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Findings and Management Implications from Benthic Nutrient Flux Surveys, 2000 - 2006

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Executive Summary

Geoscience Australia has conducted four surveys in the Swan River Estuary to investigate benthic nutrient fluxes and their impact on water quality. Surveys were undertaken in March 2000, March 2001, September 2001, and October 2006, and both the upper and lower sections of the estuary were sampled. Sites were selected to represent different facies within the estuary; muddy basins, river channels, and sandy margins.

This report details the findings of the most recent benthic nutrient flux survey (October 2006) and compares benthic fluxes at selected sites during all four surveys.

Extreme seasonality of river flow causes the estuary to alternate between fully marine (summer) and almost fresh (winter). The annual winter rains deliver nutrient-rich freshwater to the estuary, however these rains are generally insufficient to flush the entire estuary and the lower estuary (central basin) usually only contains a thin layer of fresher water ‘floating’ on the marine waters. The larger volume of the central basin (compared to the river channel in the upper estuary) also results in dilution of nutrients arriving with the freshwater. These nutrients can also be washed out to sea during the winter.

The upper estuary is significantly different to the lower estuary in terms of water area, freshwater influence, nutrient supply from the catchment, rates of organic matter decomposition and nutrient release, nutrient transformation processes, and sediment nutrient pool sizes. During the October 2006 survey, very high nutrient fluxes were recorded in the upper estuary muddy sites. In fact TCO_2, NH_4^+, PO_4^{3-} and SiO_4^{4-} fluxes were among the highest we have ever measured. Combined with very low denitrification efficiencies, large sediment nutrient pool sizes and hypoxic bottom waters, these muds are a significant source of bioavailable nutrients to the water column.

Between 2000 and 2006 there has been a significant increase in the amount of organic matter decomposition and nutrient release from the muddy sediments in the upper estuary. This is of major concern as it is combined with a lowering of the denitrification efficiency and a diminished capacity of the sediments to bind phosphorus. A similar pattern is observed in the central basin, however, the change is not as severe.

An oxygen plant in the upper estuary is designed to increase the O_2 concentration of the bottom waters, and therefore, decrease the supply of bioavailable nutrients from the sediments to the water column. However, the fine sediments from the catchment have been identified as a large external source of nutrients to the estuary and therefore a reduction in the supply of fine sediments and associated organic matter would immediately improve the water quality in the upper estuary.

The shallow sandy margins of the lower estuary are sites of photosynthetic production, however these differ between benthic and pelagic production depending on the light attenuation. When light is available at the sediment surface, benthic production is evident, however, if light penetration is insufficient to reach the sediment surface, pelagic production is more evident.

Dissolved metal fluxes between the sediments and overlying water at one site in the upper estuary showed the sediments were not a source of dissolved metals at the time of the survey. Bottom water concentrations of copper and zinc however, did exceed ANZECC trigger values and their source is unknown.

Acknowledgements

The authors would firstly like to thank Malcolm Robb from the Western Australian Department of Water for his continued support of this work as demonstrated by the funding he has obtained over many years. We also acknowledge the assistance and support other staff members of the Aquatic Science Branch have given us, in particular, Ben Boardman, Frances D'Souza, Melinda Ranaldi, Vanessa Forbes, and Zoe Goss.

The authors would also like to thank Colin Tindall, Ian Atkinson, Matthew Carey, John Ryan and Craig Wintle for there assistance in field sampling during some or all of the surveys.

All surveys were hugely successful due to the support of the Swan River Trust, we thank Dave Fardig and his team for providing a facility to work and, more importantly, assistance in the form of suitable boats and competent drivers.

Sample analysis has been extensive and involved many collaborators and institutions over the years. We acknowledge the great work undertaken by the staff at the Geoscience Australia Laboratory in Canberra, the Marine and Freshwater Research Institute in Victoria (Andrew Longmore and Rob Cowdell), Southern Cross University in Lismore, and the National Measurement Institute in Perth.

Finally, the authors would like to acknowledge the former Geoscience Australia scientists, David Fredericks and Duncan Palmer, who were part of the initial Swan River survey program (2000-2001). David and Duncan, along with David Heggie and Craig Smith, were the principal investigators into Nutrient Recycling during the first three surveys to the Swan River.

Abbreviations and Units

ANZECC	Australian and New Zealand Environment and Conservation Council
BMA	Benthic Microalgae
Chl-a	Chlorophyll a
C	Carbon
$\delta^{13}C$	Delta ^{13}C
cm	centimetre
CO_2	Carbon Dioxide
DIN	Dissolved Inorganic Nitrogen
DIP	Dissolved Inorganic Phosphorus
DO	Dissolved Oxygen
DON	Dissolved Organic Nitrogen
DoW	Department of Water, Western Australian Government
Fe	Iron
GA	Geoscience Australia
Kd	Light Attenuation Coefficient
km	kilometre
m	meter
m^{-1}	per metre
mg/L	milligrams per litre
mmol m^{-2} day^{-1}	millimoles per metre squared per day
M	Moles per Litre
N	Nitrogen
$\delta^{15}N$	Delta ^{15}N
N_2	Dinitrogen Gas
NH_4^+	Ammonium
NO_2^-	Nitrite
NO_3^-	Nitrate
NO_X	Nitrate + Nitrite
O_2	Oxygen
PAR	Photosynthetically Active Radiation
PO_4^{3-}	Phosphate
SiO_4^{4-}	Silicate
TCO_2	Total Carbon Dioxide
TDN	Total Dissolved Nitrogen (NH_4 + NO_X + N_2 + DON)
TIN	Total Inorganic Nitrogen (NH_4 + NO_X + N_2)
TN	Total Nitrogen
TP	Total Phosphorus
WRC	Water and Rivers Commission, Western Australia (integrated into DoE in 2004)
µM	micromolar
°C	degrees Celsius
%Sat	percent saturation

Contents

1. Introduction

1A. AIMS

Geoscience Australia (GA) has conducted four surveys in the Swan River Estuary to investigate benthic nutrient fluxes and their impact on water quality. The first three surveys were carried out in March 2000, March 2001, and September 2001, in order to monitor changes in nutrient fluxes over time. The final survey five years later (October 2006) aimed to determine any longer term temporal trends as well as provide baseline information to assist in the effective operation of a new oxygenation plant for the Upper Swan Estuary. In addition, this latest survey included a preliminary assessment of possible metal fluxes at one site in the upper estuary.

A report entitled *Benthic Fluxes and Nutrient Recycling in the Swan Estuary* (Fredericks *et al*., 2002) presents the findings of the first three surveys. The results and discussion section of this report presents the findings of the latest survey (Part A) and compares the results from all four surveys (Part B).

Part A aims to:

- compare benthic fluxes at different sites throughout the estuary and assess their impact on water quality;
- provide baseline information for assisting in the effective operation of an oxygenation plant in the Upper Swan Estuary; and
- assess the importance of metal fluxes at a site (SR33) located in the upper estuary.

Part B aims to:

- compare benthic nutrient fluxes between the four surveys at selected sites.

The final section of this report discusses the management implications of these findings.

1B. BACKGROUND

The Swan River Estuary (Figure 1) covers an area of approximately 40 km^2 and ~ 60 km upstream from Fremantle and ~ 6 km up the Canning River. The lower estuary comprises the main basin of Melville Water and the smaller Perth Water (Figure 2a). Melville Water has a deep (~ 10 m) muddy basin and extensive sandy margins and is predominantly marine influenced. The upper estuary, comprising the Swan River channel (Figure 2b), drains a large (18,000 km^2) catchment and is dominated by freshwater runoff events. The channel is up to 30 m wide and around 2 - 3 m deep, apart from some deeper areas ~ 5 m. The channel sediments consists typically of mud in the upper reaches and muddy sand in the lower reaches.

The Swan River Estuary is naturally susceptible to algal blooms due to the poor nutrient-binding capacity of the surrounding sandy soils, the hot summers, large changes in salinity, and poor flushing (WRC, 2005). In recent years, the prevalence of harmful algal species together with low bottom water oxygen levels and fish kills have been of particular concern for river managers.

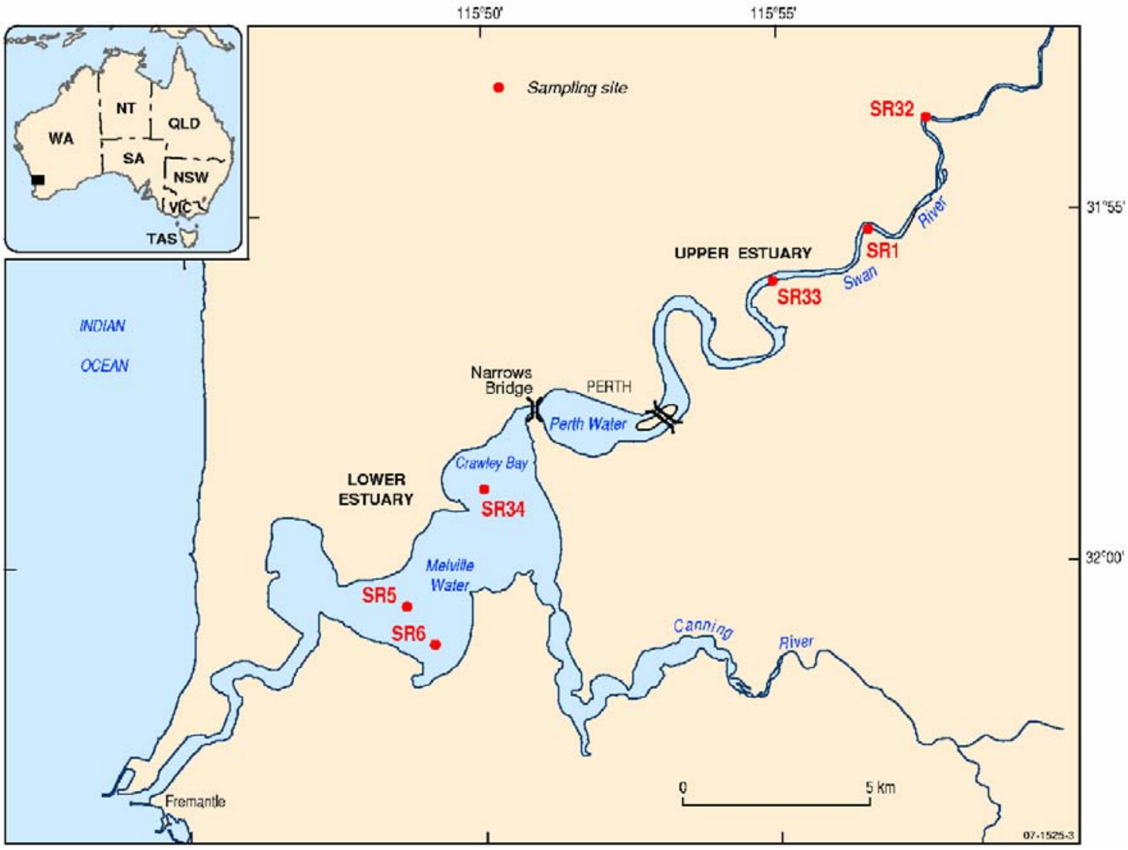


Figure 1. Swan River Estuary study site locations.

a.)

b.)

Figure 2. a.) Satellite image of the lower Swan River Estuary and b.) photo of a section of the Upper Swan River Estuary.

1C. BENTHIC NUTRIENT FLUX SURVEYS 2000 - 2006

All sites were selected in conjunction with the WA Department of Water (DoW) and were chosen to represent different environments within the upper and lower estuary (Figure 1 and Appendix 1). SR1, SR5 and SR6 were sampled in all four surveys, and SR32, SR33 and SR34 were included for the final survey (Table 1). Additional sites (SR2, SR3 and SR4) were sampled during the first three surveys, however the results have been previously reported in Fredericks *et al.* (2002) and are not discussed in this report.

Table 1. Sites sampled during each survey in the Swan River Estuary. Ticks represent benthic chamber sampling and crosses represent where sediment cores or surface sediments were collected.

	Lower Estuary			**Upper Estuary**		
	SR5	**SR6**	**SR34**	**SR33**	**SR1**	**SR32**
Depth **Sediment Type**	10 mud	2 sand	2 sand	3 muddy sand	4 mud	3 mud
Survey 1 (14 - 24 March 2000)	✓✗	✓✗			✓✗	
Survey 2 (21 March – 2 April 2001)	✓✗	✓✗			✓✗	
Survey 3 (27 September – 7 October 2001)	✓✗	✓✗			✓✗	
Survey 4 (18 – 29 October 2006)	✓	✓✗	✓✗	✓✗	✓	✓✗

Methods for the first three surveys are given in Fredericks *et al*. (2002). Benthic chamber and coring operations and analytical methods for Survey 4 are described in Murray *et al*. (2007). Additionally, extra benthic chamber and sediment porewater samples were collected from SR33 during Survey 4 for dissolved metal analysis.

2. Results and Discussion

2A. Results of the October 2006 Survey

2A1. SEASONAL CONTEXT AND WATER COLUMN CONDITIONS

Salinity and Dissolved Oxygen

Water column conditions in the Swan River Estuary during the October 2006 survey were typical for springtime. The salinity distribution shows the influence of freshwater inflows from seasonal winter rains along with the upstream migration of a tidal salt wedge (Figure 3; WRC, 2002). However, winter rainfall prior to the survey had been considerably lower than average, especially in May, June, and July. Winter rains occurring from late July to September developed a freshwater plume that resulted in stratification of the upper estuary. However, flows were not sufficient to flush the entire system and freshwater did not extend very far into the lower estuary.

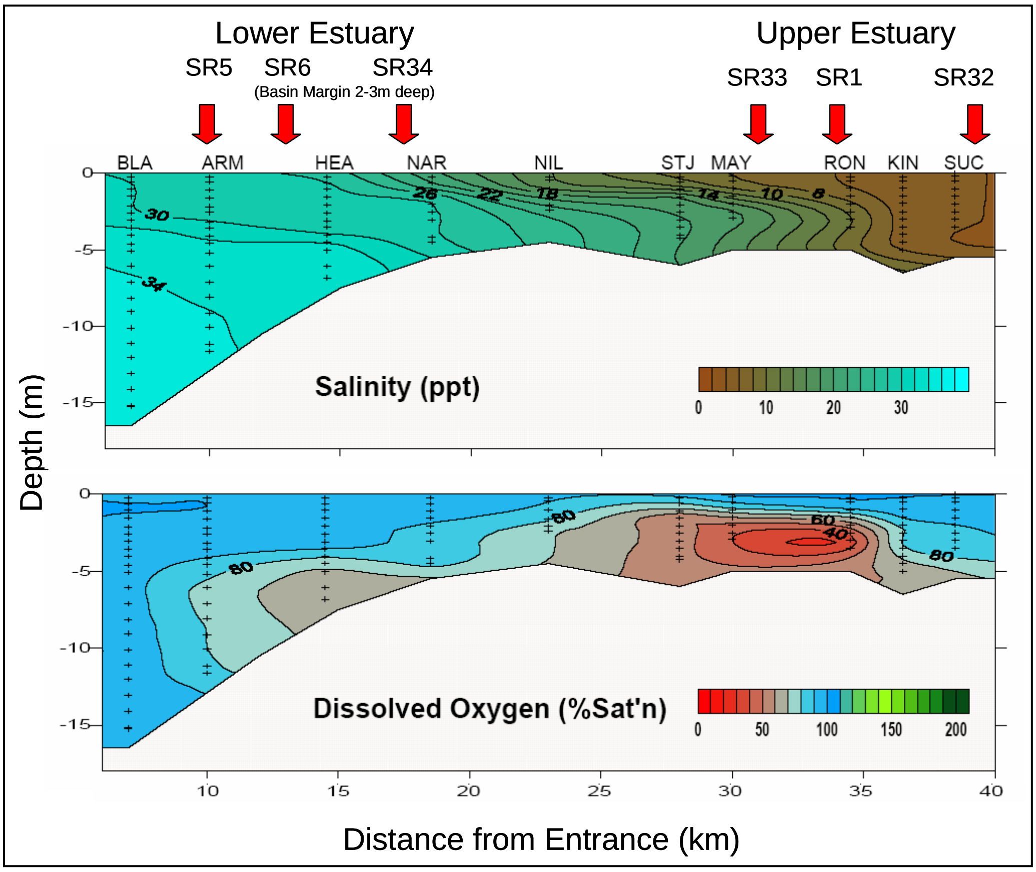


Figure 3. Longitudinal profiles of salinity and dissolved oxygen in the Swan River Estuary (23rd October 2006). Source: Swan River Trust website (www.swanrivertrust.wa.gov.au). The three-letter codes are Swan River Trust weekly water quality monitoring sites. Note that SR6 and SR34 are located off-centre of the longitudinal profile on the shallower margins of the central basin.

At the time of the survey, salinity and dissolved oxygen levels differed markedly between the lower and upper estuary (Figure 3). The lower estuary was saline, ranging from 34 in the bottom waters of the deep central basin (SR5) to 25 in the surface waters at SR34. The water column in the lower estuary was also generally well-mixed and well-oxygenated (Figure 4), with around 100% or greater dissolved oxygen saturation in the surface waters of all three sites (SR5, SR6, SR34), and in shallow areas (2-3 m water depth; SR6 and SR34), oxygen saturation was above 90% throughout the entire water column. In the deep central basin (~10 m water depth; site SR5), dissolved oxygen levels decreased with water depth to around 80% at the estuary bottom, indicating net consumption of oxygen at the sediment surface. This was expected, since light penetration into the water column on the day of sampling was such that photosynthesis was likely to occur only to a depth of 4.4 m (Table 2). Thus, there was no photosynthetic production of oxygen at the estuary bottom to counteract consumption of oxygen from organic matter breakdown in the sediment.

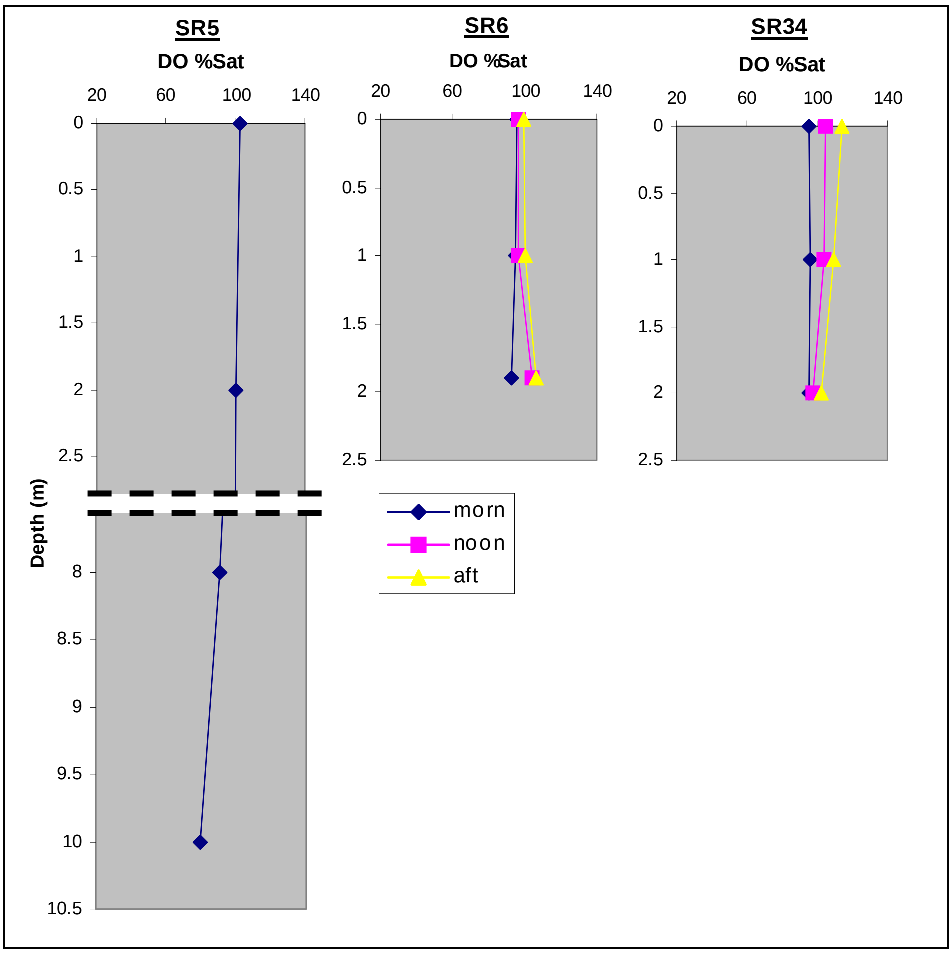


Figure 4. Dissolved Oxygen profiles for lower estuary sites. Multiple profiles were measured at some sites over the course of a day (morning, noon, and afternoon).

