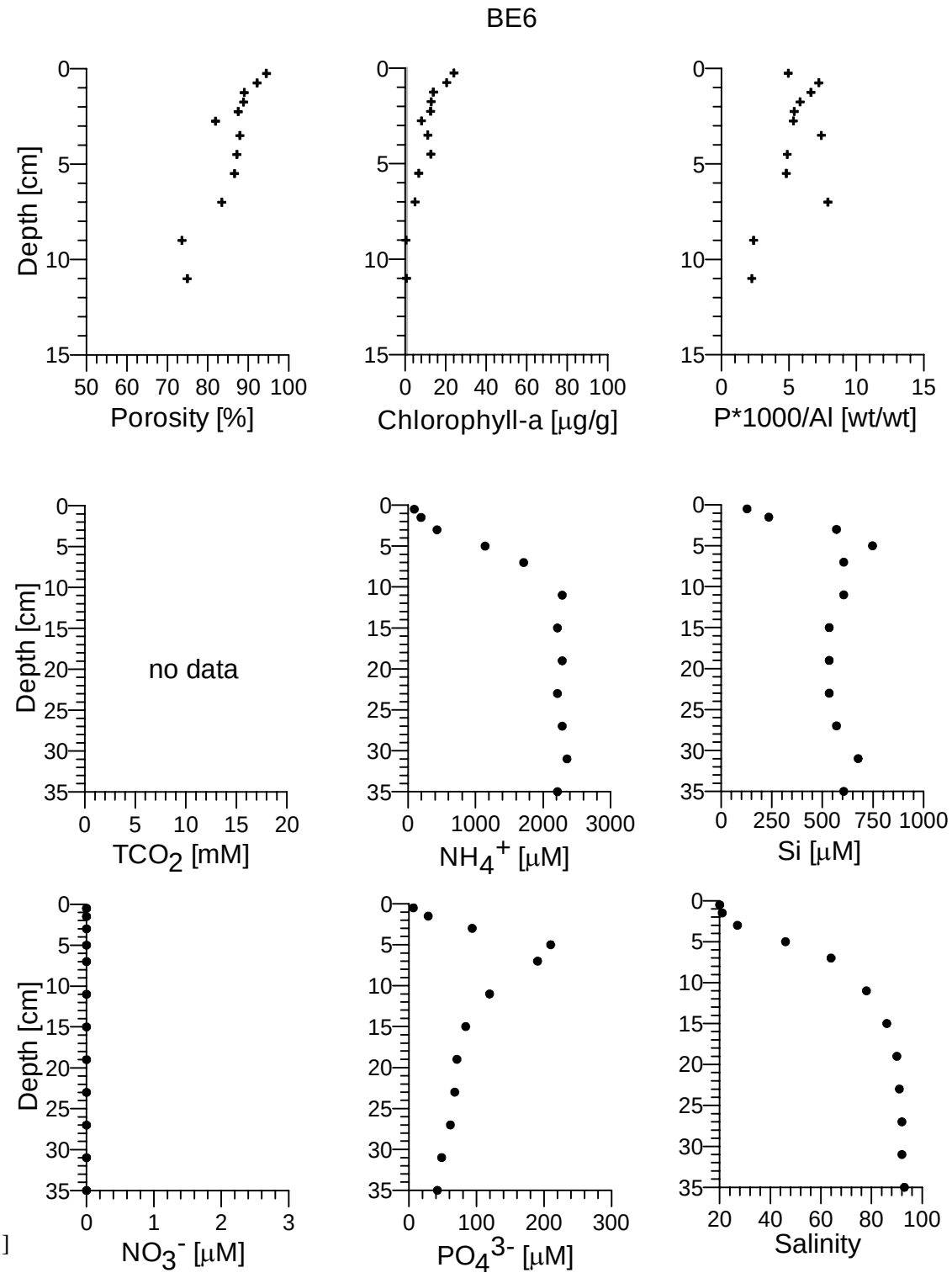

WE9
Depth [cm]
Porosity [%]
Chlorophyll-a [µg/g]
P*1000/Al [wt/wt]
TCO2 [mM]
NH4+ [µM]
Si [µM]
NO3- [µM]
PO43- [µM]
Salinity


GO6
Depth [cm]
Porosity [%]
Chlorophyll-a [μg/g]
P*1000/Al [wt/wt]
TCO2 [mM]
NH4+ [μM]
Si [μM]
NO3- [μM]
PO43- [μM]
Salinity