*Table 2. Maximum depth possible for benthic primary production, and the likelihood of photosynthesis occurring at the sediment surface, based on average vertical light attenuation coefficients (Kd). Kd values were calculated from photosynthetically active radiation (PAR) profiles measured at each site during the day of benthic chamber sampling. The maximum depth possible for benthic primary production was calculated assuming a minimum light demand by benthic algae of 200 µM m^{-2} s^{-1}, no cloud cover (=1800 µM m^{-2} s^{-1} PAR reaching the water surface during midday) and accounts for the measured light attenuation coefficient. n.a. not available: light levels were insufficient to measure PAR at this site because the sky was overcast on the day of sampling. * photosynthesis at the sediment surface was considered unlikely at this site based on observations by divers who were unable to see more than 2-3 cm in front of them while at the estuary bottom.*

	Site	Kd (m^{-1})	Water Depth (m)	Maximum depth possible for benthic primary production (m)	Photosynthesis at sediment surface?
Upper Estuary	SR32	n.a.	3	n.a.	unlikely*
	SR1	2.6	4	0.8	unlikely
	SR33	2.5	2	0.9	unlikely
Lower Estuary	SR34	1	2.5	2.2	possible
	SR6	0.5	2.5	4.4	very likely
	SR5	0.5	10	4.4	unlikely

Interestingly, SR6 and SR34 had contrasting dissolved oxygen profiles, despite these two basin margin sites having similar water depths and sandy sediments. Over the course of the day, between morning and afternoon, dissolved oxygen levels in the bottom waters of SR6 increased, whereas at SR34, they remained constant (Figure 4). The increase in dissolved oxygen levels at SR6 indicated that photosynthesis was occurring at the sediment surface, likely from benthic microalgae (BMA), and/or seagrasses and macroalgae. Indeed, seagrasses and macroalgae were observed to be growing at this site. In addition, the measured Kd value (Table 2), revealed that light penetration into the water column was more than adequate to allow photosynthesis at the sediment surface. In contrast, the estimated maximum depth possible for benthic primary production at SR34 was half that of SR6, and was marginally too shallow to reach the sediment surface. This explains why dissolved oxygen did not increase at the sediment surface of this site, since oxygen production from photosynthesis was either not occurring, or was in balance with oxygen consumption from respiration. Seagrasses and macroalgae were observed to be growing on the sediments at SR34, indicating that at times water clarity and light penetration is adequate for photosynthesis. A significant conclusion for this site is that benthic primary productivity is very sensitive to changes in water clarity. Compared to SR6, this site is possibly more exposed to sediment resuspension by wind driven waves and the inflow of relatively turbid waters from upstream.

SR6 and SR34 also contrasted in regards to surface water changes in dissolved oxygen (Figure 4), where levels increased between morning and afternoon at SR34, but remained constant at SR6. This suggests that photosynthesising phytoplankton were present in the water column of SR34, but not SR6. Likely, photosynthesising BMA and benthic plants at SR6 had used up most of the available nutrients in the water column, leaving very little for phytoplankton growth.

In the upper estuary, salinity decreased upstream (Figure 3) becoming relatively fresh (~ 4) throughout the water column at the most upstream site (SR32). In the mid-reaches, between SR34 and SR1, the water column was moderately stratified reflecting the influence of residual freshwater from winter rains lying above the more saline water of a tidal salt wedge. As such, salinities at SR33 and SR1 increased with depth from 7 in surface waters to ~ 14 in bottom waters.

The tidal salt wedge was associated with low dissolved oxygen levels (Figure 3), because stratification, combined with high rates of organic matter breakdown (respiration) in the sediments of large areas of the upper estuary, has depleted the saline bottom water of oxygen. In addition, photosynthetic production of oxygen in the salt wedge was unlikely because the upper estuary was highly turbid (indicated by high Kd values), and the maximum depth for benthic photosynthesis was only 80 to 90 cm (Table 2). This was significantly shallower than at the lower estuary sites. The lowest levels of dissolved oxygen occurred in areas with the highest degree of stratification (Figure 3). This was most obvious at SR33 and SR1 (Figure 5) where in the afternoon, dissolved oxygen levels were 122% and 137% in surface waters compared to 24% and 63% in bottom waters respectively.

Comparing upper and lower estuary dissolved oxygen profiles (Figure 4 and Figure 5), the increase in surface water dissolved oxygen over the course of a day was far greater in the upper estuary indicating a greater degree of water column primary production and likely abundance of phytoplankton here. Chlorophyll-a concentrations confirm this observation with far greater levels in the surface waters of the upper estuary compared to the lower estuary (Figure 6). Interestingly, at SR32 oxygen levels increased throughout the water column rather than just in the surface layer, as it did at SR33 and SR1. It seems the lack of stratification at SR32 allowed this to occur since light penetration to the estuary bottom was insufficient to allow benthic photosynthesis at this site. The degree of stratification in the upper estuary appeared to be weakening at the time of the survey, with the cessation of significant freshwater inflows following the end of the winter rainy period and the continued upstream migration of the tidal saltwater wedge.

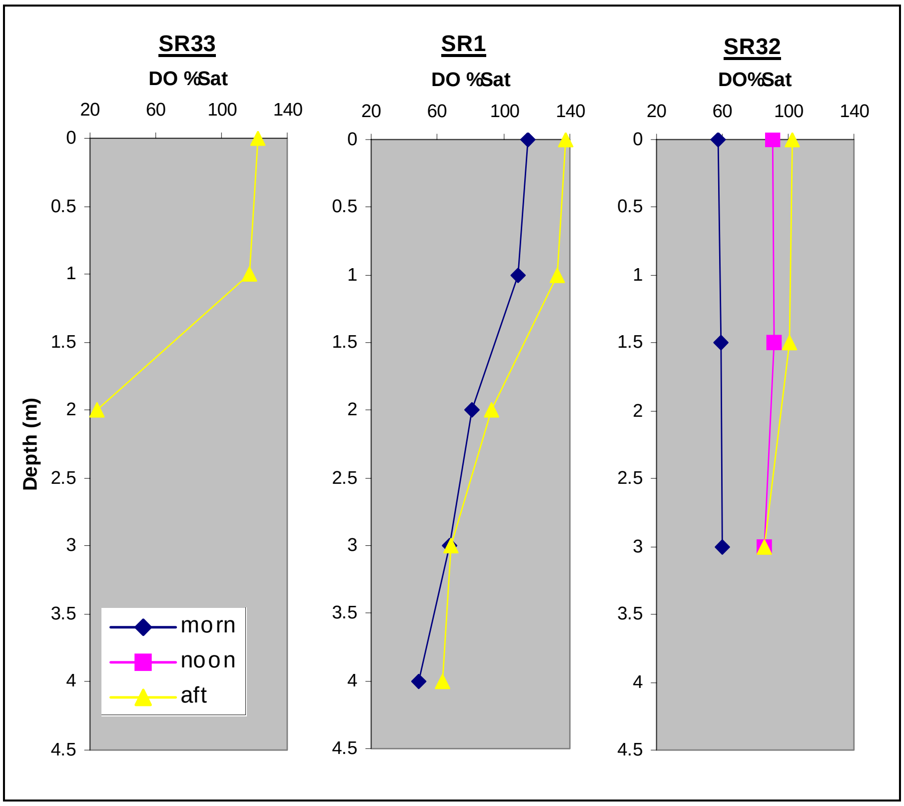


Figure 5. Dissolved Oxygen profiles for upper estuary sites. Multiple profiles were measured at some sites over the course of a day (morning, noon, and afternoon).

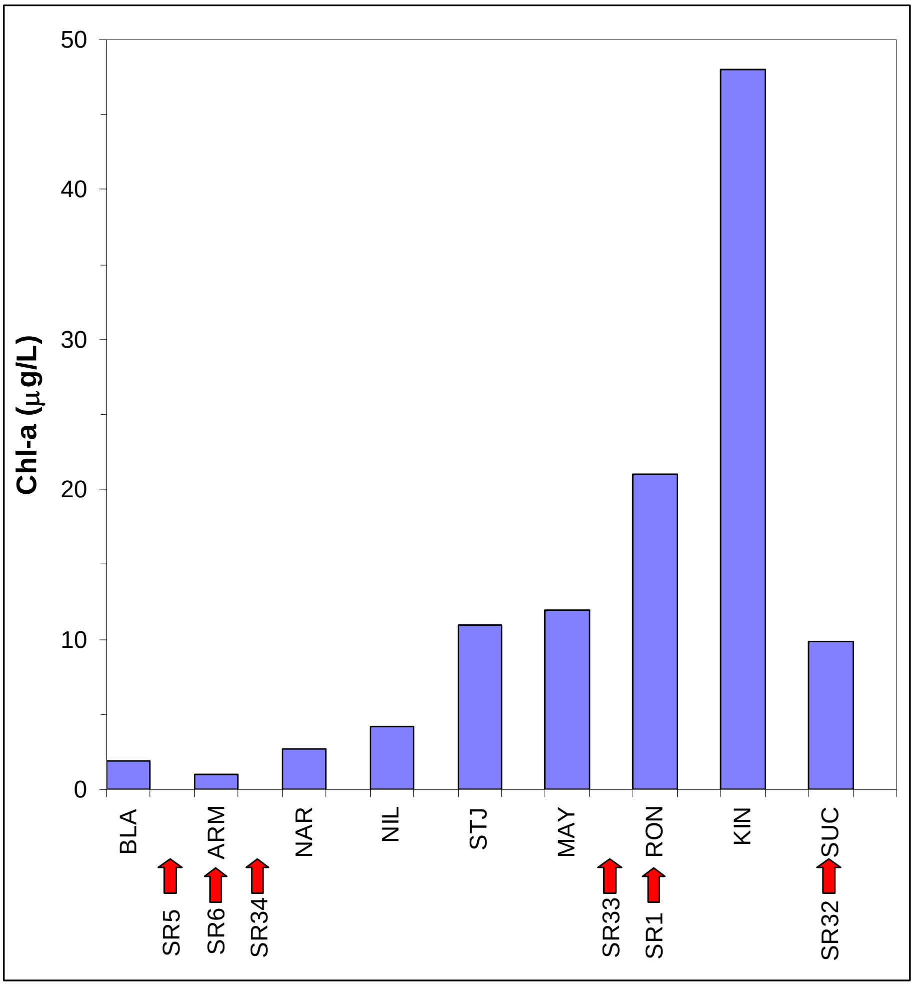


Figure 6. Chlorophyll-a concentrations in the Swan River Estuary (23rd October 2006). Source: Swan River Trust. .

Water Column Nutrients

Nutrient distributions in surface and bottom waters (Figure 7) at the time of the survey were a direct result of catchment inputs and internal recycling processes. Catchments typically deliver oxidised nitrogen (NO_X) rather than ammonia (NH_4^+) to estuaries. The high NH_4^+ found in the upper estuary (particularly in bottom waters) is a sign of high organic matter degradation in the sediments releasing the NH_4^+ to the overlying water column.

Interestingly, dissolved organic nitrogen (DON) concentrations were significant in both surface and bottom waters (Figure 7) and were consistently higher in the upper estuary compared to the lower estuary. Dilution of catchment-derived DON by marine water likely explains this pattern. However, significant DON fluxes measured at SR1 and SR32 (Figure 9) indicate there was some contribution of DON from the sediments in the upper estuary. Silicate (SiO_4^{4-}) concentrations in surface and bottom waters showed a similar pattern to DON concentrations and were also likely reflecting the dilution of catchment-derived runoff by marine water. However, once again, there was evidence for some release of SiO_4^{4-} from the sediments at SR1 and SR32 (Figure 9).

Dissolved phosphorus (PO_4^{3-}) concentrations in the bottom waters of SR1 were significantly higher than at any other site (Figure 7). Notably, the surface water concentration of PO_4^{3-} at SR1 was negligible. Therefore, the high bottom water concentrations are likely reflecting relatively high sediment release of PO_4^{3-}, enhanced by the existence of stratification and hypoxic bottom waters. Indeed, measured benthic PO_4^{3-} fluxes were very high at this site (Figure 9). PO_4^{3-} levels were negligible in surface waters throughout the upper estuary suggesting that catchment runoff was either very low in PO_4^{3-} or PO_4^{3-} was binding to suspended sediment particles and settling to the bottom in the upper estuary. In addition, phytoplankton growing in the upper estuary (Figure 6) is likely consuming all the available surface water P, along with most N. Therefore, in springtime, the relatively muddy, organic-rich sediments of the upper estuary are a significant source of bioavailable P and N for sustaining this phytoplankton growth.

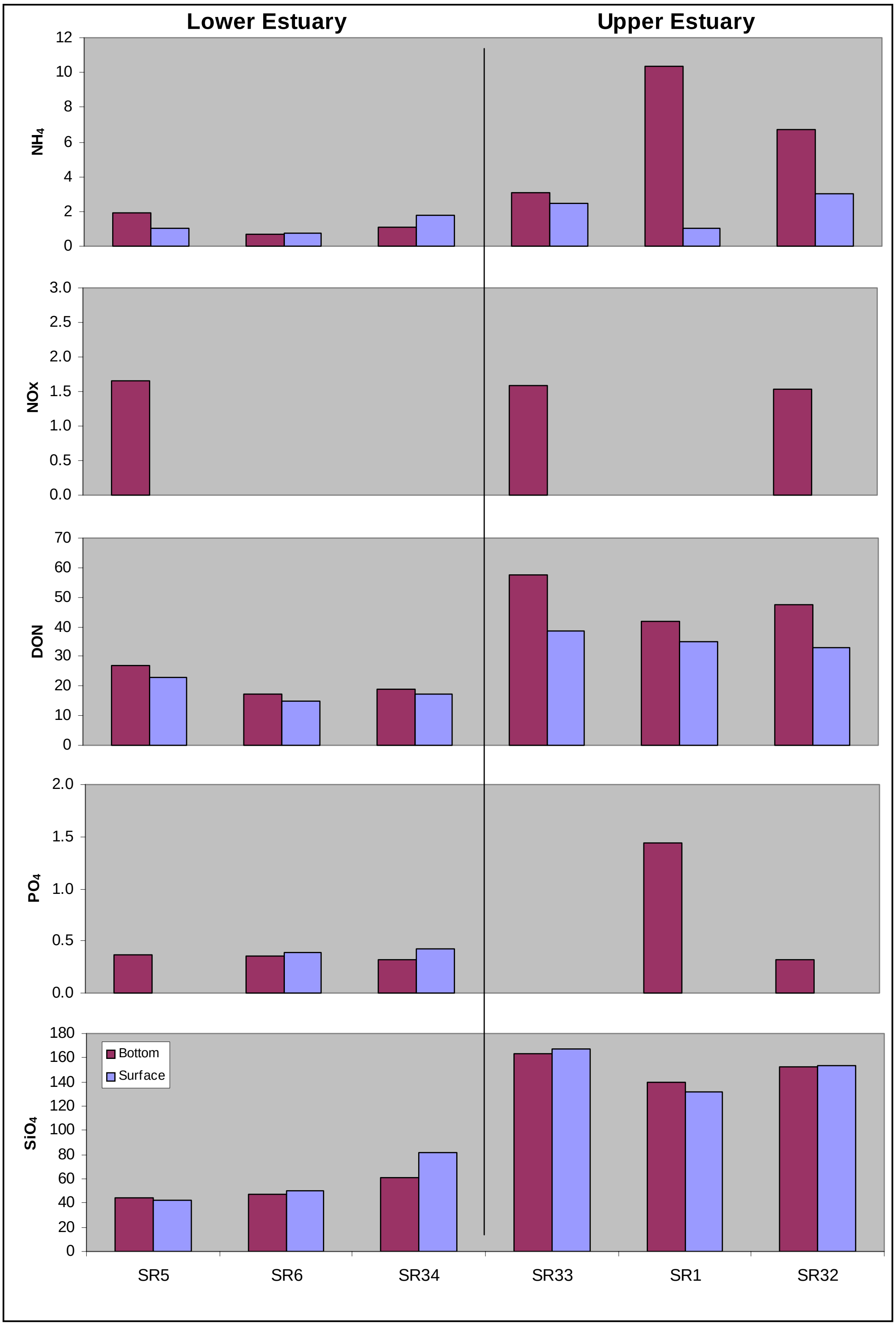


Figure 7. Bottom water (dark purple) and surface water (light purple) nutrient concentrations at each site in µM. Sites are arranged left to right, from most downstream to most upstream.

Surface water total nitrogen (TN) levels were much higher in the upper estuary compared to the lower estuary while total phosphorus (TP) levels were only significant at SR33 and SR1 (Figure 8). The relatively low dissolved inorganic N and P levels in surface waters (Figure 7) indicate that a significant proportion of N and P in surface waters was either organic or particulate. This could be explained by the enhanced primary productivity (as seen in the higher Chl-a concentrations: Figure 6) at these sites supplying more particulate N and P via the increased biomass. Another possible explanation could be resuspension of sediments from the estuary bottom from *particle entrainment* (O'Callagahan, 2004), a process whereby friction from tidal action at the leading edge of the salt wedge forces sediment particles into the overlying water.

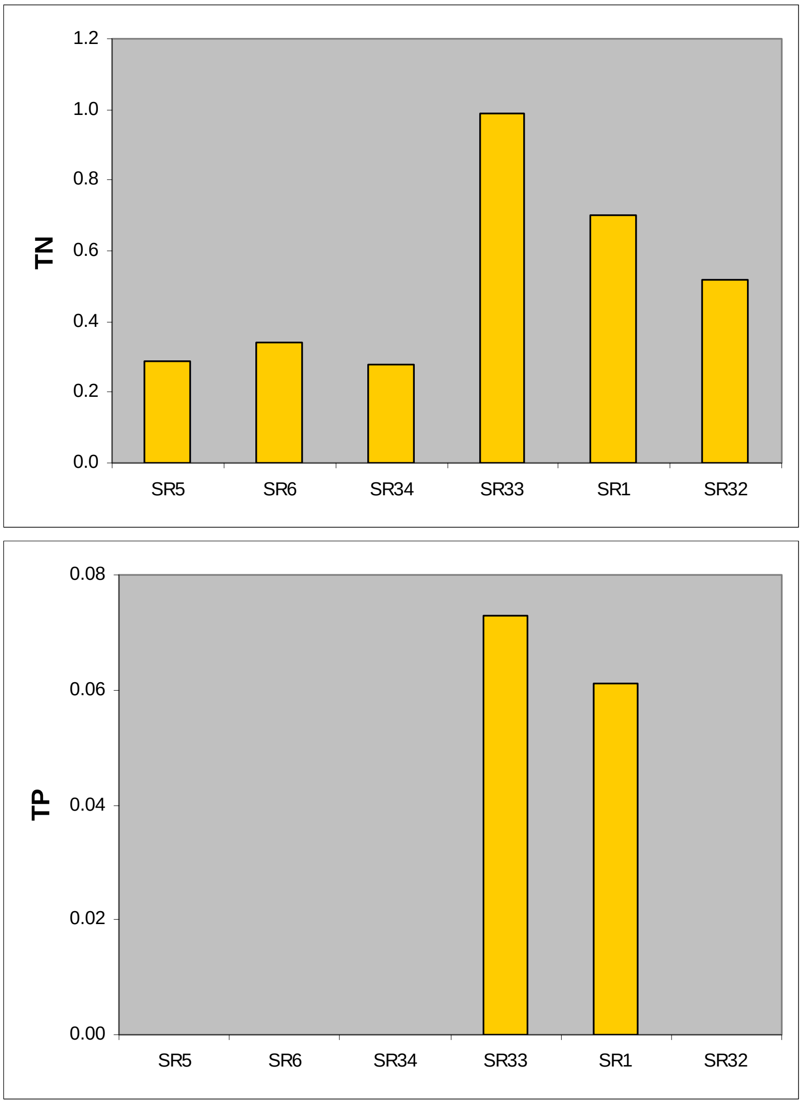


Figure 8. Surface water total nitrogen (TN) and total phosphorus (TP) concentrations at each site in mg/L. Sites are arranged left to right, from most downstream to most upstream.

2A2. BENTHIC NUTRIENT FLUXES

Organic matter supply to the sediment and nutrient release

In the Swan River Estuary, rates of nutrient release from the sediment (benthic fluxes) were most distinctly governed by sediment type (i.e mud versus sand) and the environmental setting (i.e. lower versus upper estuary). Muds occurring in the upper estuary (SR32 and SR1) had much higher rates of nutrient release compared to all sandy sites (SR33, SR34, and SR6) and also muds occurring in the lower estuary (SR5; Figure 9; Appendix 2). Nutrient fluxes measured at SR32 and SR1 were also much more variable than at any other site. For example, carbon dioxide (TCO_2) fluxes at SR32 ranged from 90 to 1550 mmol m^{-2} day^{-1}. Of the eight parameters determined (TCO_2, O_2, NH_4^+, NO_X, N_2, DON, PO_4^{3-}, and SiO_4^{4-}), only O_2, NO_X, and N_2 did not fit this pattern of benthic flux magnitude and within-site variability.

Note that the graphs in Figure 9 only show fluxes measured under dark conditions, and therefore, result from respiration processes (organic matter breakdown) only. Dark conditions existed at the sediment surface at SR32, SR1, and SR33, according to PAR profiles (Table 2), and/or observed by divers. Therefore, all benthic chamber deployments at these sites were considered dark incubations even though two of the chambers at SR32 and three of the chambers at SR33 and SR5 were transparent and sampled during daylight hours. Sunlight penetrated the water column, illuminating the sediment surface at SR34 and SR6. Benthic fluxes measured under these ‘light’ conditions are presented in Figure 10 in the next section.

The high rates of carbon dioxide (TCO_2) and nutrient release at SR1 and SR32 (Figure 9) indicate these sediments are very organic-rich and have a ready supply of fresh organic material, either delivered from the catchment with winter runoff, or from localised phytoplankton growth such as algal blooms during spring and summer, within the upper estuary itself. Conversely, in a cyclical sense, these organic-rich muds would also sustain ongoing phytoplankton blooms by providing abundant bioavailable N and P in spring and summer when catchment inputs of nutrients are low but light availability and temperatures are high. Determining the extent of these organic-rich muds throughout the estuary is therefore important for determining an overall nutrient budget for the Swan River Estuary. Notably, their distribution in the upper estuary is not necessarily ubiquitous. The sandier sediments at SR33 had far lower nutrient fluxes than the muds at SR1 and SR32 (Figure 9) despite having a relatively stratified water column (Figure 3 and Figure 5) and potentially often having hypoxic bottom waters. Similarly, not all muds in the estuary necessarily have high fluxes. For example, muds in the deep central basin (SR5) had relatively low rates of nutrient release compared to the muds at SR1 and SR32 (Figure 9).

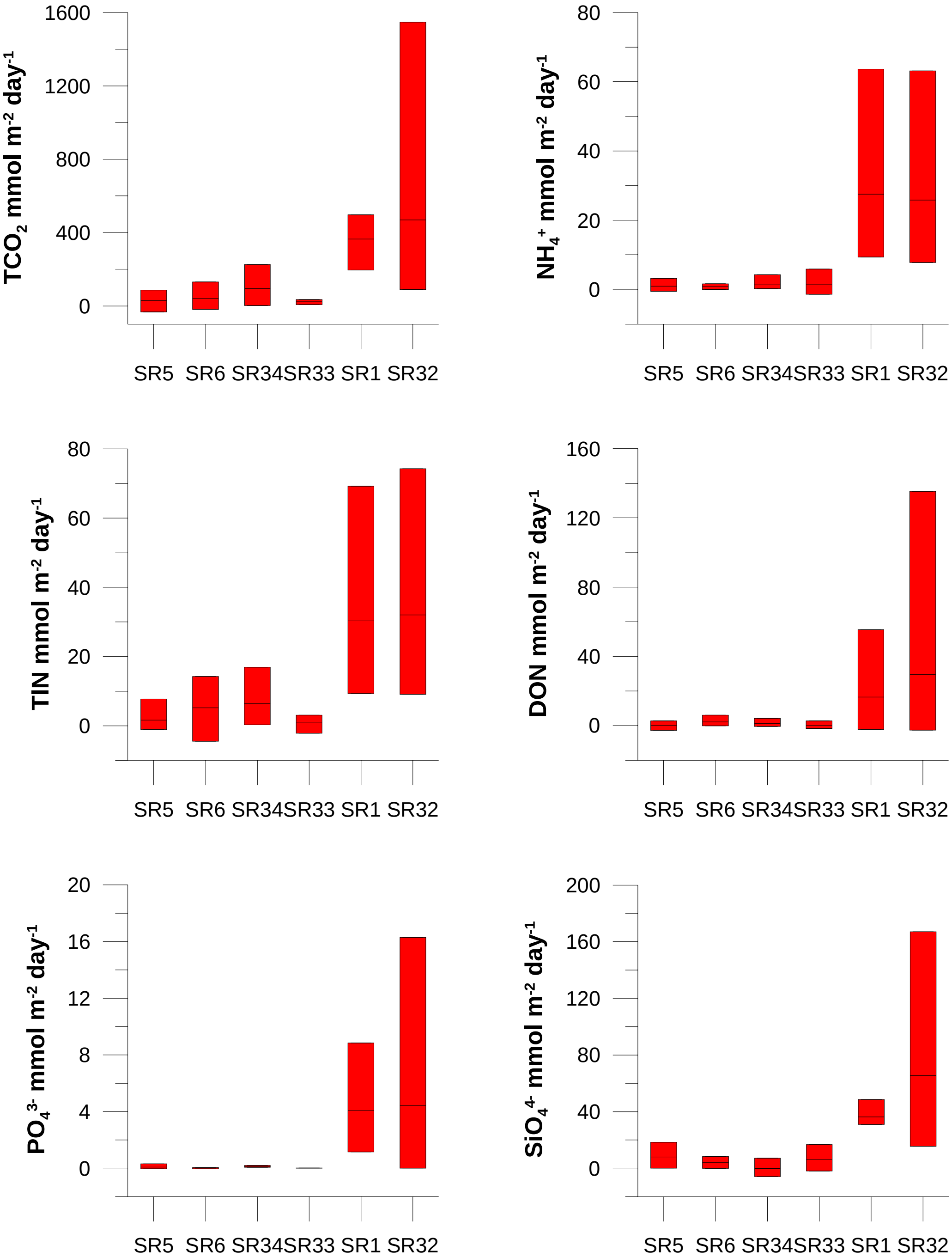


Figure 9. Benthic fluxes for all sampling sites in mmol m^{-2} day^{-1}. The red boxes show the range in flux measurements at each site. The average is marked by a horizontal line within each red box. Sites are arranged left to right, from most downstream to most upstream. See Appendix 1 for individual benthic flux rates measured in each chamber at each site.

In contrast to the upper estuary, relatively smaller benthic nutrient fluxes in the lower estuary (Figure 9) indicate that nutrient availability in the water column is much more reliant on recent nutrient inputs from the catchment. This, along with clearer waters and greater light penetration (Table 2), has led to differences in the nature and extent of plant growth in the lower estuary compared to the upper estuary. As mentioned previously, the relatively high benthic nutrient fluxes in the upper estuary can sustain relatively high growth rates of phytoplankton in spring and summer, a time when light and temperature are most favourable for growth but catchment nutrient inputs are low. In the lower estuary however, higher phytoplankton growth rates would usually be restricted to early springtime, when nutrients are available from recent winter runoff. Additionally, in shallow areas where sunlight can illuminate the estuary bottom, nutrient uptake by benthic plants further reduces the nutrients available to phytoplankton.

Benthic photosynthesis

Limited light availability at the sediment surface of three upper estuary sites (SR32, SR1, and SR33) and at the deep central basin site (SR5; Table 2) indicate benthic photosynthesis was absent at these sites. Photosynthesis was, however, occurring at the sediment surface at the shallow sandy margin sites in the lower estuary (SR6 and SR34) as seen by the positive O_2 and negative TCO_2 fluxes (Figure 10). The extent of benthic photosynthesis at SR6 was greater than at SR34, as indicated by greater net TCO_2 uptake and O_2 release in both transparent chambers at SR6 (Figure 10). This was consistent with greater light availability at the sediment surface at SR6 (Table 2) and a larger increase in bottom water dissolved oxygen levels between morning and afternoon (Figure 4). Light availability for benthic photosynthesis at SR34 was marginal at the time of sampling, with one transparent chamber indicating net photosynthesis (negative TCO_2 and positive O_2 fluxes) and the other transparent chamber indicating net respiration (positive TCO_2 and negative O_2 fluxes). This suggests that benthic plants grow in the lower estuary under ideal conditions, that is, a clear water column, and long, sunny days in spring and summer. Benthic plant growth is very sensitive to changes in water clarity, cloud cover and the change in seasons and benthic plants likely begin to die in late summer and autumn when light levels are reduced. This subsequently provides organic material to the sediments and results in the dominance of respiration processes and a drop in bottom water dissolved oxygen levels.

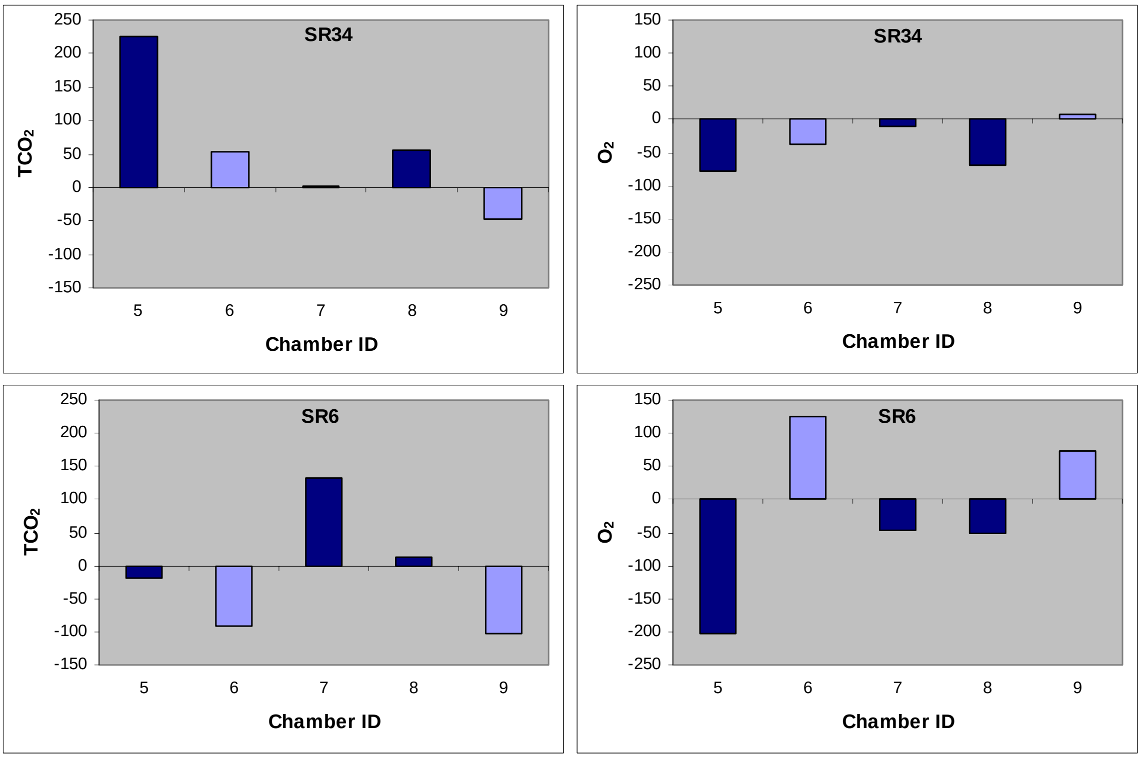


Figure 10. TCO_2 and O_2 benthic fluxes in mmol m^{-2} day^{-1}, measured in each benthic chamber deployed at SR34 and SR6, both located on the sandy margins of the central basin in the lower estuary. Transparent chambers are light blue and opaque chambers are dark blue.

Denitrification

Denitrification is a process of organic matter breakdown where nitrogen is released from the sediments as N_2 gas, as opposed to NH_4^+ or other such forms of dissolved nitrogen. Unlike these dissolved forms, plants cannot directly use N_2 gas for growth and nitrogen is therefore lost from the estuary to the atmosphere. The degree to which denitrification is occurring in the sediments can indicate the susceptibility of an estuary to eutrophication. The proportion of total nitrogen released from the sediment as N_2 gas is shown in Figure 11. In general, chambers at the muddy sites in the upper estuary (SR1 and SR32) had low rates of denitrification (25% or lower). The deep central basin site (SR5) and SR33 in the upper estuary had moderate to high denitrification (above 50%) and sites on the sandy margin of Melville Water (SR6 and SR32) had the highest rates of denitrification (close to 100%).

Low rates of denitrification in the muddy sediments of the upper estuary are concerning, especially since these sites also have very high rates of organic matter supply to the sediments and high *absolute* rates of nutrient release. There are virtually no moderating controls on nutrient release from the sediments of these sites. In addition to low rates of denitrification, the sediments at these sites are a poor trap for P (Figure 9) and there are no freshwater flows to flush nutrients downstream in spring and summer when conditions are favourable for phytoplankton growth. Light penetration into the water column is also limited so there are no benthic plants to take up nutrients. This is further exacerbated in spring when stratification from the upstream migration of a salt wedge effectively blocks resupply of oxygen to the bottom waters, resulting in anoxia and anaerobic respiration.

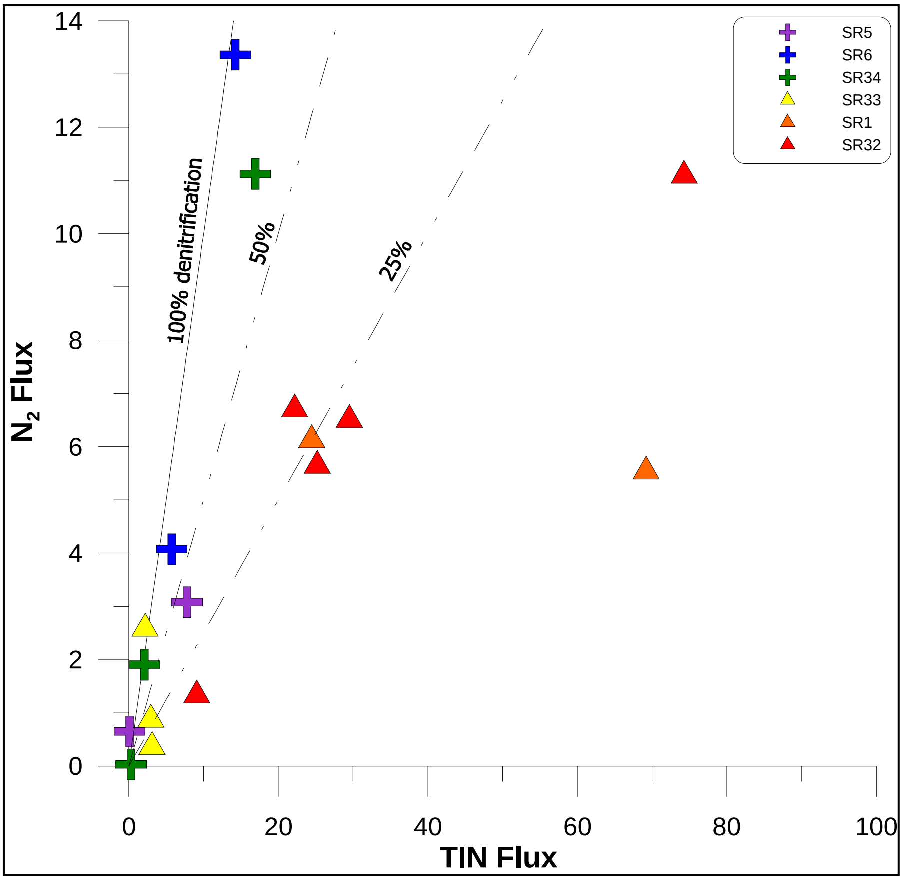


Figure 11. N_2 versus TIN benthic fluxes in mmol m^{-2} day^{-1}, measured in each benthic chamber at all sites. The lines indicate the percentage of total nitrogen released as N_2 (i.e the amount of denitrification).

2A3. SEDIMENT COMPOSITION AND POREWATER NUTRIENTS

The total organic carbon concentration correlates positively with the porosity of the sediment, i.e. the very muddy sediment at SR32 had the highest total organic carbon concentration, whereas the silty to sandy sediments at SR33 and SR34 had the lowest organic carbon concentration (Figure 12).

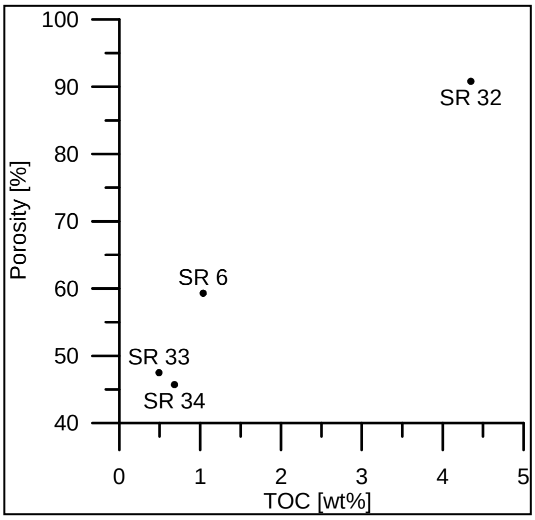


Figure 12. Correlation of the total organic carbon (TOC) concentration and porosity in surface sediments at sites SR6, SR32, SR33, SR34.

The stable carbon and nitrogen isotopic composition of the bulk organic matter from surface sediments at SR6, SR32, SR33 and SR34 is shown in Figure 13. Also shown are areas representing typical isotopic composition of organic matter from different sources (Cloern *et al*., 2002). The sediments at the two lower estuary sites (SR6 and SR34) plot apart from the upper estuary sites (SR32 and SR33) in terms of $\delta^{13}C$. $\delta^{13}C$ in the lower estuary sites range from -20.2 to -22.2, indicating that the decomposing organic matter is predominantly of marine source. $\delta^{13}C$ in the upper estuary sites range from -26.7 to -27.6, indicating terrestrial inputs account for much of the decomposing organic matter.

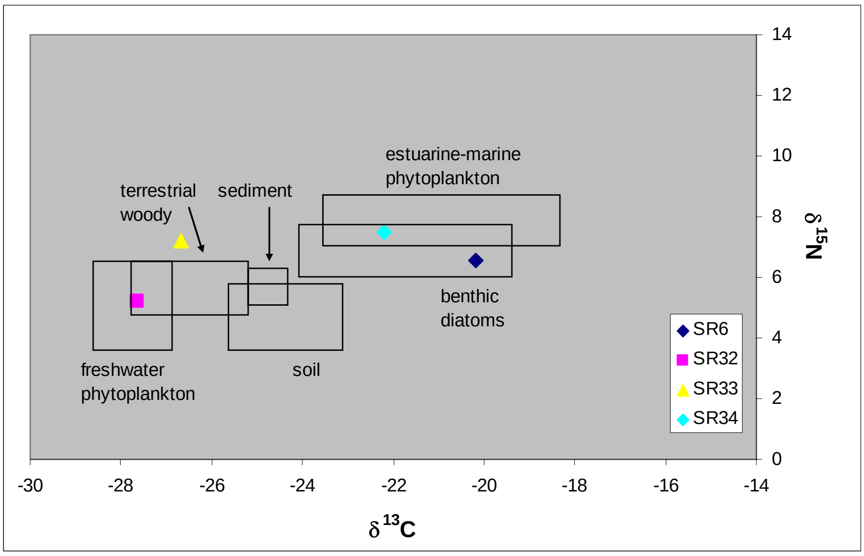


Figure 13. Stable carbon and nitrogen isotopic composition of bulk organic matter samples (modified after Cloern et al., 2002).