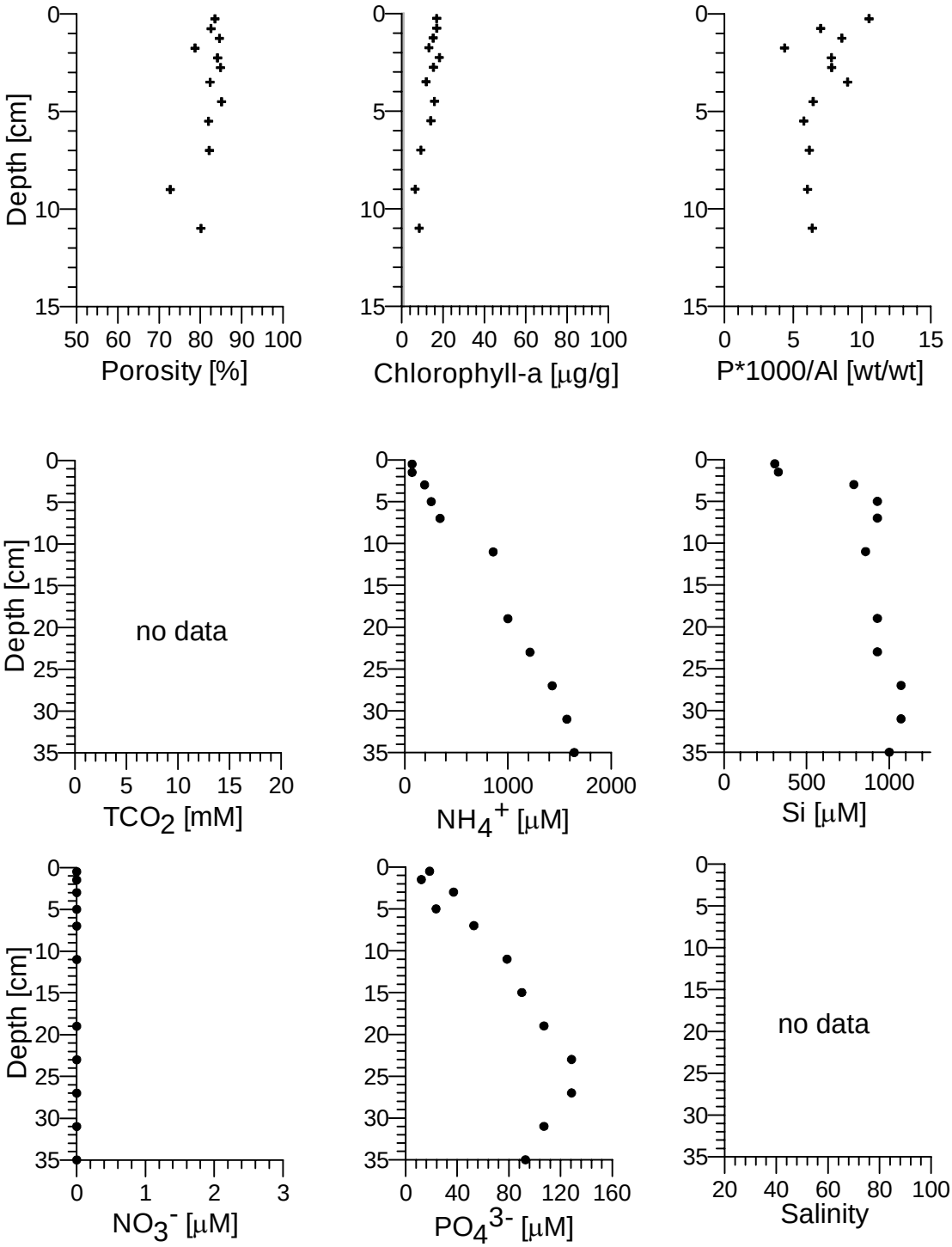

GO7
Depth [cm]
Porosity [%]
Chlorophyll-a [µg/g]
P*1000/Al [wt/wt]
TCO2 [mM]
NH4+ [µM]
Si [µM]
NO3- [µM]
PO43- [µM]
Salinity


GO8
Depth [cm]
Porosity [%]
Chlorophyll-a [μg/g]
P*1000/Al [wt/wt]
TCO2 [mM]
NH4+ [μM]
Si [μM]
NO3- [μM]
PO43- [μM]
Salinity