Sediment cores were collected from three sites that had not previously been sampled in the first three surveys (SR32, SR33, and SR34). Profiles of porewater nutrient concentrations measured in these cores (Figure 14) showed that nutrient concentrations increased sharply with depth at SR32 whereas porewater nutrient concentrations at SR33 and SR34 were comparatively much smaller and there was little change with depth. These profiles were consistent with the higher benthic nutrient fluxes at SR32 (Figure 9), and further highlights that the muds at SR32, comprise a very high proportion of fresh organic material which is rapidly breaking down. This is in contrast to the sands in the upper estuary (SR33) and around the shallow margin of the lower estuary (SR34) where organic matter breakdown and release rates are low. Porewater nutrient pool sizes calculated for the top 20 cm of sediment at each site (Figure 15) indicate the greater degree of organic matter breakdown at SR32 where the porewater pool of both NH_4^+ and PO_4^{3-} were about 20 times greater than at SR33 and SR34.

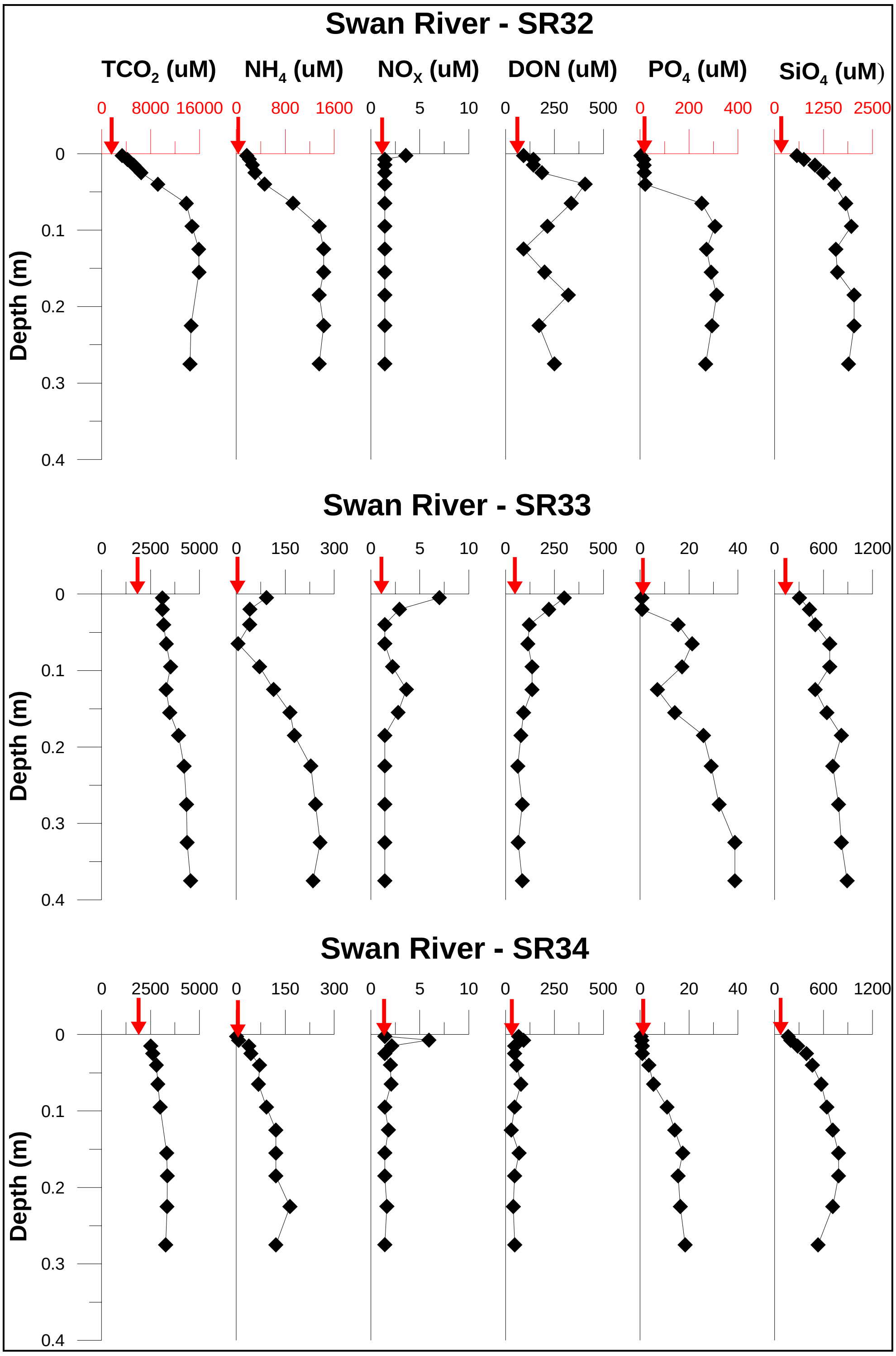


Figure 14. Porewater nutrient profiles for SR32, SR33 and SR34 in the Swan River Estuary. Note the red arrows indicate the bottom water nutrient concentrations. The axes are the same for each nutrient unless they are coloured red.

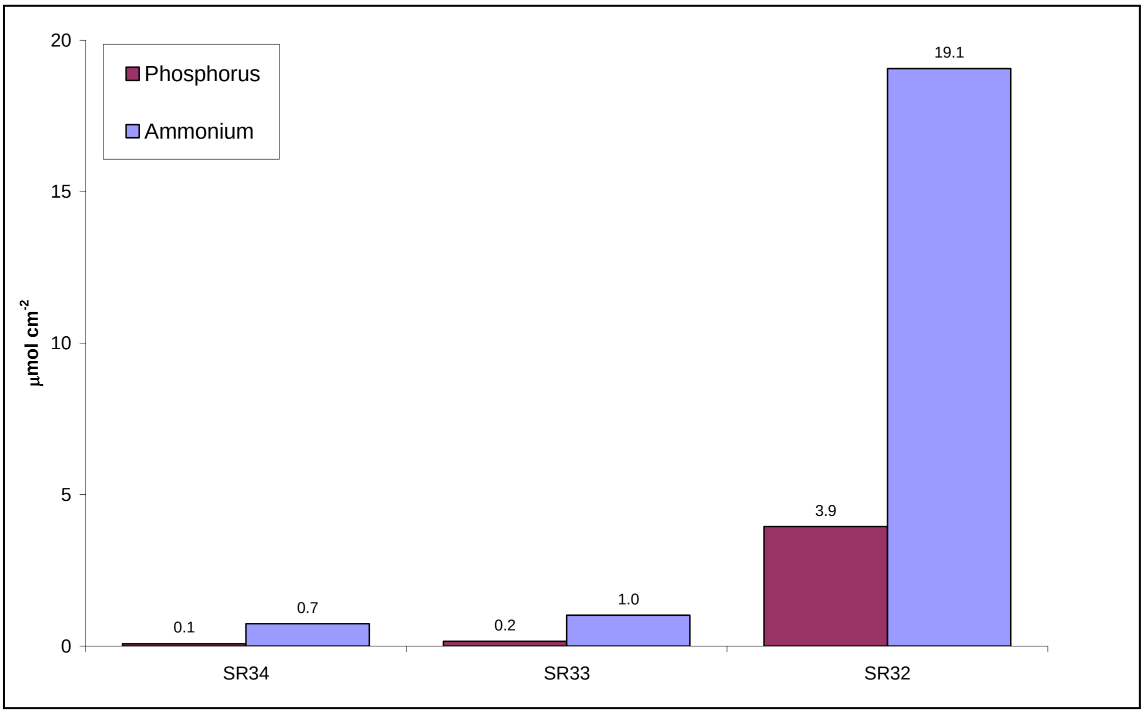


Figure 15. Porewater pool sizes for phosphorus and ammonium at the core sites. Sites are arranged left to right, from most downstream to most upstream. Porewater pool sizes were calculated from porewater profiles using the mass of each dissolved nutrient in the top 20 cm of sediment (where a depth of 20 cm was estimated as the limit of the most active zone of organic matter degradation) based on the measured nutrient concentration in each depth layer and the porosity.

The porewater nutrient profiles from SR32 are comparable to those measured at SR1 in previous surveys (Fredericks *et al*., 2002). Given that both these sites also have similarly high benthic nutrient fluxes (Figure 9) it can be assumed that the muds at these sites are subject to similar environmental conditions and organic matter input. Importantly however, porewater profiles at SR33, which is also located in the upper estuary, are significantly different to SR1 and SR32. Therefore, similarly to the conclusions drawn from the benthic flux results, the highly organic-rich muddy sediments are not necessarily ubiquitous throughout the upper estuary. It should be a high priority to map the extent of these sediments that are releasing a significant proportion of the nutrients sustaining phytoplankton growth in spring and summer.

2A4. METALS

Sediment porewaters and benthic chamber water samples were analysed for dissolved metals to assess if the sediments were a source of metals at SR33. It has been suggested that groundwater flows could be importing metals to this upper estuary.

Cores

Porewater profiles of aluminium (Al) and copper (Cu) are similar (Figure 16) indicating that the redox conditions must be suitable for the solubilisation of these two metals in the top 8 cm of the sediment. The PO_4^{3-} and SiO_4^{4-} concentrations (Figure 14), are high in the same region (4-9 cm depth), while the NH_4^+ and NO_X concentrations are at their lowest. This fluctuating trend in nutrient concentrations is not seen in the SR32 and SR34 core porewater samples.

Porewater arsenic (As), cadmium (Cd) and vanadium (V) increase to maximum concentrations at 12 cm indicating a change in redox potential and sediment chemistry at that depth. Although there is dissolved As, Cd and V in the porewater profiles, these metals are strongly bound in the sediments close to the sediment-water interface and are not released into the water column. Zinc (Zn) also shows a slight increase in concentration at depths of 6-9 cm, after a rapid drop in the first 0.5 cm.

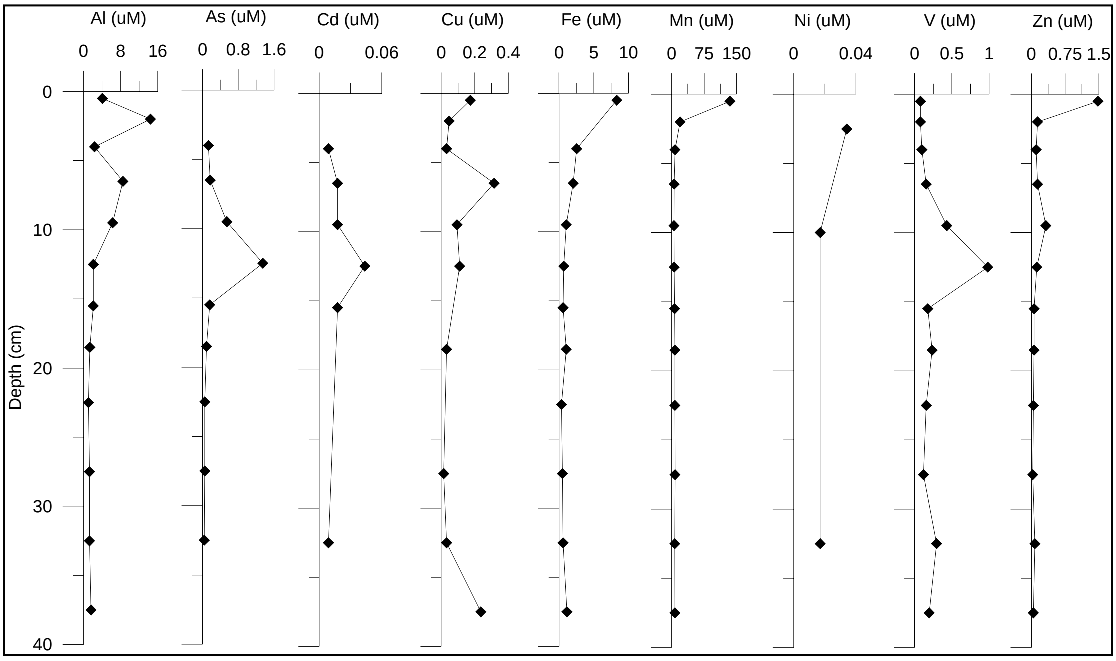


Figure 16. Down core dissolved metal concentrations from SR33

Chambers

The average bottom water concentration of Al, Cd, manganese (Mn) and nickel (Ni) observed in the chambers was well below the respective ANZECC 99% species trigger values for fresh and marine waters (Table 3). In general the marine trigger values are higher than their freshwater equivalents. The bottom water at SR33 had a salinity of approximately 10, which is typical of an estuary and the actual trigger values most likely lie somewhere in between the marine and freshwater ones shown in Table 3. It has been observed in other estuaries that dissolved metal concentrations, particularly Cu, Zn and in some cases Cd, are highest in areas with mid range salinities (Zwolsman *et al*., 1997).

Table 3. The dissolved metal concentrations measured in the Bottom Water for chamber deployments at SR33 plus the average concentration along with their associated ANZECC Freshwater and marine trigger values All values are in µM.

Chamber	Al	Cd	Cu	Mn	Ni	Zn
33A-1	0.34	0.000	0.09	7.46	0.03	0.26
33A-2	0.41	0.000	0.06	6.73	0.00	2.45
33A-3	0.56	0.000	0.08	7.46	0.02	0.99
33B-1	0.44	0.002	0.06	5.10	0.03	1.68
33B-2	0.27	0.001	0.06	5.82	0.03	1.53
33B-3	0.78	0.001	0.08	5.46	0.05	5.20
Average	**0.47**	**0.001**	**0.07**	**6.34**	**0.03**	**2.02**
ANZECC Fresh						
Protect 99% Species	1	0.2	0.02	22	0.14	0.04
Protect 80% Species	6	1.3	0.04	66	0.29	0.47
ANZECC Marine						
Protect 99% Species	N/A	N/A	0.00	N/A	0.1	0.11
Protect 80% Species	N/A	N/A	0.13	N/A	9.5	0.66

Cu and Zn concentrations were consistently greater than the 99 and 80% ANZECC trigger values for freshwater. The average bottom water concentration of Cu was 0.07µM (Table 3), which is double even the ANZECC 80% species trigger value and therefore of concern. The average bottom water zinc concentration (2 µM) was 4 times higher than the ANZECC 80% trigger value freshwater (Table 3). The average Cu and Zn concentrations in the chambers were higher than in the sediment porewaters and the fluxes were either very small or slightly negative (Table 4). This indicates that the sediment at SR33 is a potential sink for Cu and Zn, rather than a source.

Table 4. Dissolved metal fluxes from SR33 (mmol m^{-2} day^{-1})

	Metal Flux (mM/m^2/day)					
Site	**Al**	**Cd**	**Cu**	**Mn**	**Ni**	**Zn**
33A 1	0.07	0.00	-0.01	-0.36	0.00	-0.57
33A 2	0.05	0.00	-0.01	2.34	0.00	0.23
33A 3	0.15	0.00	0.00	2.45	0.01	-0.83
33B 1	0.02	0.00	0.02	1.67	0.03	0.19
33B 2	0.05	0.00	0.00	0.87	0.00	0.18
33B 3	-0.03	0.00	0.06	1.27	0.00	-1.00

2B. Survey Comparison 2000 - 2006

2B1. SEASONAL CONTEXT AND WATER COLUMN CONDITIONS

There are distinct differences in the water column conditions between the surveys at each site. Changes in rainfall (and hence flow) are the main drivers for the physical and chemical characteristics of the water column at each site. Therefore, the time of year the survey was undertaken is important. The four surveys were conducted at different times of the year; the first two surveys were conducted in autumn and the last two surveys were conducted in spring of their respective years. Table 5 shows the temperature, salinity and percent dissolved oxygen saturation within the surface and bottom waters of each site during the four survey periods. These parameters are important in terms of estuarine health as they can result in stratification, which in turn can drive the creation of algal bloom through increased nutrient fluxes from the sediments.

Table 5. Water column temperature (^{o}C), salinity and dissolved oxygen (%) at SR1, SR5 and SR6 during each survey

Site	Survey	Depth	Temperature	Salinity	Dissolved Oxygen
SR1	1	Surface	25.7	8.7	131.9
		Bottom	24.8	17.8	4.1
	2	Surface	20.9	27.0	82.0
		Bottom	21.4	28.2	70.0
	3	Surface	16.1	3.9	99.5
		Bottom	16.1	3.9	99.5
	4	Surface	23.2	7.5	114.3
		Bottom	23.2	12.4	49.0
SR5	1	Surface	24.2	26.5	112.7
		Bottom	23.4	33.3	45.4
	2	Surface	20.2	36.5	95.0
		Bottom	19.7	36.5	84.6
	3	Surface	18.2	15.7	104.0
		Bottom	17.4	32.5	49.2
	4	Surface	20.0	28.2	103.0
		Bottom	19.0	32.8	79.6
SR6	1	Surface	24.4	28.1	95.5
		Bottom	24.4	29.2	78.1
	2	Surface	19.4	37.2	104.0
		Bottom	19.2	37.4	102.8
	3	Surface	17.1	20.9	106.3
		Bottom	17.1	22.6	72.7
	4	Surface	21.3	24.8	104.7
		Bottom	20.2	27.1	97.7

Survey 1 (14th – 24th March, 2000)

Prior to the March 2000 survey, unseasonably heavy rainfall associated with Cyclone Steve fell in the catchment of the Swan-Avon River system. The resultant runoff was enough to fill the Swan-Canning Rivers and estuary five and a half times over (WRC, 2000), and lowered the salinity of the upper estuary considerably (8.7 in the surface waters of SR1; Table 5). In Melville Water (SR5) salinity remained high in the bottom waters (33.3) but was reduced in the surface waters (26.5), indicating a freshwater lens overlying the denser marine waters and causing stratified conditions. Dissolved oxygen was severely reduced in the bottom waters compared to the surface waters, particularly in the deeper sites. SR1 DO was 131.9% in the surface water and 4.1% in the bottom waters and at SR5 DO was 112.7% in the surface waters and 45.4% in the bottom waters. The super-saturated surface waters at SR1 and SR5 are indicative of phytoplankton production, possibly associated with a bloom. Estuary conditions during this survey were more typical of winter-time conditions but with higher water temperatures.

Survey 2 (21st March – 2nd April, 2001)

Lower than average rainfall prior to this survey resulted in marine water intrusion into the Upper Swan (salinity of 28.2 in the bottom waters of SR1) and hyper-saline conditions in Melville Waters (36.5 in the bottom waters of SR5 and 37.4 in the bottom waters of SR6; Table 5). The water column was well mixed (Figure 17) with no stratification apparent at any site. Dissolved oxygen was only slightly depleted in the bottom waters of the deeper sites (70.0% at SR1 and 84.6% at SR5). There is some super-saturation of surface waters in the upper estuary (Figure 17), which could be associated to phytoplankton blooms.

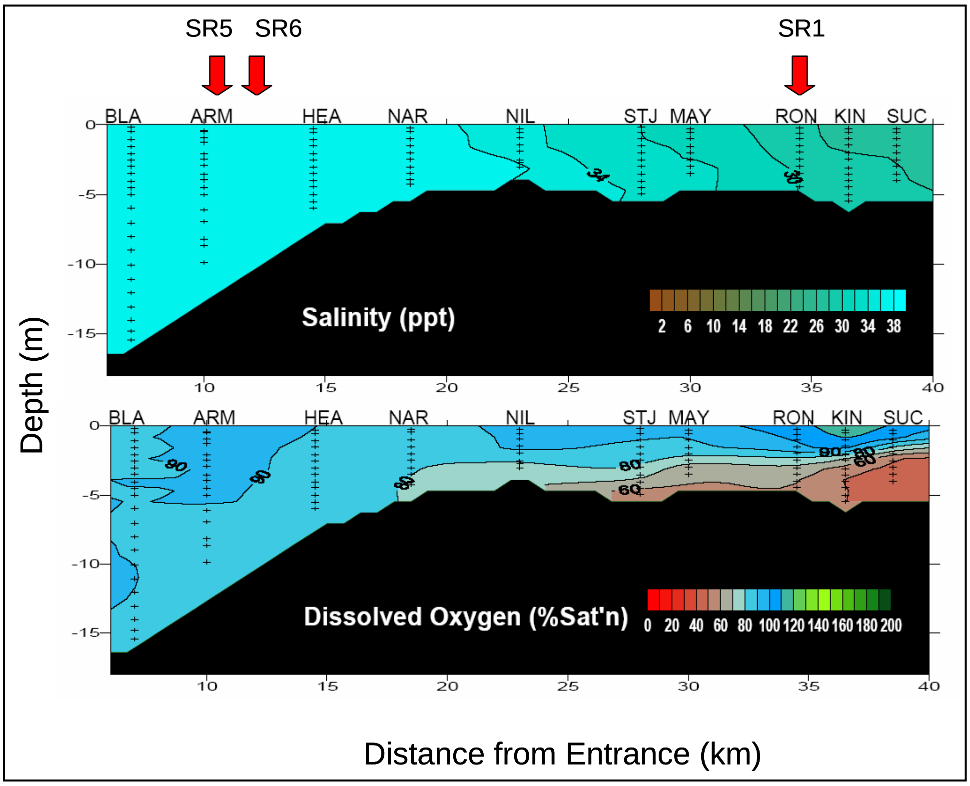


Figure 17. Longitudinal profiles of salinity and dissolved oxygen in the Swan River Estuary during Survey 2 (27th March 2001). Source: Swan River Trust website (www.swanrivertrust.wa.gov.au). The three-letter codes are Swan River Trust weekly water quality monitoring sites. Note that SR6 is located off-centre of the longitudinal profile on the shallower margins of the central basin.

Survey 3 (27th September- 7th October, 2001)

Survey 3 was conducted when a salt wedge was migrating upstream after the cessation of the winter rains (Figure 18). The salt water intrusion had extended part way up the Swan River but not as far as SR1. As a consequence, water column conditions varied markedly between the upper and lower estuary. Salinity at SR1 was less than 4 indication freshwater conditions. At SR5 there was some stratification with salinities of 15.7 in the surface waters and 32.5 in the bottom water and dissolved oxygen depleted to less than 50% of surface water saturation (Table 5).

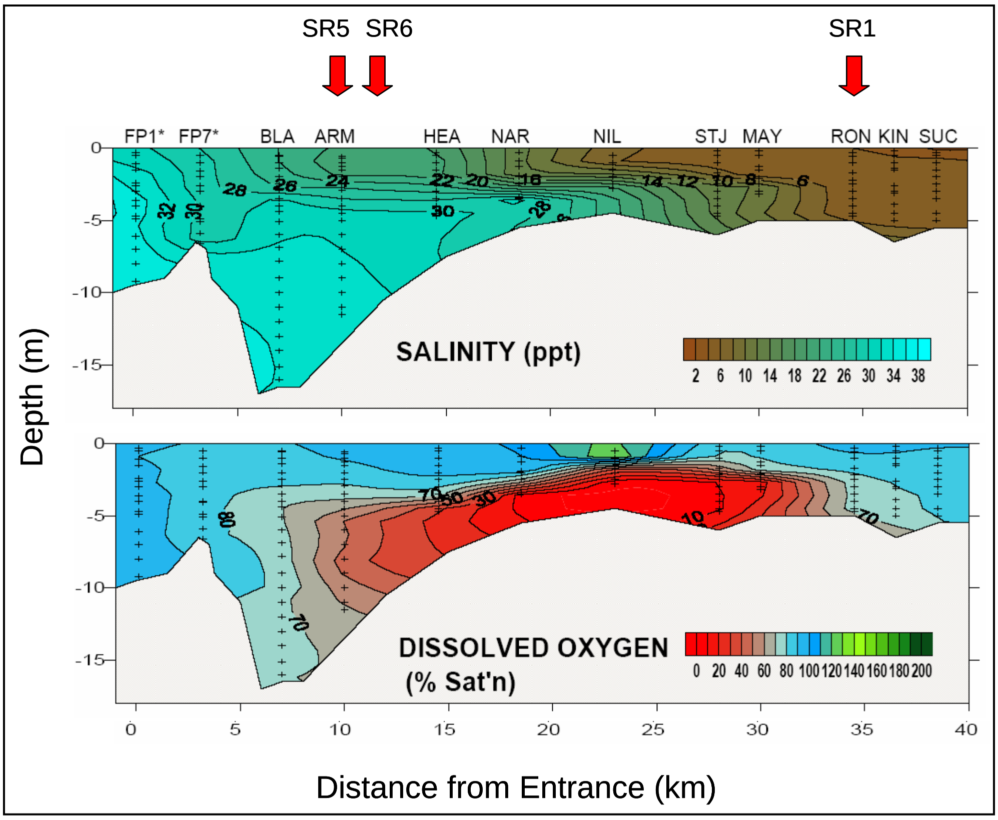


Figure 18. Longitudinal profiles of salinity and dissolved oxygen in the Swan River Estuary during Survey 3 (24th September 2001). Source: Swan River Trust website (www.swanrivertrust.wa.gov.au). The three-letter codes are Swan River Trust weekly water quality monitoring sites. Note that SR6 is located off-centre of the longitudinal profile on the shallower margins of the central basin.

Survey 4 (18th – 29th October, 2006)

There was average rainfall for the 2 months prior to survey 4, however, much lower than average rainfall fell prior to that. The water column conditions were still typical of spring/early summer conditions (Figure 3). Salinity varied from 7 to 12 at SR1 to around 30 in Melville Waters. Dissolved oxygen was much more depleted in the bottom waters of the upper estuary (SR1) than in the bottom waters of Melville Waters. For a more detailed explanation of site conditions during Survey 4, see section 2A1.

Water Column Nutrients

Changing nutrient concentrations between surveys are either a direct response to changes in hydrodynamic conditions or a result of altered catchment conditions and increased urbanisation.

Water column concentrations of NH_4^+, NO_X and SiO_4^{4-} (Table 6) were generally higher during the spring surveys (surveys 3 and 4) than the autumn surveys (surveys 1 and 2). This is likely due to the winter rains bringing nutrient-rich freshwater into the estuary prior to these spring surveys. As expected the upper estuary (SR1) experiences increases in greater nutrient concentrations (*eg* SiO_4^{4-} concentrations increased from 25-47 µM to over 130 µM between autumn and spring). Additionally, SR5 (the most downstream site) has the greatest marine influence and therefore has the smallest nutrient increases between autumn and spring. N:P ratios at all sites during all surveys indicate that N is most probably the limiting nutrient for phytoplankton growth, although PO_4^{3-} concentrations tend to decrease over time.

Table 6. Bottom water nutrient concentrations at sites SR1, SR5 and SR6 during each survey. All concentrations are in µM

Site	Survey	NH_4^+	NO_X	N_2	PO_4^{3-}	SiO_4^{4-}
SR1	Mar-00	0.3	0.0	477.8	1.9	24.5
	Mar-01	1.9	0.2	443.0	1.0	47.0
	Sep-01	3.9	9.1	553.0	1.4	134.9
	Oct-06	4.3	1.4	490.3	0.7	131.7
SR5	Mar-00	3.7	0.9	411.4	0.8	12.2
	Mar-01	0.5	0.4	408.2	0.6	23.9
	Sep-01	4.6	1.2	463.1	0.8	29.4
	Oct-06	1.9	1.7	421.0	0.4	44.5
SR6	Mar-00	2.2	0.2	429.9	1.1	22.5
	Mar-01	0.9	0.1	409.3	0.6	22.2
	Sep-01	1.0	0.7	480.8	0.3	49.1
	Oct-06	1.5	1.4	409.2	0.4	47.9

2B2. BENTHIC NUTRIENT FLUXES

Appendix 2 shows the average and standard deviation of benthic fluxes from the three sites within the Swan River Estuary. There is no significant light penetration to the sediments of SR1 and SR5 (see section 2A1), therefore all chambers were treated as dark. Fluxes from SR6 were averaged into light and dark fluxes for each survey, as this site was shallow and benthic productivity was evident, a net 24-hour flux was calculated.

Upper Estuary (SR1)

Average O_2 fluxes (Figure 19) at SR1 are similar between all surveys ranging from 33.9 to 54.3 mmol m^{-2} day^{-1}. However, the average TCO_2 fluxes are much larger during survey 4 (365 mmol m^{-2} day^{-1}) compared to the first 3 surveys (59.5 to 97.3 mmol m^{-2} day^{-1}). This indicates that there has been a large increase in the rate of organic matter decomposition, but there has been insufficient oxygen for its degradation. This is also reflected in the bottom water oxygen concentrations (Table 5) that show a reduced level (49.0% saturation) during the last survey. In the absence of oxygen, sulphate reduction or methanogenesis are likely to be significant. Due to the high reactivity of this organic matter, it is believed that it was deposited in a recent event, most probably with the 2006 winter rains.

Average TIN fluxes (Figure 19) were very low during the first survey (NH_4^+, NO_X and N_2 fluxes of 0.18, 0.03, and 0.52 mmol m^{-2} day^{-1} respectively) and increased with each subsequent survey (NH_4^+, NO_X and N_2 fluxes of 27.54, 0.00, and 3.01 mmol m^{-2} day^{-1} respectively during survey 4). Denitrification Efficiencies (calculated as the percentage N_2 within the TIN flux) were between 40% and 72% during the first 3 surveys, but decrease to 10% in the last survey. It appears that the additional carbon load during this final survey is using up the available oxygen; this in turn creates anoxic conditions that are impacting the denitrification pathway. Anoxia prevents nitrification and therefore limits denitrification. The net result is more nitrogen is retained in the biologically-available NH_4^+ form.

The average fluxes of PO_4^{3-} and SiO_4^{4-} (Appendix 2) follow a similar trend to the nitrogen species with smaller fluxes during the first three surveys and an increase during the final survey. This larger release of nutrients during the final survey supports the notion of increased organic matter breakdown. The increase in PO_4^{3-} during the final survey is also due to the reduced P-binding capacity of the sediments at this site. When iron oxyhydroxides are used as oxidants, the PO_4^{3-} bound to their surface can be released from the sediments into the overlying water. This is of concern as the nutrients that are being released are bioavailable and can be used to support phytoplankton blooms in the upper estuary.

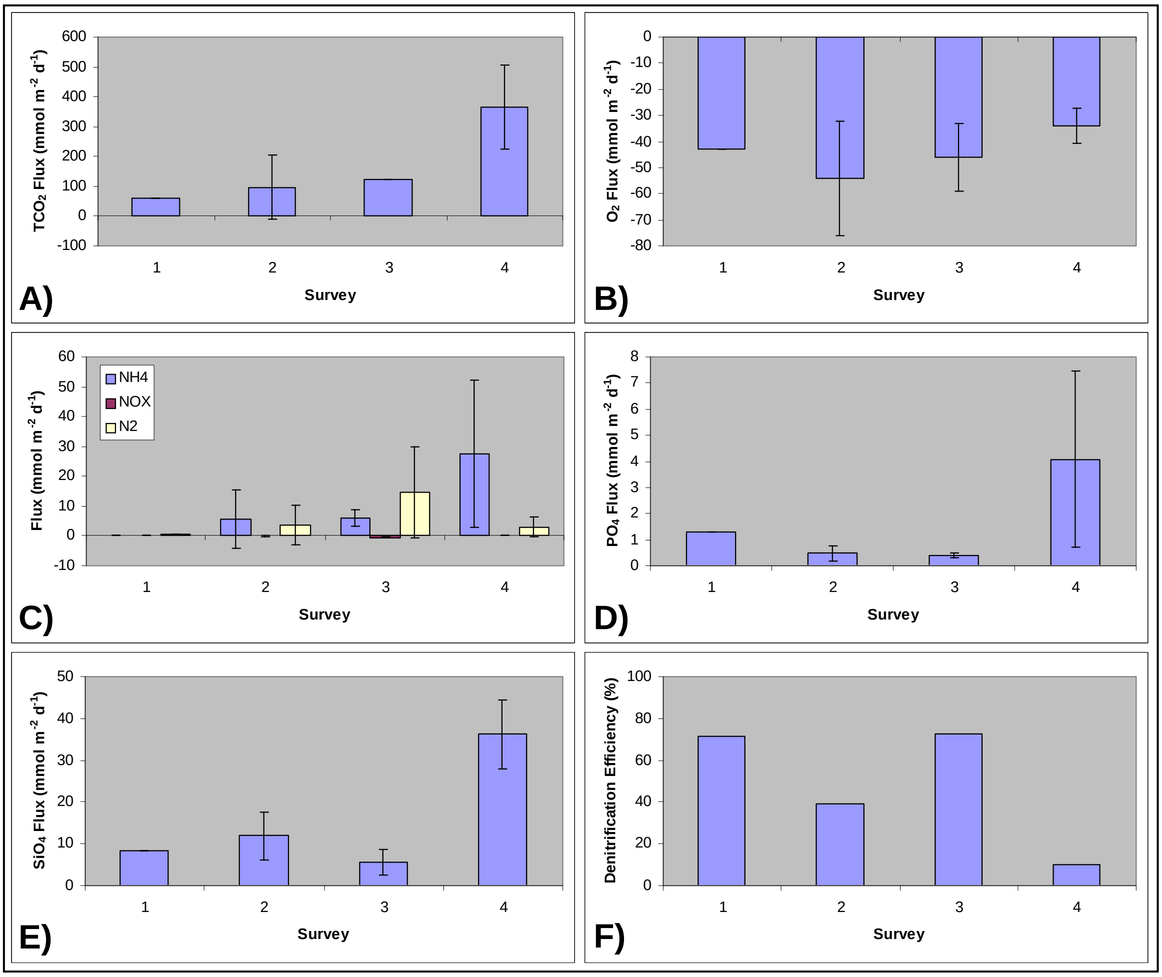


Figure 19. Average TCO_2 (A), O_2 (B), NH_4^+ + NO_X + N_2 (C), PO_4^{3-} (D) and SiO_4^{4-} (E) fluxes, and Denitrification Efficiencies (F) from site SR1 during the 4 surveys. Error bars show the standard deviations.

Central Basin (SR5)

The average O_2 fluxes (Figure 20) at SR5 were quite low with uptake rates ranging from 15.4 mmol m^{-2} day^{-1} to 58.4 mmol m^{-2} day^{-1}. The highest average rate was measured during the second survey and corresponded with the highest level of available oxygen in the bottom waters (84.6% saturation; Table 5). Average TCO_2 fluxes were relatively during the first 3 surveys (25.9 to 33.0 mmol m^{-2} day^{-1}) and increased during the last survey (74.1 mmol m^{-2} day^{-1}). This may be due to a higher organic load in the upper estuary being transported downstream to the central basin.

There was a large difference between TCO_2 flux and O_2 flux during Survey 4 with 51.4 mmol m^{-2} day^{-1} more TCO_2 produced than O_2 consumed suggesting other oxidants are likely to be degrading the organic matter.

The average TIN fluxes (Figure 20) at SR5 were variable and relatively low compared to SR1. Average NH_4^+ fluxes range from 1.24 – 2.05 mmol m^{-2} day^{-1}, while average NO_X fluxes are small (< 0.7 mmol m^{-2} day^{-1}). N_2 fluxes are quite variable between the surveys, with a major concern being the low flux recorded during the last survey. The lower N_2 flux has resulted in a denitrification efficiency of around 10%, compared with 33 – 62% for the first 3 surveys.

Average TIN and PO_4^{3-} fluxes were lowest during Survey 4 (Figure 20). TCO_2:SiO_4^{4-} during all 4 surveys suggest that a diatomaceous source of organic matter is dominant in the sediments of the central basin. As such, C:N and C:P ratios should follow the Redfield Ratio (C:N:P 106:16:1:

Redfield *et al.* 1963). Both C:N and C:P ratios were close to the Redfield Ratio for the first 3 surveys, however, there was lower than predicted N and P during the final survey. NH_4^+ was relatively constant throughout the four surveys, but NO_X was higher and N_2 lower during the final survey. This could be due to the uncoupling of the nitrification-denitrification processes preventing the conversion of NO_X into N_2.

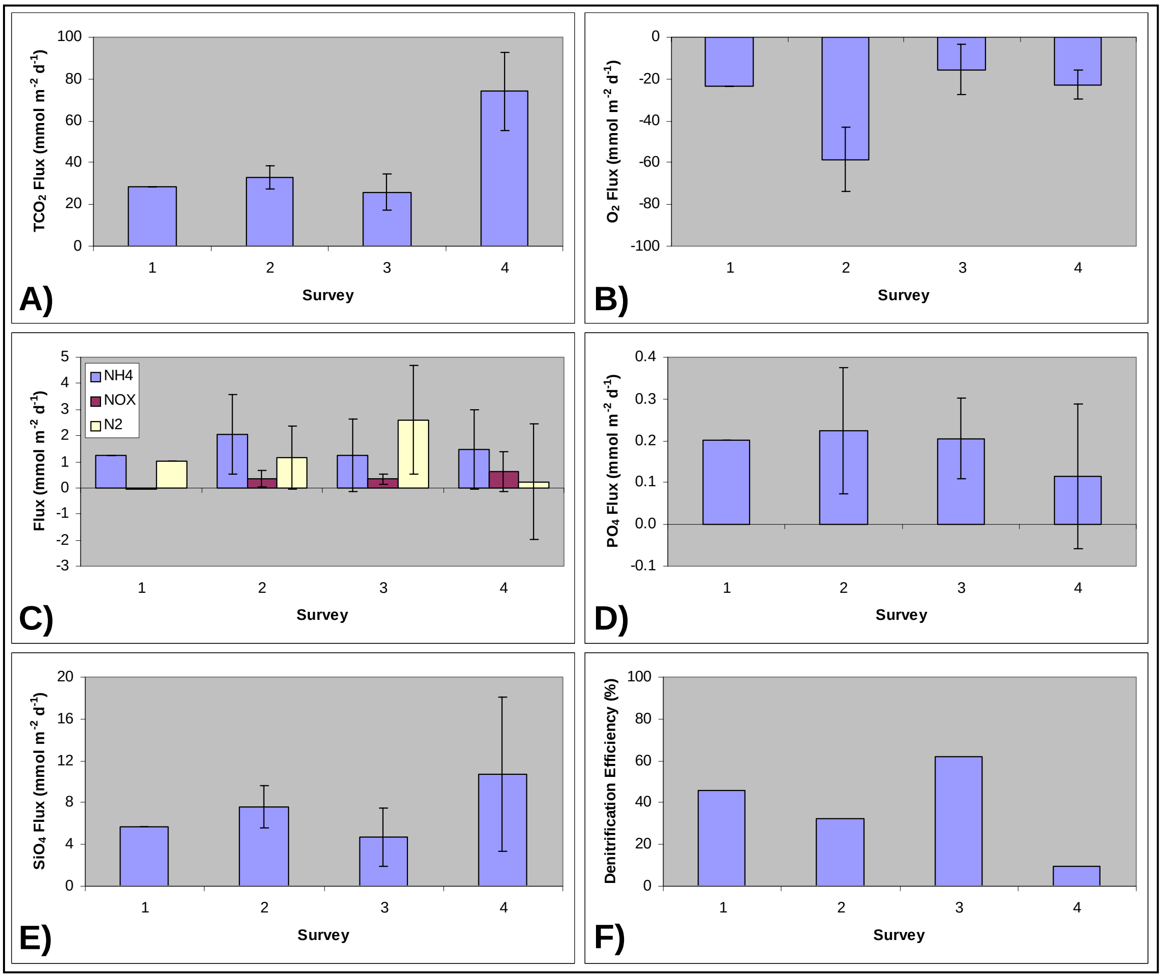


Figure 20. Average TCO_2 (A), O_2 (B), NH_4^+ + NO_X + N_2 (C), PO_4^{3-} (D) and SiO_4^{4-} (E) fluxes, and Denitrification Efficiencies (F) from site SR5 during the 4 surveys. Error bars show the standard deviations.

Sandy Margins (SR6)

In the sandy margins of Melville Waters (SR6) net respiratory conditions were observed during first and third surveys and net photosynthetic conditions observed during the final survey (Figure 21). However, both respiration and photosynthesis processes were observed during the second survey. This is consistent with the bottom water dissolved oxygen concentrations (Table 5) that were higher during the second and final surveys, indicating greater photosynthetic activity than during the first and third surveys.