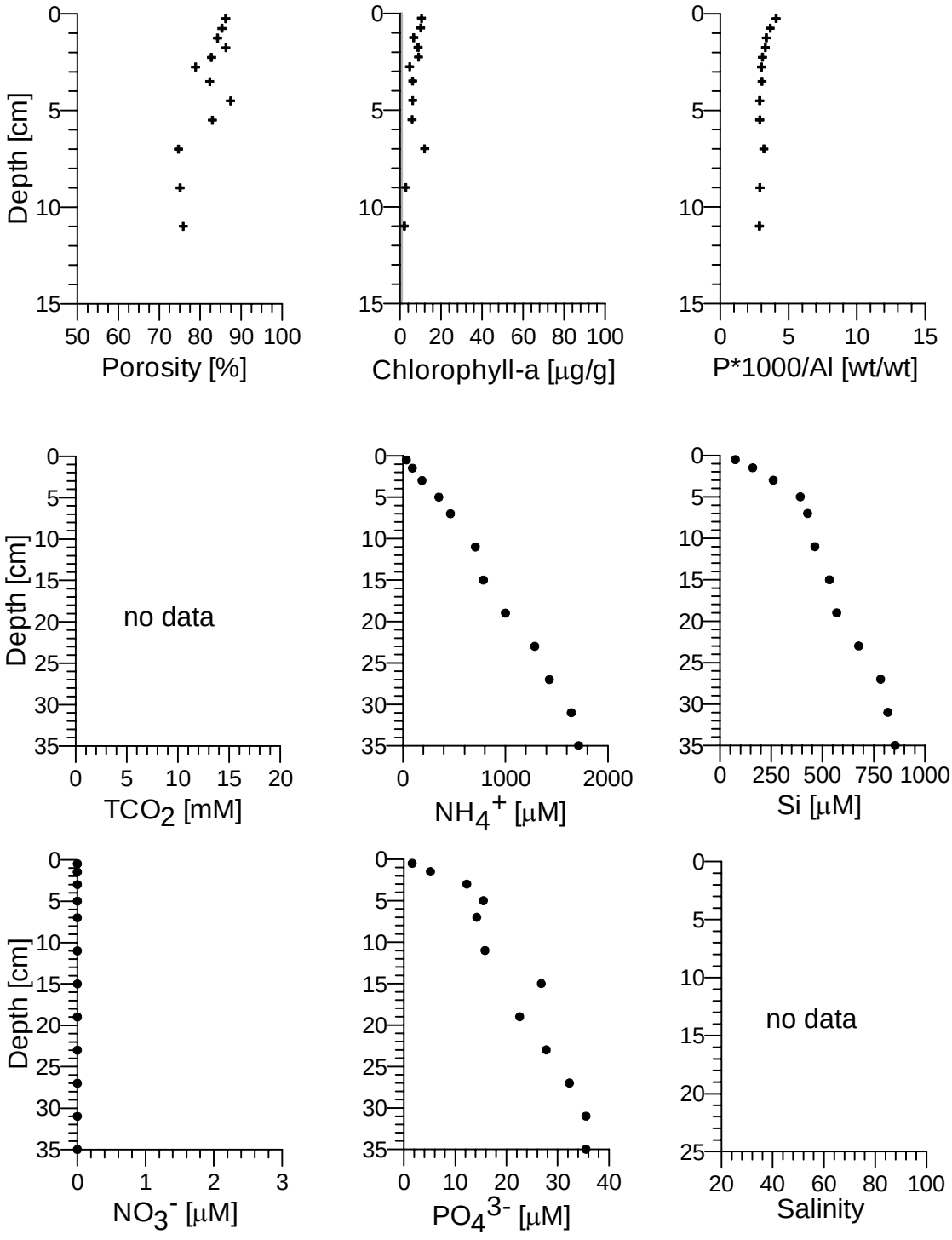

GO9
Depth [cm]
Porosity [%]
Chlorophyll-a [µg/g]
P*1000/Al [wt/wt]
TCO2 [mM]
NH4+ [µM]
Si [µM]
NO3- [µM]
PO43- [µM]
Salinity