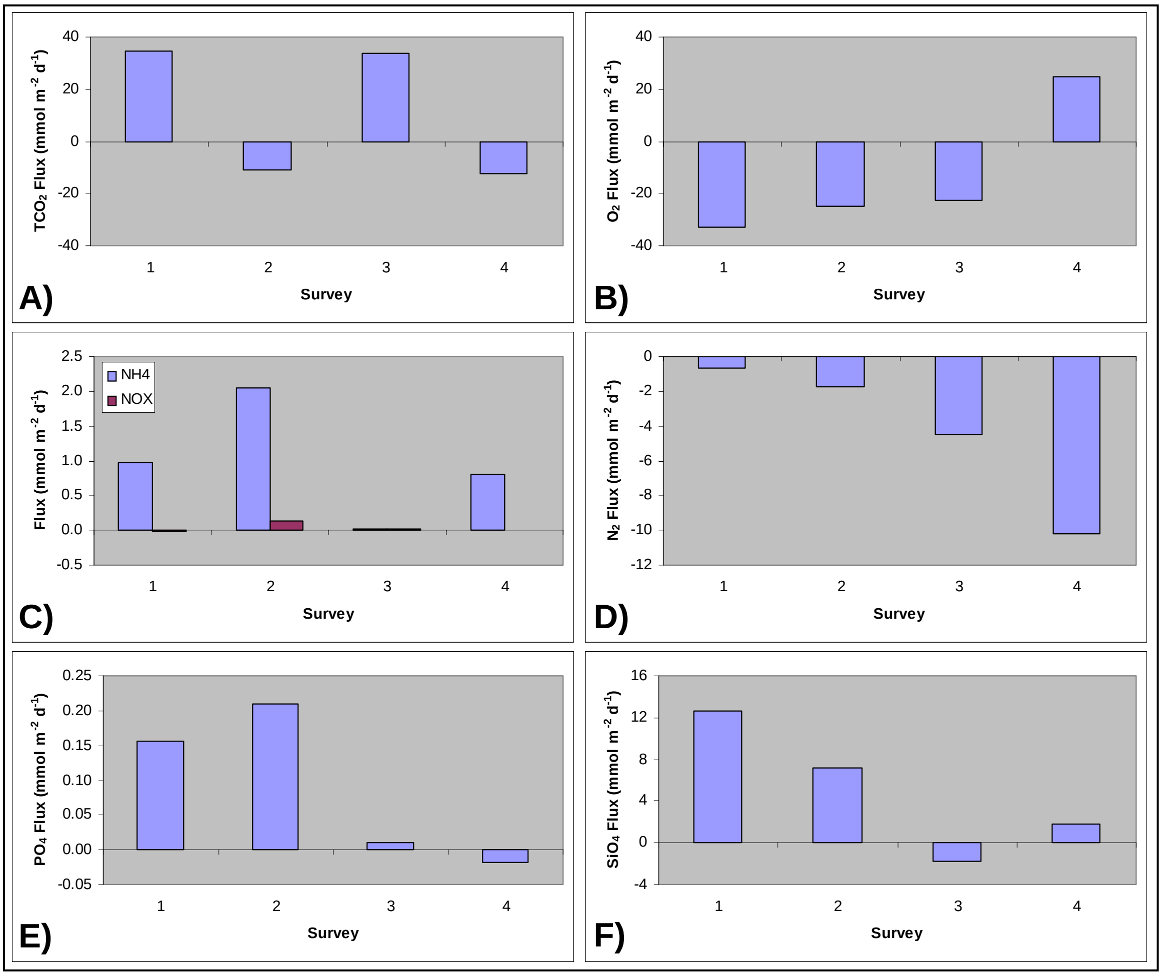


Figure 21. Net TCO_2 (A), O_2 (B), NH_4^+ + NO_X (C), N_2 (D), PO_4^{3-} (E) and SiO_4^{4-} (F) fluxes from site SR6 during the 4 surveys.

Seasonal patterns are observed in the net NH_4^+, PO_4^{3-} and SiO_4^{4-} fluxes. Generally, higher net fluxes occurred during autumn (survey 1 and 2) than during spring (surveys 3 and 4). This could be due to more intense organic matter decay in autumn than in spring. Spring is typically a growth period for algae and phytoplankton whereas autumn is a period when a large fraction of aquatic plants are dying and decaying.

The net N_2 fluxes plot are negative indicating that nitrogen fixation dominates denitrification in the sandy margins, however N_2 stripping during photosynthesis could be responsible for some of the observed N_2 uptake. The increasing N_2 uptake trend is reflected in the O_2 fluxes that become less negative and then positive in the last survey. This indicates an increasing rate of photosynthesis, which may lead to greater N_2 uptake via stripping.

3. Management Implications

3A. O_2 PLANT

Fine sediments and associated organic matter have been shown to be a major sink for O_2 and a major source of nutrients. The extent of reactive sediments in the upper estuary is unknown. When stratification occurs over these areas of reactive sediments, it is likely that high rates of nutrient release may occur. Managers already have information about the extent of stratification from the weekly monitoring program. Mapping the extent of each sediment types in the Swan River would enable a more accurate measure of the oxygen demand in the upper estuary and the likely impact of the oxygen plant.

It is likely the reactive sediments extend for at least the 6 km stretch between SR1 and SR32 in the upper estuary. Given the average O_2 consumption rate of approximately 50 mmol m^{-2} day^{-1} during the last survey, 9 000 M (280 kg) of O_2 would be consumed by the sediments over this area each day. The last survey was conducted at a time when the water column was well mixed and the bottom waters would have been “resupplied” with O_2 from the atmosphere resulting in oxic bottom waters. During other times of the year (December for example), the water column becomes stratified due to the advancing salt wedge and the exchange of O_2 between surface and bottom waters is impaired. At these times, O_2 concentrations may be much lower in the bottom waters of the upper estuary. The oxygen plant would need to supply at least 280 kg of O_2 over the area of reactive sediments per day in order to keep the bottom waters oxic.

3B. METAL FLUXES

There are high levels of copper and zinc in the bottom water at SR33 and these do not appear to be coming from the sediment at the time of the survey. Therefore, it is concluded that another source of these metals must exist. Since the levels are above ANZECC guidelines, it would be important to identify the source of the contamination and prevent further increases in copper and zinc levels.

3C. CHANGES IN BETHIC FLUXES OVER TIME

The latest survey has indicated a large increase in the amount of organic matter and associated nutrients compared to previous surveys. There has been a period of five years between the first three surveys and survey 4, and it remains unclear whether the increase in carbon loading results from a recent event (possibly from the last winter rains) or a slow increase over time. The organic matter is attached to fine sediment and is deposited largely in the upper estuary creating a large area of highly reactive sediments. Decomposition of this organic matter has decreased the O_2 concentration in the bottom waters and released bioavailable nutrients (PO_4^{3-} and NH_4^+). The P-binding capacity of the sediments and denitrification efficiencies have decreased. Fine sediments are a large external source of nutrients and a reduction in the fine sediment load is necessary to impove water quality in the Swan River estuary. TCO_2 fluxes reached almost 1550 mmol m^{-2} day^{-1} in the upper estuary during the 2006 survey. A possible target for this area would be no more than 100 mmol m^{-2} day^{-1}. TCO_2 fluxes in the central basin increased from about 25 to 75 mmol m^{-2} day^{-1} between 2000 and 2006, and this was enough to observe a decrease in the denitrification efficiency at this site. A target of around 50 mmol m^{-2} day^{-1} may be more suitable for such sites.

4. References

Cloern, J.E., Canuel, E.A. and Harris, D. (2002). Stable carbon and nitrogen isotopic composition of aquatic and terrestrial plants of the San Francisco Bay estuarine system. *Limnology and Oceanography*, **47(3)**, 713-729.

Fredericks, D.J., Palmer, D.W., Smith, C.S. and Heggie, D.T. (2002). Benthic Fluxes and Nutrient Recycling in the Swan Estuary. Geoscience Australia, Professional Opinion, 2002/03.

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. Geoscience Australia Record, **2007/03**. Commonwealth Government, Canberra.

O'Callaghan, J.M. (2004). Tidal and sediment dynamics of a partially mixed, micro-tidal estuary. PhD Thesis, The University of Western Australia, Perth.

Redfield, A.C., Ketchum, B.H. and Richarhs, F.A. (1963). The influence of organisms on the composition of sea water. P. 73-124. In *Marine Geochemistry*. Schultz, H.D. and Zabel, M. (eds). Springer-Verlag.

WRC (2000). 'Summer Surprise' The Swan River blue-green algal bloom, February 2000. River Science, Issue **2**, September 2000.

WRC (2002). Seasonal Nutrient Dynamics in the Swan Estuary, 1995-2000. River Science, Issue **8**, October 2002.

WRC (2005). Algal blooms in the Swan-Canning estuary: Patterns, causes and history. River Science, Issue **3**, February 2005.

Zwolsman, J.J.G., Van Eck, B.T.M. and Van Der Weijden, C.H. (1997). Geochemistry of dissolved trace metals (cadmium, copper, zinc) in the Scheldt estuary, south-western Netherlands: Impacts of seasonal variability. *Geochimica et Cosmochimica Acta*, **61(8)**, 1635-1652.

Appendix 1. Site

Site	Location	Sediment	Latitude	Longitude
SR1	Ron Courtney Island	Mud	-31.92023	115.94217
SR5	Central Basin – Melville Water	Mud	-32.00988	115.81133
SR6	Sandy Margin – Melville Water	Sand	-32.01895	115.81918
SR32	Upper Estuary - Oxygen Plant	Mud	-31.89468	115.95883
SR33	Upper Estuary - Baigup	Muddy Sand	-31.93223	115.91515
SR34	Crawley Bay – Melville Water	Sand	-31.98227	115.83332

Appendix 2. Benthic Fluxes

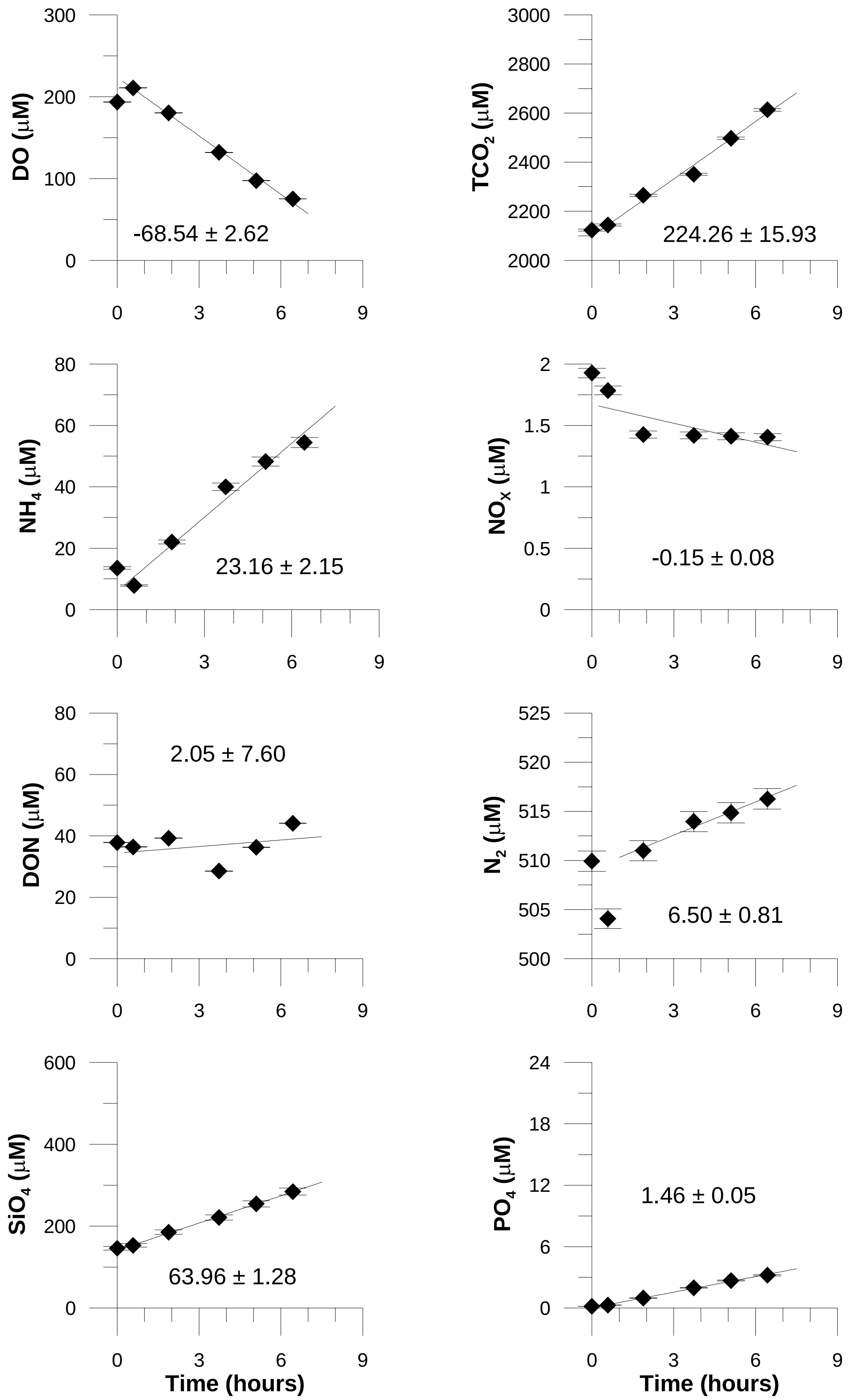
Site	Survey	Type	DO	TCO_2	error	Alk	error	NH_4^+	error	NO_X	error	DON	error	N_2	PO_4^{3-}	error	SiO_4^{4-}	error
1A_3	1	Light	-42.99	59.53	9.73	15.58	12.62	0.18	0.13	0.03	0.04			0.52	1.28	0.29	8.48	0.68
1B_4	2	Dark	-47.72	221.46	3.00	161.58	3.79	16.64	1.29	0.08	0.08			1.26	0.81	0.12	18.56	0.16
1B_6	2	Dark	-36.41	40.49	4.04	6.88	4.29	-1.97	0.33	-0.01	0.03			-1.39	0.24	0.18	9.10	2.08
1C_1	2	Light	-78.65	29.98	0.00	19.05	0.00	2.09	0.00	0.15	0.00			11.02	0.41	0.00	8.20	0.00
1D_4	3	Dark	-36.70	121.59	8.55	106.57	8.54	4.24	1.96	-0.32	0.06			4.02	0.33	0.10	3.42	1.59
1D_6	3	Dark	-55.01	121.66	8.37	106.61	8.38	7.94	0.34	-0.66	0.06			25.48	0.46	0.02	7.82	1.13
1F_1	4	Dark	-41.23	306.78	18.27	263.73	15.01	18.33	2.15	0.00	0.00	10.96	1.04	6.12	1.14	0.15	32.59	1.95
1F_2	4	Dark	-25.86	460.99	16.25	410.16	13.06	63.67	12.85	0.00	0.00	-2.05	18.39	5.53	3.83	0.27	30.97	5.65
1F_3	4	Dark	-37.47	195.15	29.15	169.10	24.67	18.79	4.01	0.00	0.00	1.68	3.30	0.44	2.50	0.37	33.04	3.46
1G_1	4	Light	-31.12	496.96	26.01	511.69	32.46	9.36	2.72	0.00	0.00	55.54	15.33	-0.05	8.85	1.39	48.54	3.75
5A_1	1	Light	-0.66	2.04	4.71	0.95	4.50	0.86	0.29	0.14	0.09			0.01	0.22	0.04	1.48	0.00
5B_2	1	Dark	-23.61	28.51	0.00	9.34	0.00	1.24	0.00	-0.03	0.00			1.03	0.20	0.00	5.69	0.00
5D_1	2	Light	-37.01	24.56	0.53	-2.43	1.55	0.10	0.01	-0.02	0.02			1.30	0.01	0.02	4.88	0.43
5D_2	2	Dark	-63.88	36.89	0.00	18.06	0.00	1.58	0.00	0.42	0.00			2.71	0.25	0.00	9.03	0.00
5E_1	2	Light	-59.72	35.60	1.07	3.67	1.79	3.05	0.43	0.75	0.04			0.83	0.35	0.02	7.40	0.48
5E_2	2	Dark	-73.01	34.97	2.93	7.20	3.04	3.47	0.10	0.24	0.03			-0.20	0.29	0.05	9.10	0.58
5F_1	3	Light	-25.68	23.51	1.40	3.41	0.44	0.52	0.05	0.59	0.00			2.85	0.15	0.01	6.08	0.20
5F_2	3	Dark	-26.42	16.90	0.00	6.44	0.00	-0.07	0.00	0.12	0.00			0.85	0.09	0.00	4.08	0.00
5G_1	3	Light		40.89	4.01	22.75	3.47	3.30	0.39	0.44	0.02			5.91	0.32	0.03	7.48	0.62
5G_2	3	Dark	-21.28	30.05	3.55	6.66	2.84	1.03	0.53	0.36	0.04			3.26	0.20	0.04	4.37	1.49
5H_1	3	Light		24.44	2.05	6.95	2.22	2.57	0.09	0.43	0.05			2.71	0.32	0.02	6.42	0.41
5H_2	3	Dark	-18.92	19.52	0.00	-0.10	3.74	0.09	0.00	0.09	0.00			-0.04	0.14	0.00	-0.27	2.19
5I_3	4	Light	-8.70	-32.90	29.38	-7.12	34.07	-0.55	1.81	-0.02	0.00	-2.75	1.55	0.65	-0.03	0.02	-0.04	3.92
5J_1	4	Dark	-25.51	60.91	24.15	10.57	22.18	3.20	0.16	1.50	0.08	-1.60	3.78	3.08	0.31	0.03	18.31	2.33
5J_2	4	Dark	-27.97	87.31	30.46	84.42	3.23	0.35	0.57	0.17	0.23	2.76	4.67	-0.70	0.00	0.07	3.56	3.51
5J_3	4	Dark	-14.69	1.07	67.10	3.72	76.35	0.84	0.23	0.21	0.12	2.45	5.01	-2.13	0.03	0.02	10.25	1.92
6A_3	1	Light	45.29	-109.59	24.29	-35.25	6.19	-0.63	0.05	0.05	0.02			1.90	0.20	0.30	6.24	2.93
6B_3	1	Light	88.66	-58.80	3.03	-10.55	4.72	-1.35	0.48	-0.02	0.05			-4.34	0.11	0.09	11.99	0.39
6B_4	1	Dark	-154.42	128.52	14.42	42.45	6.99	3.31	0.77	-0.02	0.12			2.99	0.20	0.03	13.25	0.16
6C_3	2	Light		-100.69	17.97	-8.26	16.72	0.27	0.02	0.00	0.01			-15.62	0.18	0.03	5.18	0.11
6C_4	2	Dark	-97.07	22.74	18.32	-24.48	31.52	3.86	1.83	0.26	0.09			3.02	0.23	0.00	6.71	0.37
6C_5	2	Light	47.29	-40.87	2.11	-10.92	3.31	0.49	0.05	0.13	0.02			2.40	0.17	0.01	7.07	0.21
6C_6	2	Dark		75.33	4.74	17.87	2.97	3.57	1.22	0.12	0.06			3.33	0.25	0.03	9.80	0.53
6D_5	3	Light	112.74	-14.79	22.68	29.18	18.33	-0.66	0.14	-0.07	0.03			4.84	-0.05	0.01	5.47	0.89
6E_4	3	Dark	-193.70	142.76	29.73	81.96	3.60	-0.03	0.41	0.05	0.80			6.03	0.04	0.01	-2.09	0.93

6E_5	3	Light	129.62	-155.50	12.58	-57.70	2.83	0.27	0.05	-0.40	0.18			-34.33	0.01	0.05	-9.56	0.52
6E_6	3	Dark	-156.20	162.04	5.38	92.09	5.86	0.52	0.18	0.48	0.42			5.44	0.04	0.02	-0.96	0.86
6F_5	4	Dark	-203.40	-19.76	8.79	-32.74	47.78	-0.01	0.08	0.00	0.00	0.45	3.20	-4.42	0.04	0.01	-0.10	0.02
6F_6	4	Light	126.04	-90.47	11.82	-15.96	23.86	0.13	0.11	0.00	0.00	0.78	9.88	-26.34	0.00	0.00	-15.94	4.04
6F_7	4	Dark	-47.62	131.44	11.60	97.04	9.12	1.64	0.31	0.00	0.00	-0.07	1.46	4.07	0.05	0.01	8.29	1.31
6F_8	4	Dark	-52.02	12.61	11.02	-9.22	13.62	0.90	0.00	0.00	0.00	6.16	2.72	13.36	-0.04	0.01	3.96	1.35
6F_9	4	Light	72.69	-101.97	4.08	10.47	17.60	0.59	0.03	0.00	0.00	8.35	4.88	-31.75	-0.11	0.04	10.82	0.01
32A_5	4	Dark	-68.54	224.26	15.93	170.90	13.57	23.16	2.15	-0.15	0.08	2.05	7.60	6.50	1.46	0.05	63.96	1.28
32A_6	4	Light	-87.03	89.29	7.27	49.05	18.27	15.49	1.57	0.00	0.00	-1.38	5.89	6.70	0.54	0.15	35.56	1.77
32A_7	4	Dark	-55.05	348.88	9.79	304.56	9.10	19.57	3.76	0.00	0.00	14.10	1.64	5.64	3.82	0.09	45.16	0.80
32A_8	4	Dark	-95.67	1548.46	65.05	1486.44	61.01	12.22	6.29	0.00	0.00	135.35	17.87	11.09	8.88	2.53	167.04	2.83
32A_9	4	Light	-252.94	134.36	0.00	110.04	0.00	7.76	0.00	0.00	0.00	-2.66	1.68	1.33	0.00	0.00	15.53	0.00
33A_1	4	Light	-10.55	20.76	2.06			-0.77	2.00	0.02	0.02	-0.81	0.00	-4.38	0.00	0.00	3.51	4.21
33A_2	4	Light	-14.54	30.99	2.76			5.89	0.39	0.00	0.00	-1.26	9.31	-4.13	0.01	0.03	16.69	0.96
33A_3	4	Light	-22.89	24.24	11.08			2.75	0.53	0.00	0.00	2.64	6.76	0.36	0.00	0.00	6.74	2.73
33B_1	4	Dark	-30.02	34.70	1.32			2.07	0.67	0.00	0.00	-0.55	4.42	0.87	0.00	0.00	11.07	3.26
33B_2	4	Dark	-4.78	6.92	3.44			-1.39	1.72	0.00	0.00	2.78	4.60	0.02	0.00	0.00	0.78	4.81
33B_3	4	Dark	-31.68	11.00	1.79			-0.41	1.53	0.00	0.00	-1.71	2.82	-0.80	0.00	0.00	-1.98	6.98
34A_5	4	Dark	-78.17	226.26	0.00	165.15	0.00	4.25	0.00	1.54	0.00	4.19	0.00	11.12	0.19	0.00	7.09	0.00
34A_6	4	Light	-37.70	52.97	13.77	37.71	5.55	0.50	0.06	0.08	0.12	2.83	1.84	-3.32	0.10	0.05	3.82	1.96
34A_7	4	Dark	-9.69	1.99	18.25	2.96	20.48	0.26	0.25	0.00	0.00	-0.41	0.60	0.03	0.07	0.02	-5.91	1.12
34A_8	4	Dark	-70.09	54.97	7.38	38.04	4.83	0.18	0.11	0.00	0.00	0.02	1.59	1.90	0.06	0.01	-1.94	0.97
34A_9	4	Light	8.32	-46.09	31.20	-53.31	23.31	0.50	0.37	0.00	0.00	0.87	3.92	-30.39	0.23	0.04	0.00	0.00

Appendix 3. Time Course Plots, Survey 4

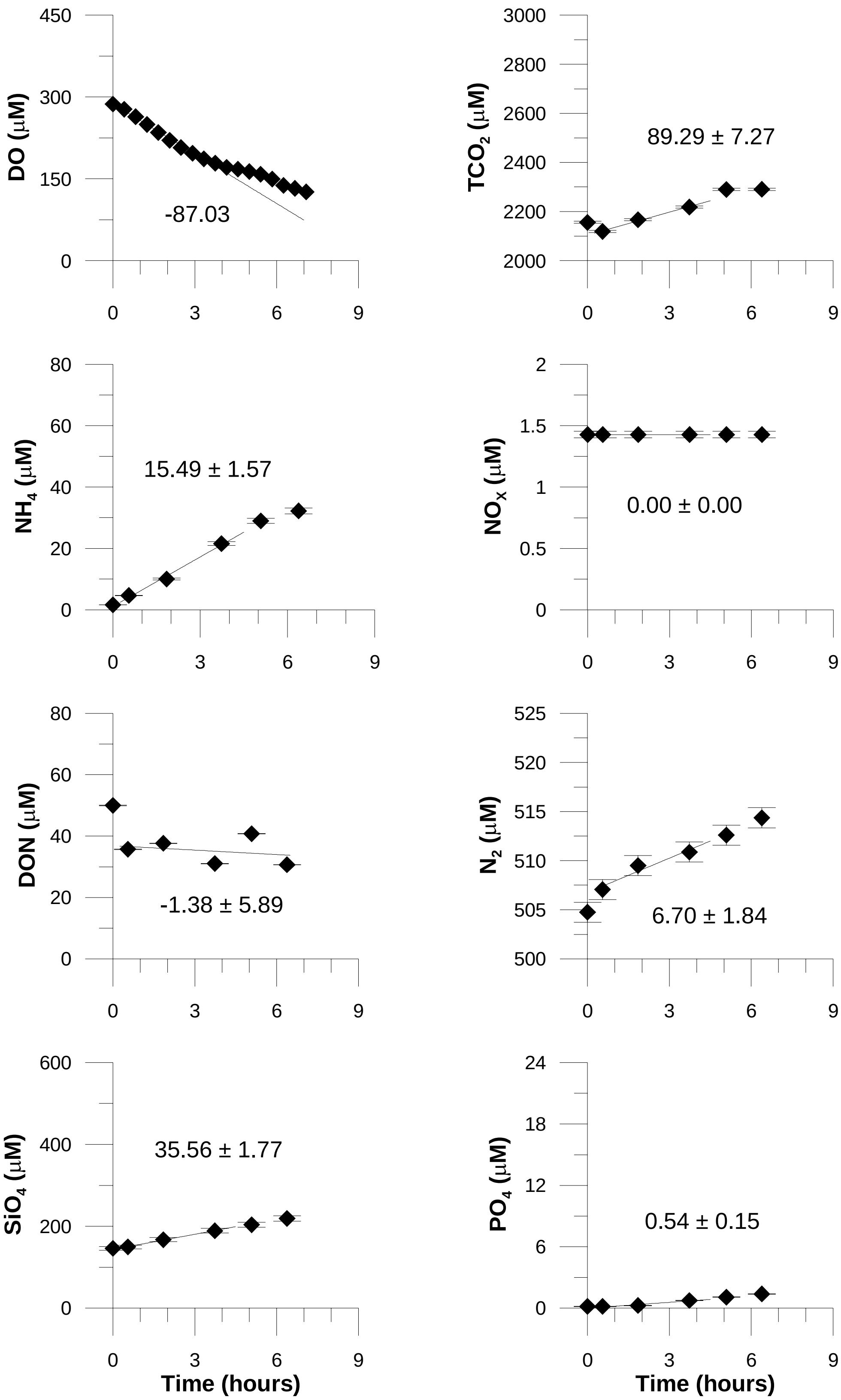
Dark

SR32A_5


DO (μM)
-68.54 ± 2.62
TCO2 (μM)
224.26 ± 15.93
NH4 (μM)
23.16 ± 2.15
NOX (μM)
-0.15 ± 0.08
DON (μM)
2.05 ± 7.60
N2 (μM)
6.50 ± 0.81
SiO4 (μM)
63.96 ± 1.28
PO4 (μM)
1.46 ± 0.05
Time (hours)
Time (hours)

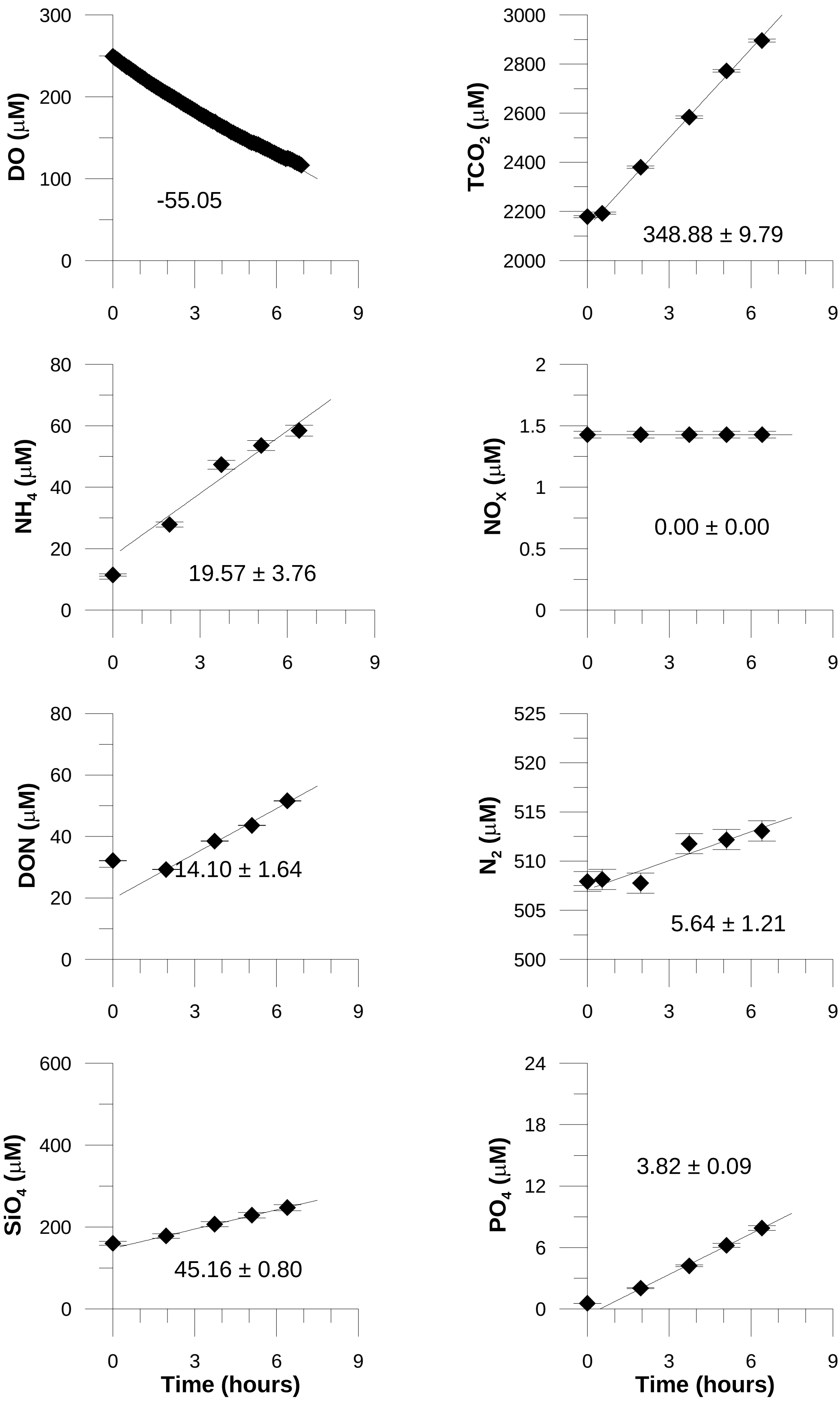
Light

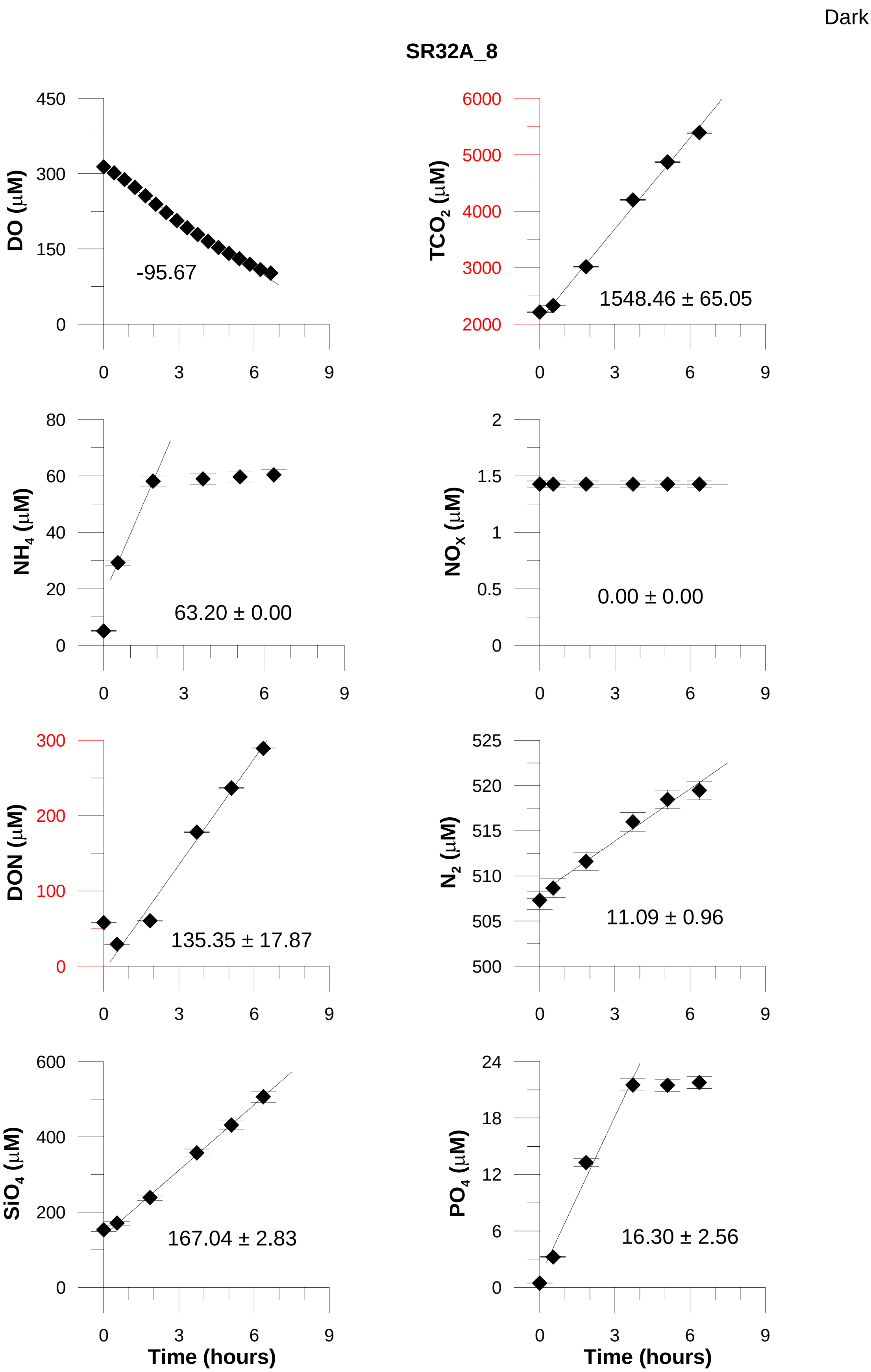
SR32A_6



Dark

SR32A_7

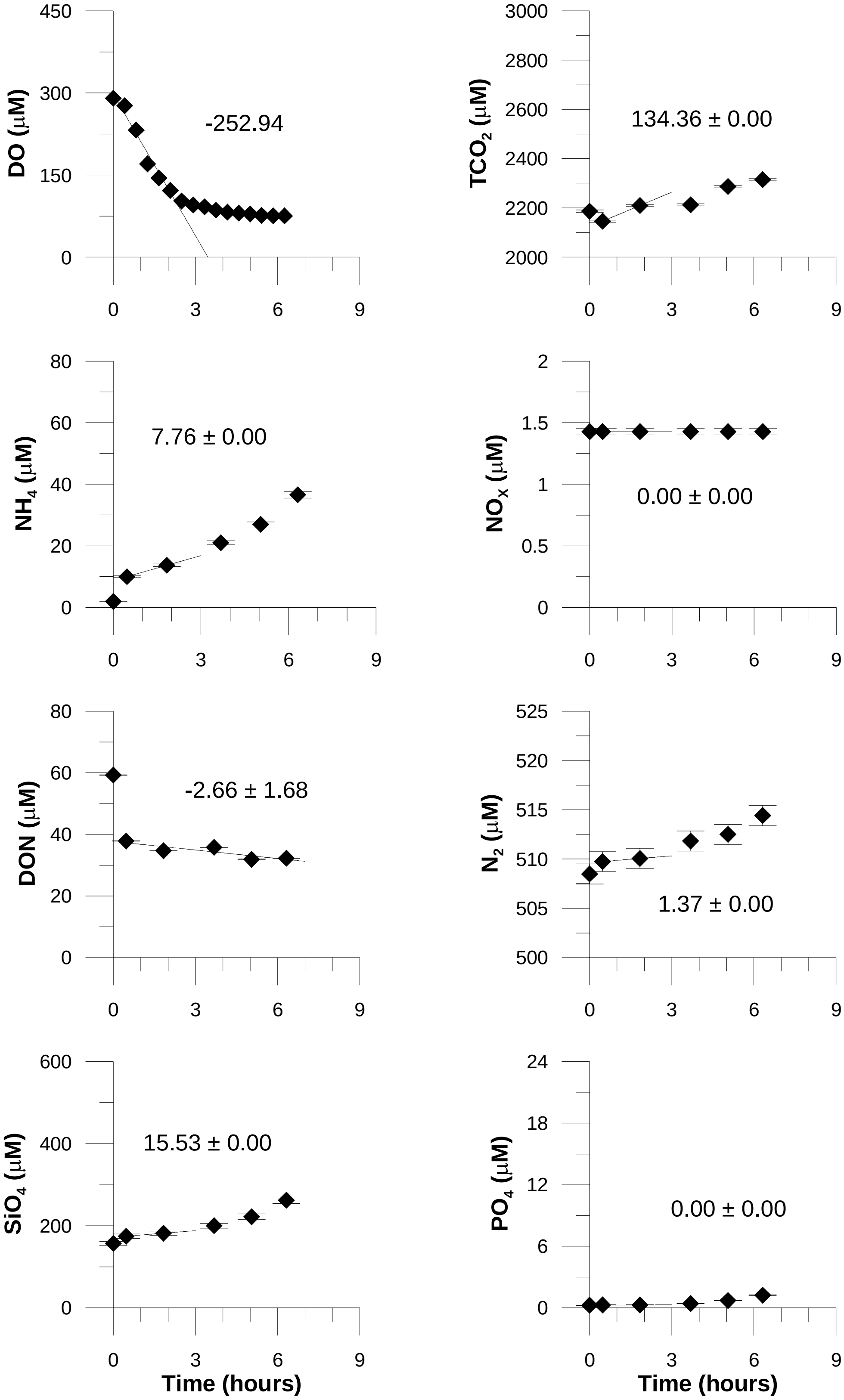

DO (μM)
-55.05
TCO2 (μM)
348.88 ± 9.79
NH4 (μM)
19.57 ± 3.76
NOX (μM)
0.00 ± 0.00
DON (μM)
14.10 ± 1.64
N2 (μM)
5.64 ± 1.21
SiO4 (μM)
45.16 ± 0.80
PO4 (μM)
3.82 ± 0.09
Time (hours)
Time (hours)



Dark
SR32A_8
DO (μM)
-95.67
TCO2 (μM)
1548.46 ± 65.05
NH4 (μM)
63.20 ± 0.00
NOx (μM)
0.00 ± 0.00
DON (μM)
135.35 ± 17.87
N2 (μM)
11.09 ± 0.96
SiO4 (μM)
167.04 ± 2.83
PO4 (μM)
16.30 ± 2.56
Time (hours)
Time (hours)