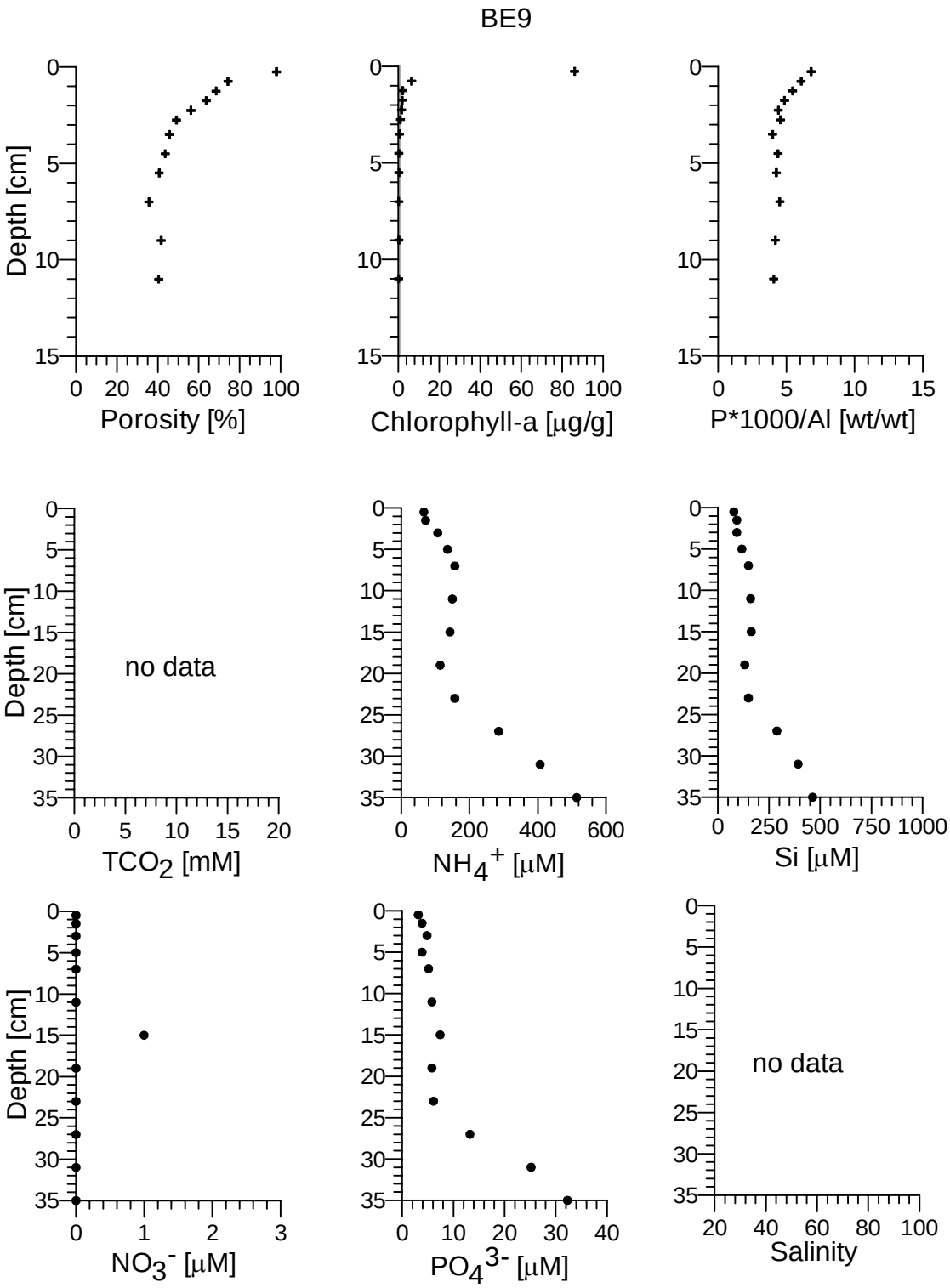

BE6
Depth [cm]
Porosity [%]
Chlorophyll-a [μg/g]
P*1000/Al [wt/wt]
no data
TCO2 [mM]
NH4+ [μM]
Si [μM]
NO3- [μM]
PO43- [μM]
Salinity

BE7


Depth [cm]
Porosity [%]
Chlorophyll-a [μg/g]
P*1000/Al [wt/wt]
no data
TCO2 [mM]
NH4+ [μM]
Si [μM]
NO3- [μM]
PO43- [μM]
no data
Salinity

BE8


Depth [cm]
Porosity [%]
Chlorophyll-a [μg/g]
P*1000/Al [wt/wt]
no data
TCO2 [mM]
NH4+ [μM]
Si [μM]
NO3- [μM]
PO43- [μM]
no data
Salinity


BE9
Depth [cm]
Porosity [%]
Chlorophyll-a [µg/g]
P*1000/Al [wt/wt]
no data
TCO2 [mM]
NH4+ [µM]
Si [µM]
NO3- [µM]
PO43- [µM]
no data
Salinity

Appendix 7 – Biomarker/Pigment Analysis

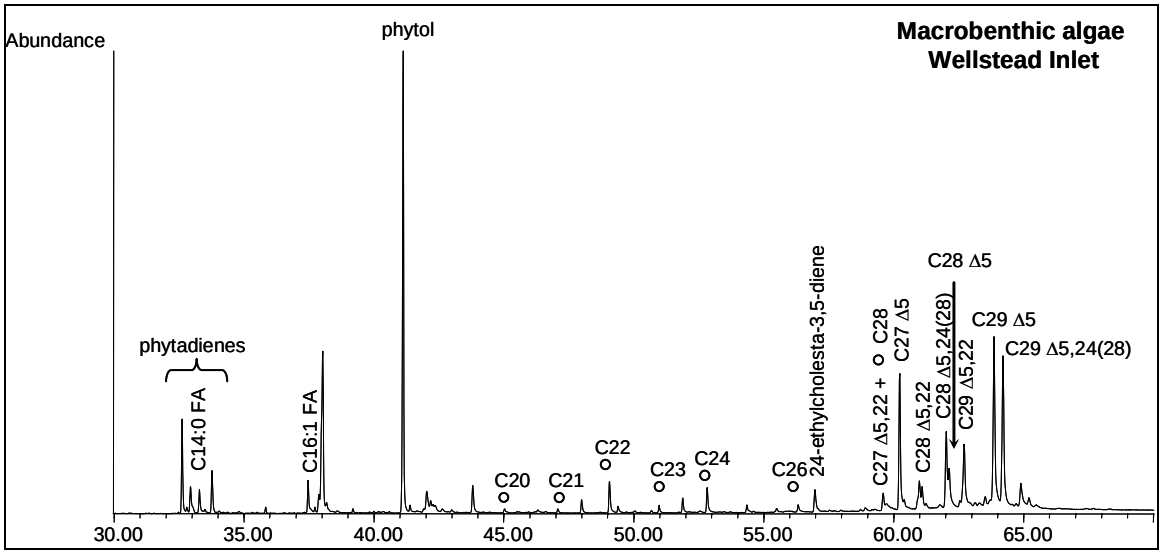


Figure A. Total ion chromatogram of the silylated extractable organic matter fraction of macrobenthic (floating) algae collected at Wellstead Estuary. For sterol annotations refer to Table A.

Table A. Sterol names and peak identification symbol.

Symbol	**Nomenclature name**	**Common name**
C27Δ5,22	Cholesta-5,22E-dien-3β-ol	dehydrocholesterol
C27Δ22	Cholest-22E-en-3β-ol	dehydrocholestanol
C27Δ5	Cholest-5-en-3β-ol	cholesterol
C27Δ0	5α-cholestan-3β-ol	cholestanol
C28Δ5,22	24-methylcholesta-5,22E-dien-3β-ol	brassicasterol
C28Δ5	24-methylcholest-5-en-3β-ol	Campesterol
C28Δ5,24(28)	24-methylcholesta-5,24(28)-dien-3β-ol	24-methylenecholesterol
C29Δ5,22	24-ethylcholesta-5,22E-dien-3β-ol	stigmasterol
C29Δ5	24-ethylcholesterol	sitosterol
C29Δ5,24(28)Z	24-ethylcholesta-5,24(28)Z-dien-3β-ol	isofucosterol

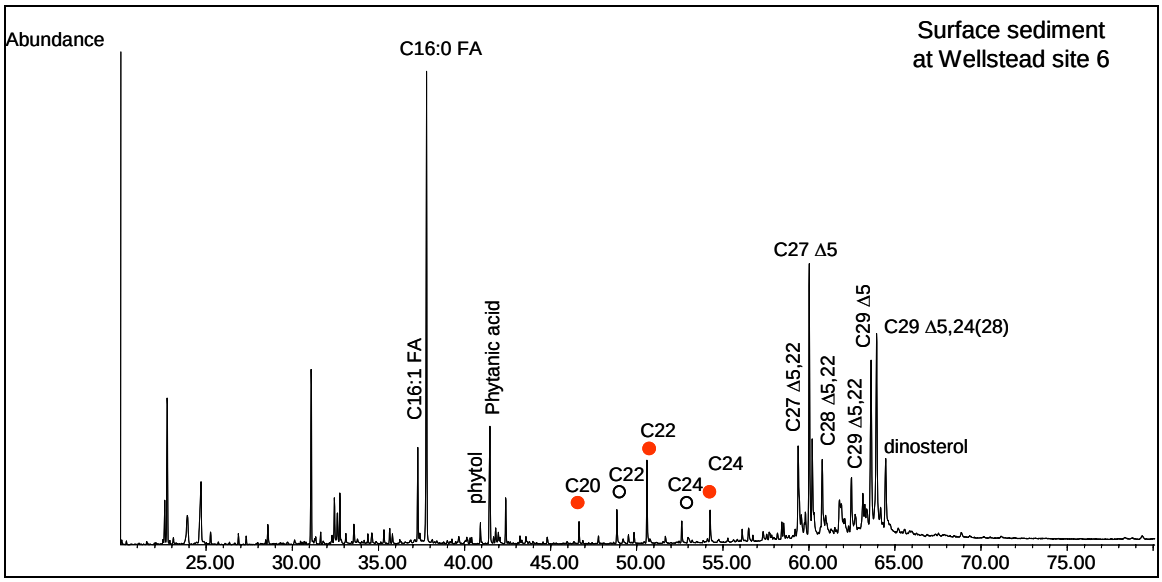


Figure B. Total ion chromatogram of the silylated extractable organic matter fraction of surface sediment (0-0.5 cm) collected at Wellstead Estuary site WE6. For sterol annotations refer to Table A.

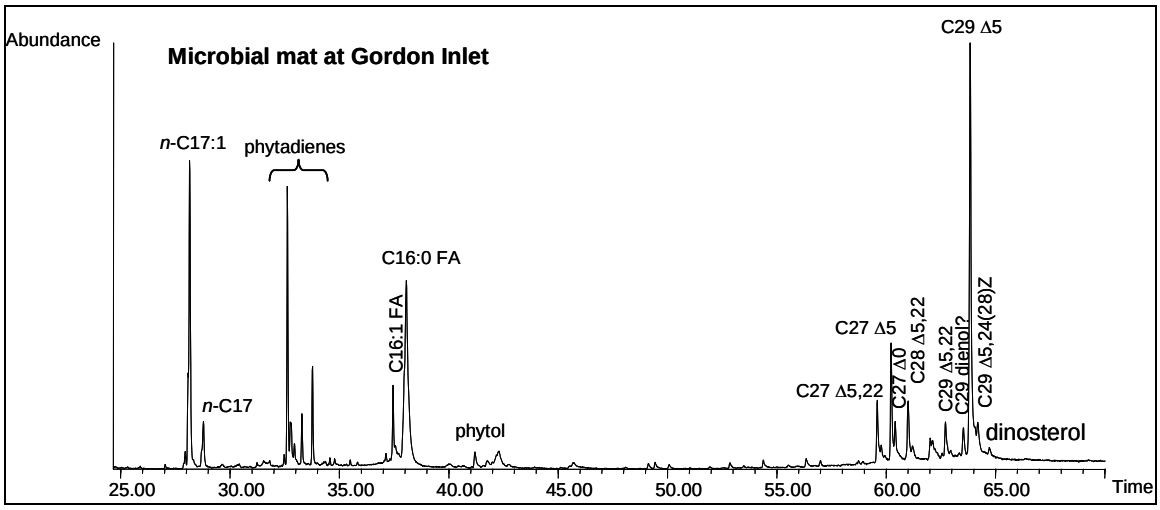


Figure C. Total ion chromatogram of the silylated extractable organic matter fraction of microbial mat collected at Gordon Inlet. For sterol annotations refer to Table A.

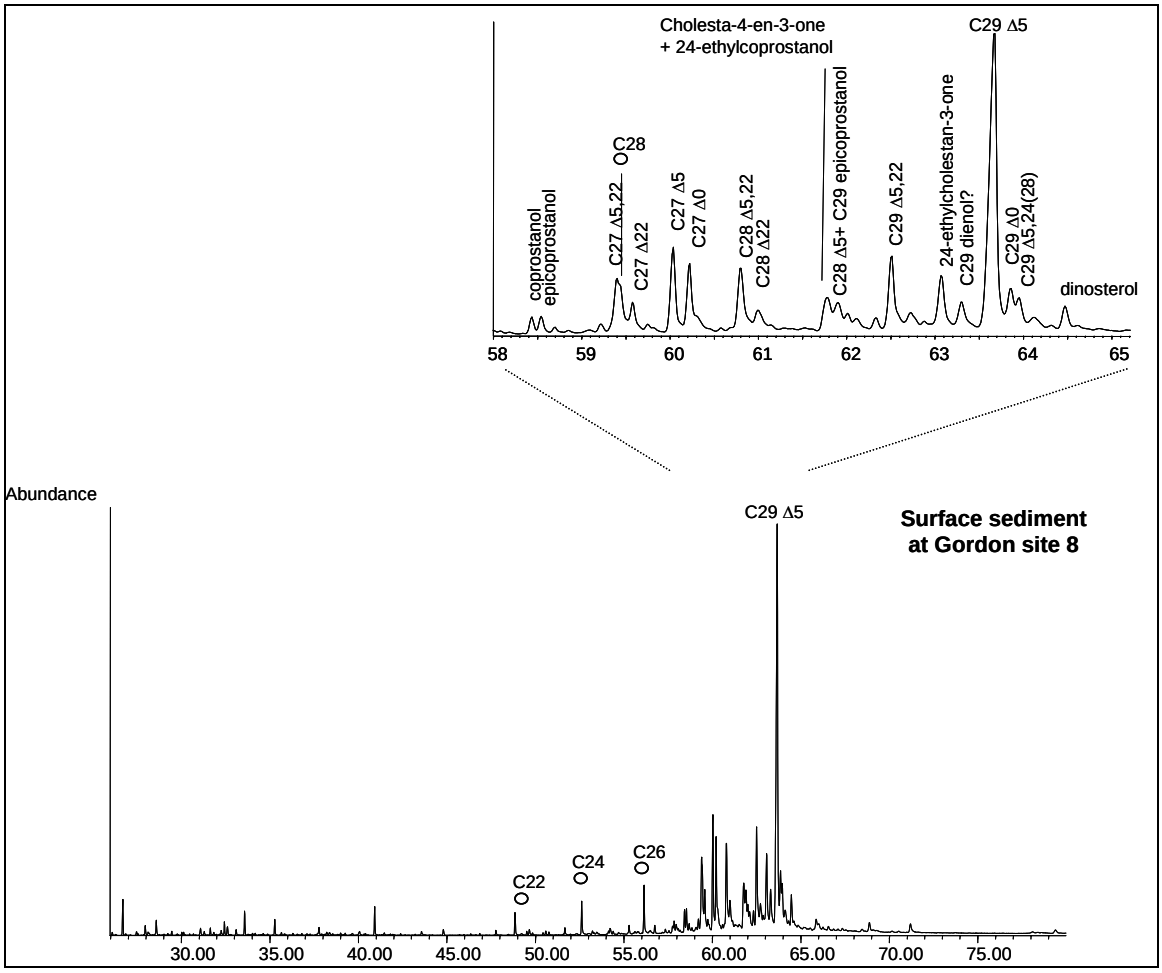


Figure D. Total ion chromatogram of the silylated extractable organic matter fraction of surface sediment (0-0.5 cm) collected at Gordon Inlet site GO8. For sterol annotations refer to Table A.

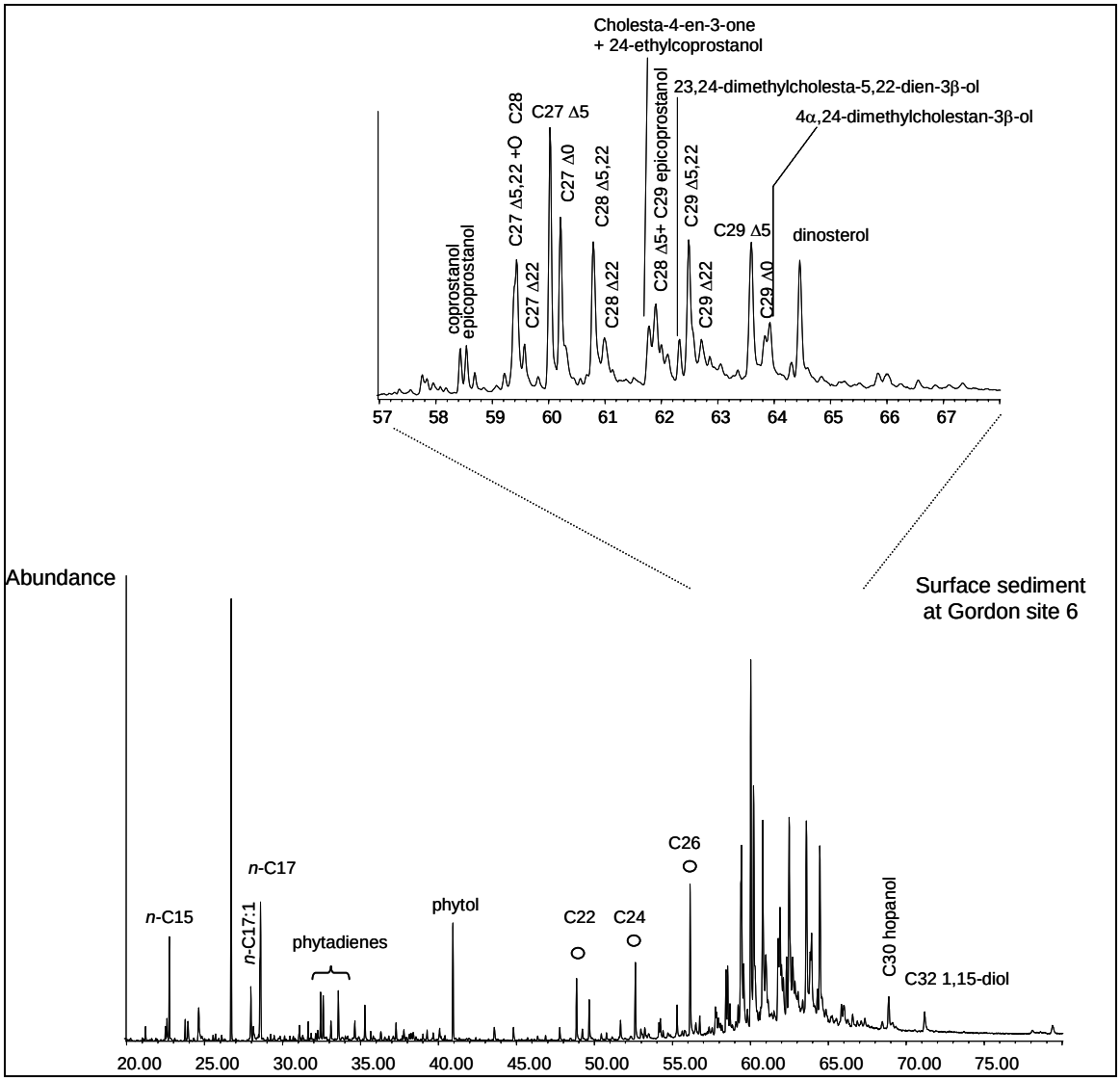


Figure E. Total ion chromatogram of the silylated extractable organic matter fraction of surface sediment (0-0.5 cm) collected at Gordon Inlet site GO6. For sterol annotations refer to Table A.

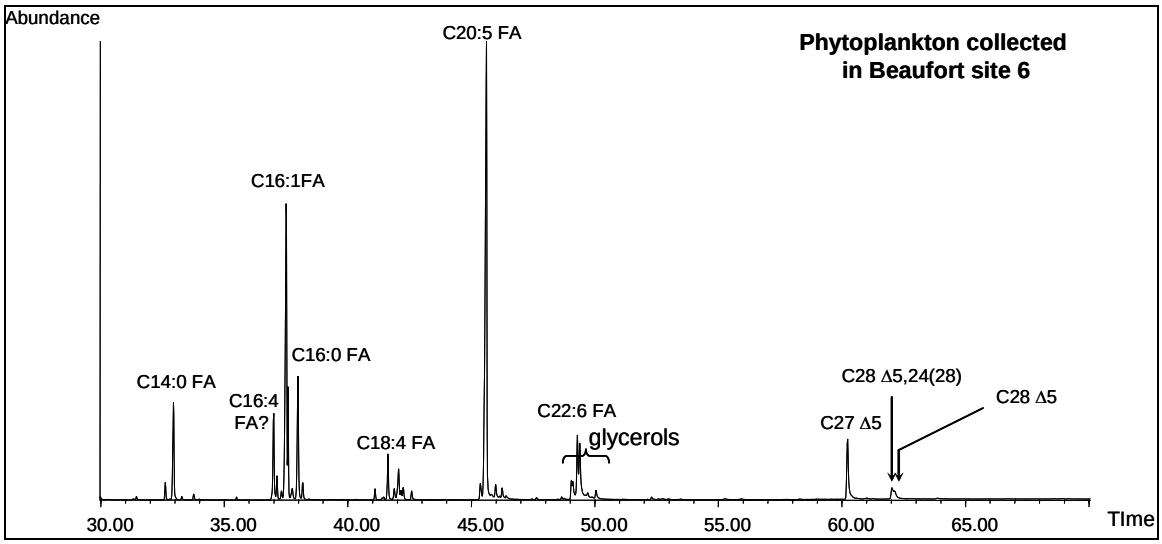


Figure E. Total ion chromatogram of the silylated extractable organic matter fraction of phytoplankton collected at Beaufort Inlet site BE6. For sterol annotations refer to Table A.

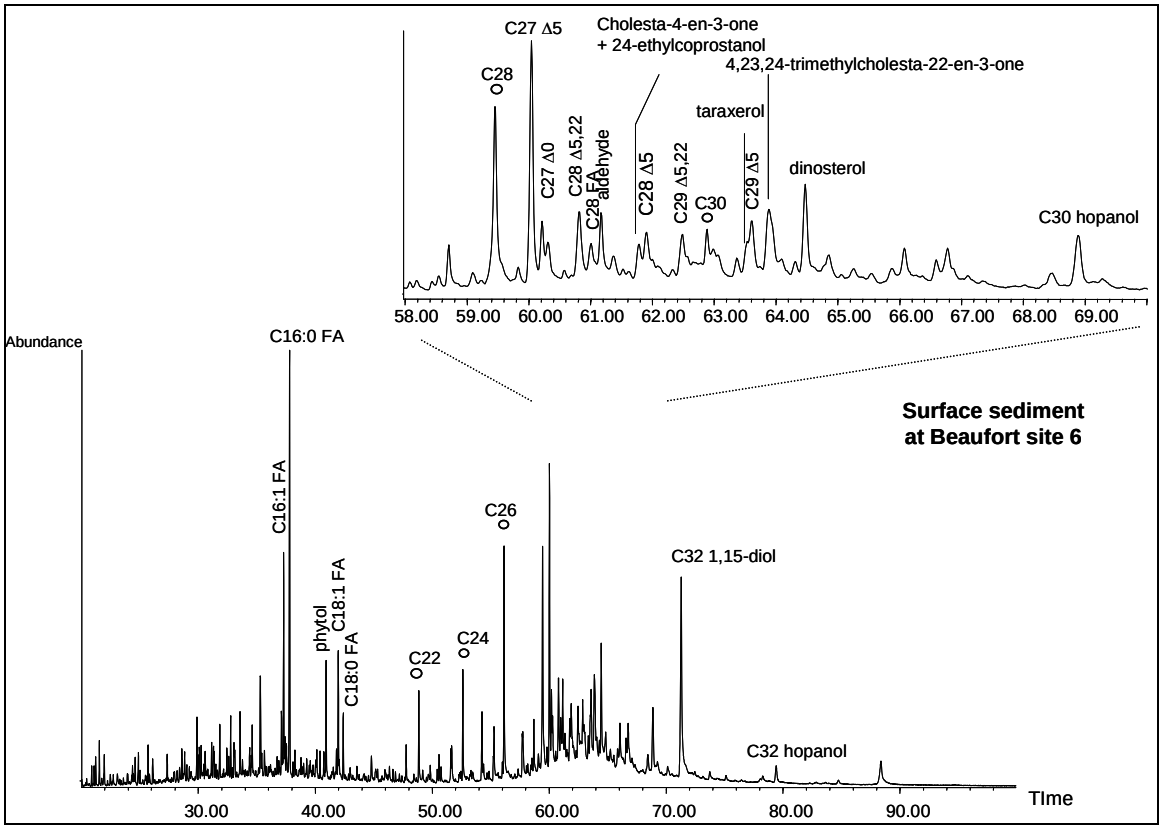


Figure F. Total ion chromatogram of the silylated extractable organic matter fraction of surface sediment (0-0.5 cm) collected at Beaufort Inlet site BE6.

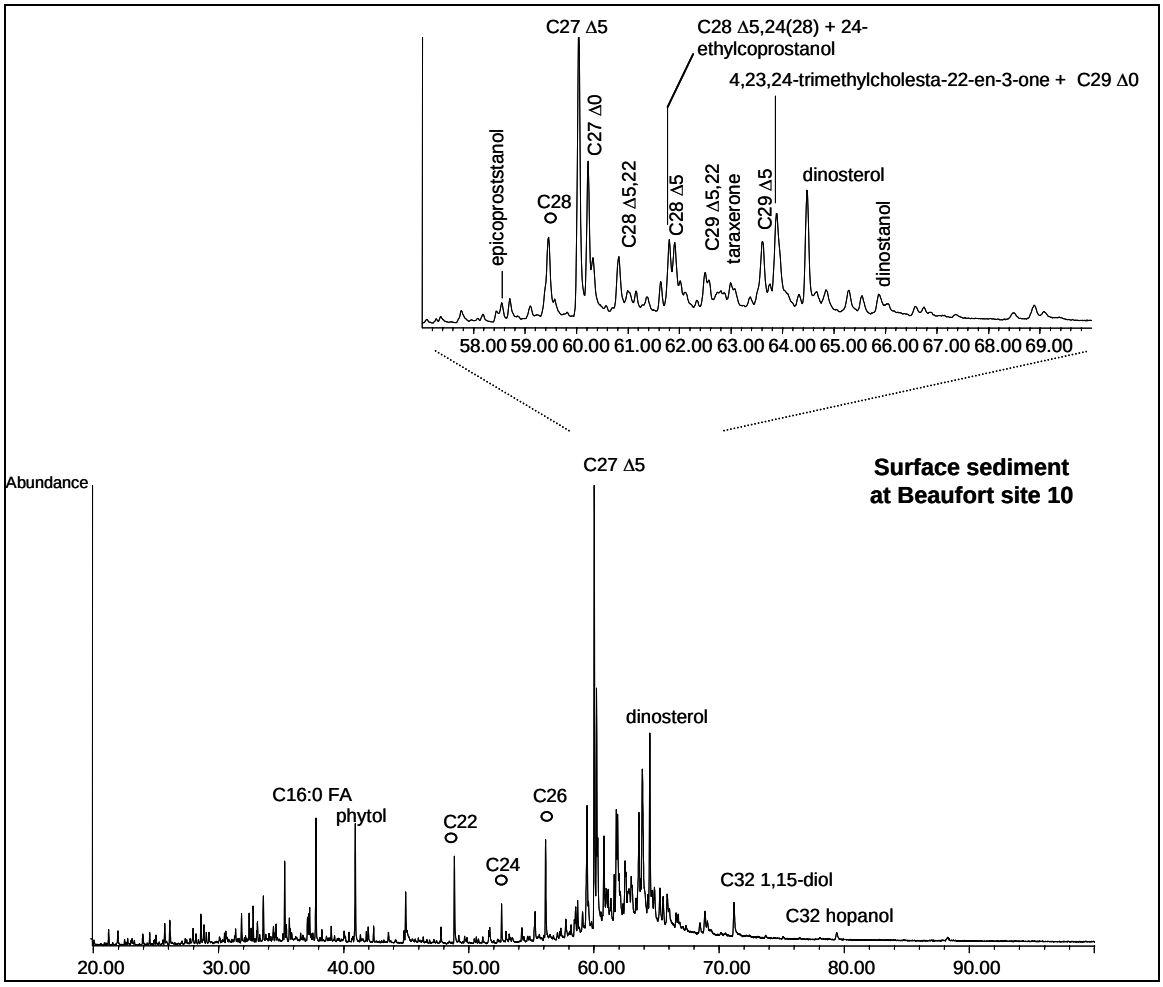


Figure G. Total ion chromatogram of the silylated extractable organic matter fraction of surface sediment (0-0.5 cm) collected at Beaufort Inlet site BE10.