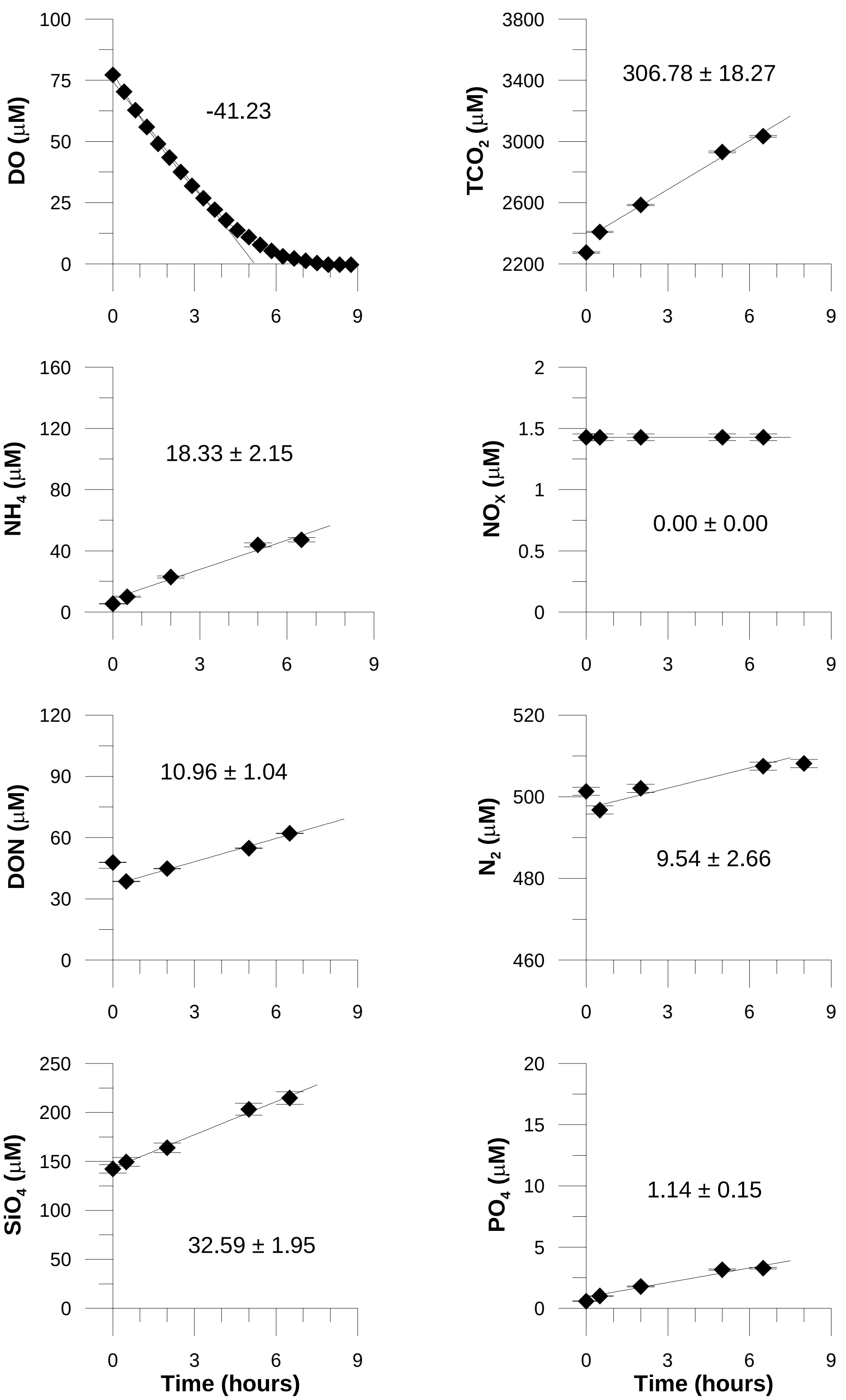
Light

SR32A_9



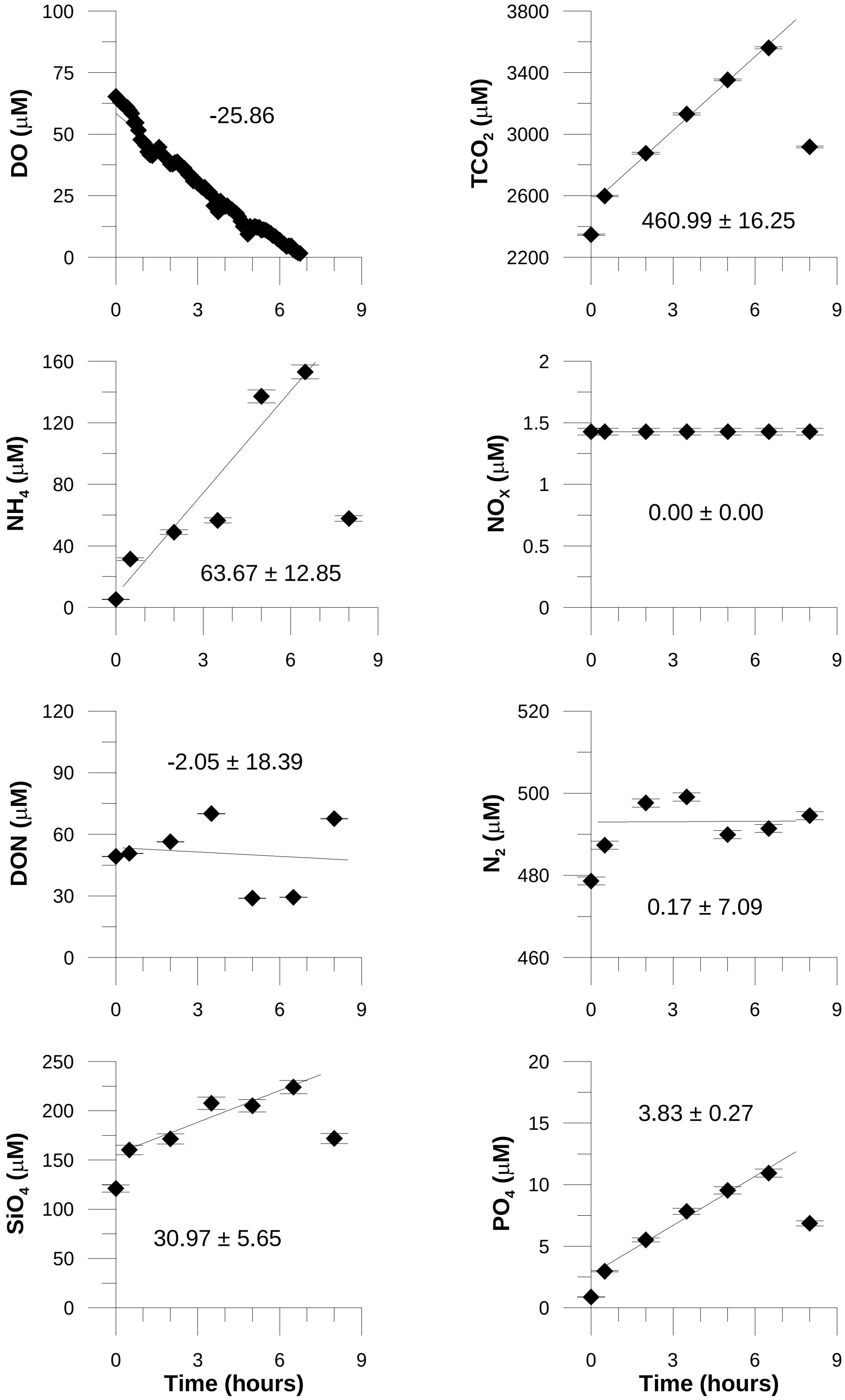
Dark

SR1F_1


DO (µM)
-41.23
TCO_2 (µM)
306.78 ± 18.27
NH_4 (µM)
18.33 ± 2.15
NO_X (µM)
0.00 ± 0.00
DON (µM)
10.96 ± 1.04
N_2 (µM)
9.54 ± 2.66
SiO_4 (µM)
32.59 ± 1.95
PO_4 (µM)
1.14 ± 0.15
Time (hours)
Time (hours)

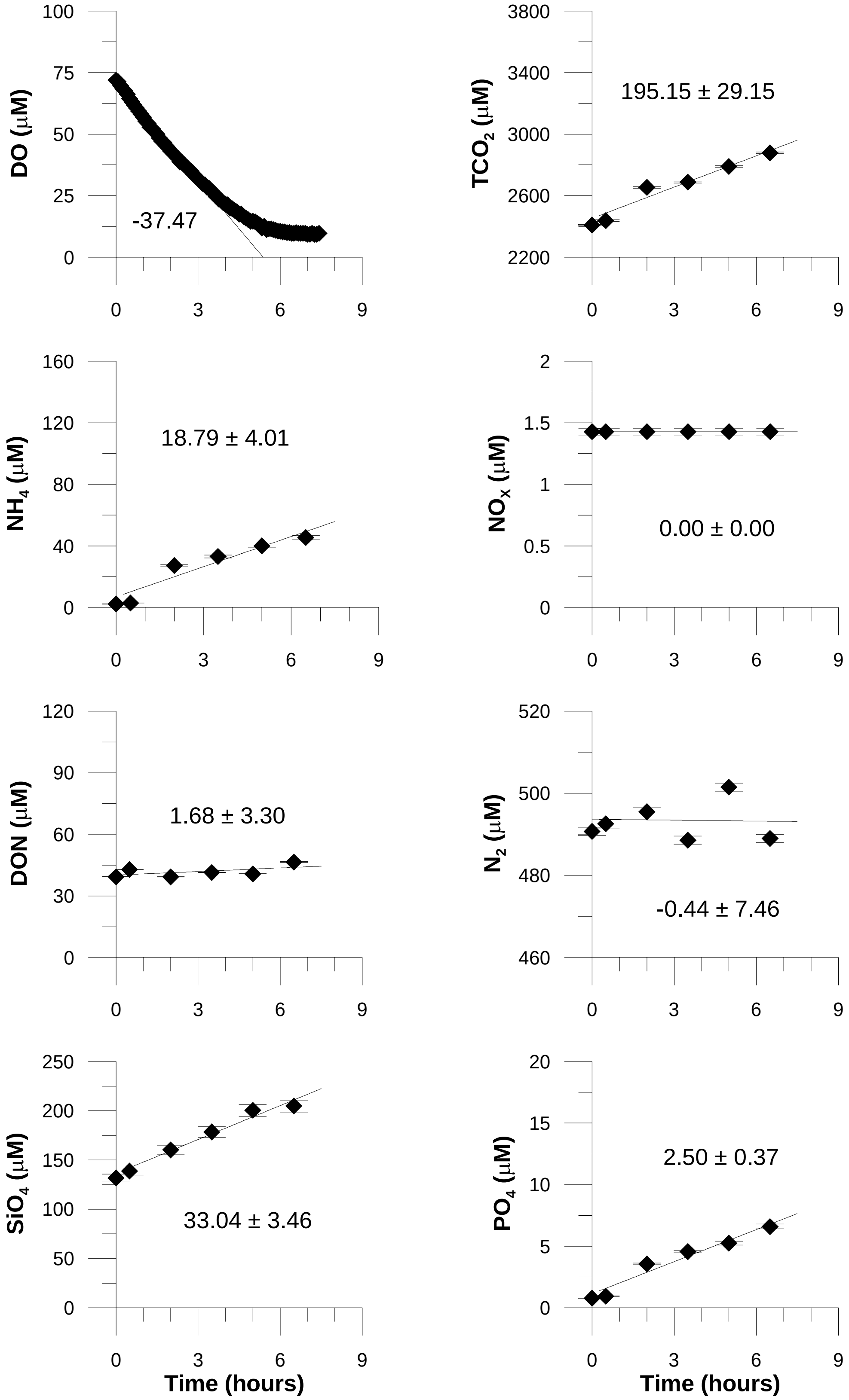
Dark

SR1F_2


DO (µM)
-25.86
TCO2 (µM)
460.99 ± 16.25
NH4 (µM)
63.67 ± 12.85
NOX (µM)
0.00 ± 0.00
DON (µM)
-2.05 ± 18.39
N2 (µM)
0.17 ± 7.09
SiO4 (µM)
30.97 ± 5.65
PO4 (µM)
3.83 ± 0.27
Time (hours)
Time (hours)

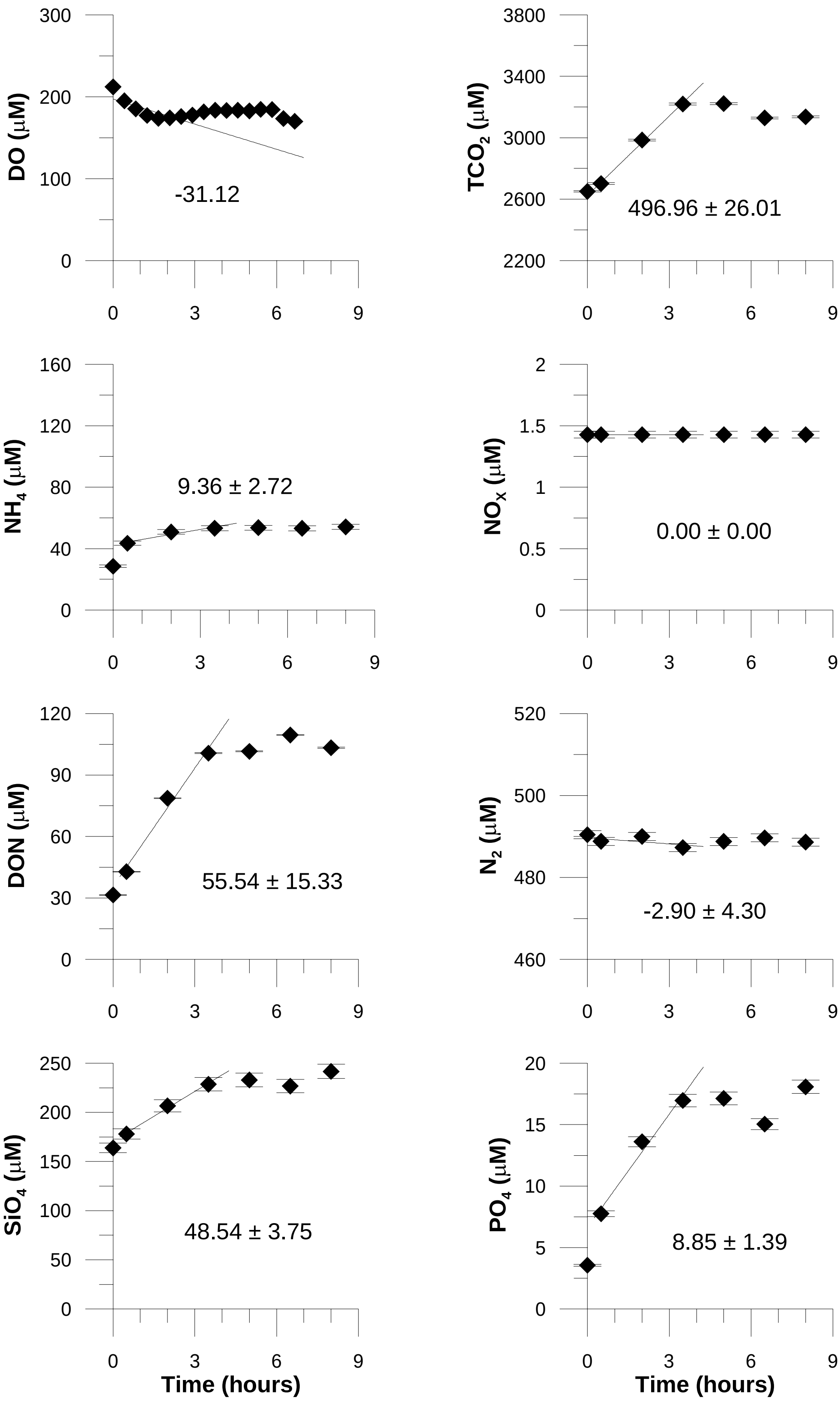
Dark

SR1F_3


DO (μM)
-37.47
TCO₂ (μM)
195.15 ± 29.15
NH₄ (μM)
18.79 ± 4.01
NOx (μM)
0.00 ± 0.00
DON (μM)
1.68 ± 3.30
N₂ (μM)
-0.44 ± 7.46
SiO₄ (μM)
33.04 ± 3.46
PO₄ (μM)
2.50 ± 0.37
Time (hours)
Time (hours)

Dark

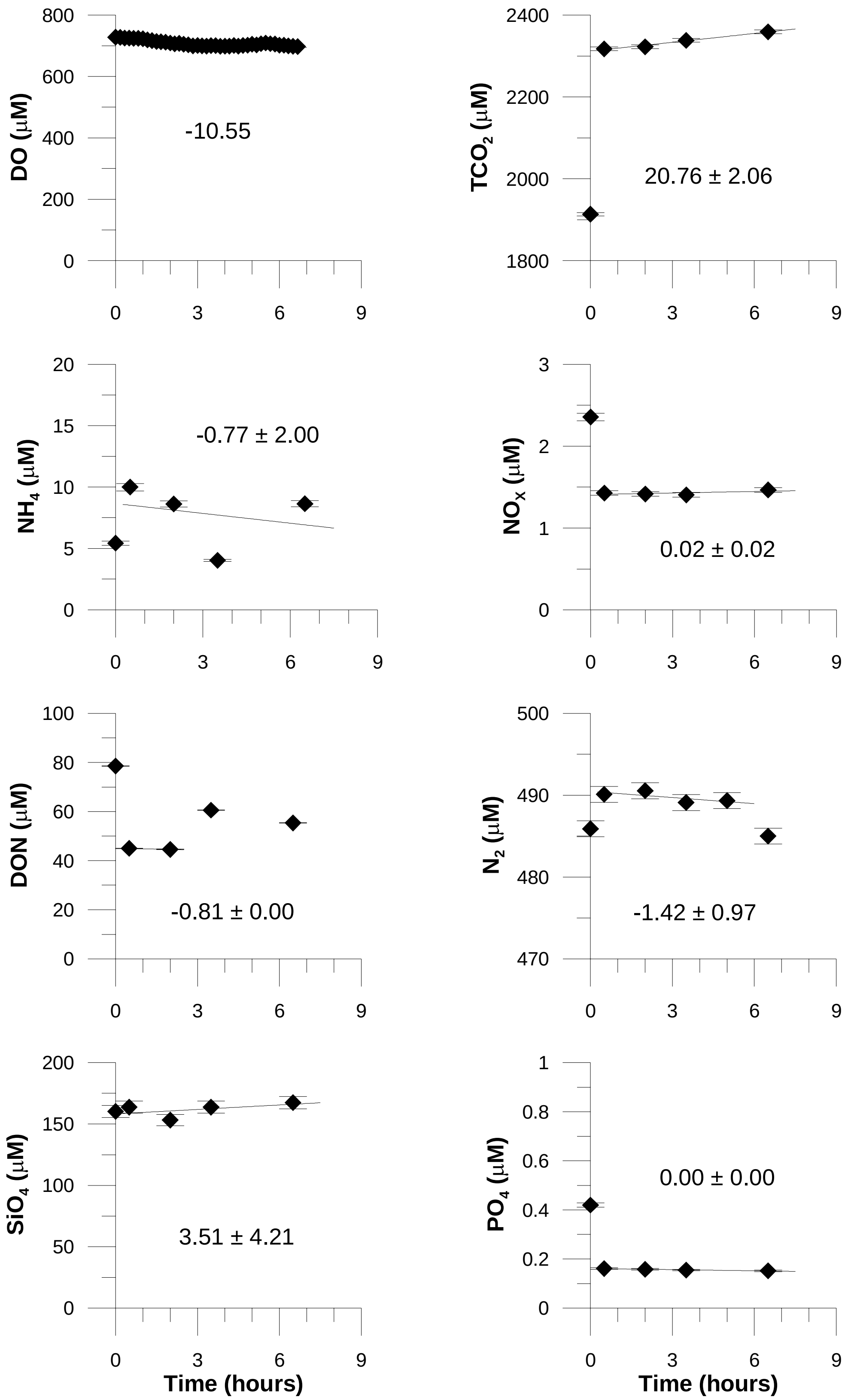
SR1G_1



DO (µM)
300
200
100
0
-31.12
0
3
6
9
TCO2 (µM)
3800
3400
3000
2600
2200
496.96 ± 26.01
NH4 (µM)
160
120
80
40
9.36 ± 2.72
NOx (µM)
2
1.5
1
0.5
0.00 ± 0.00
DON (µM)
120
90
60
30
55.54 ± 15.33
N2 (µM)
520
500
480
460
-2.90 ± 4.30
SiO4 (µM)
250
200
150
100
50
48.54 ± 3.75
PO4 (µM)
20
15
10
5
8.85 ± 1.39
Time (hours)
Time (hours)

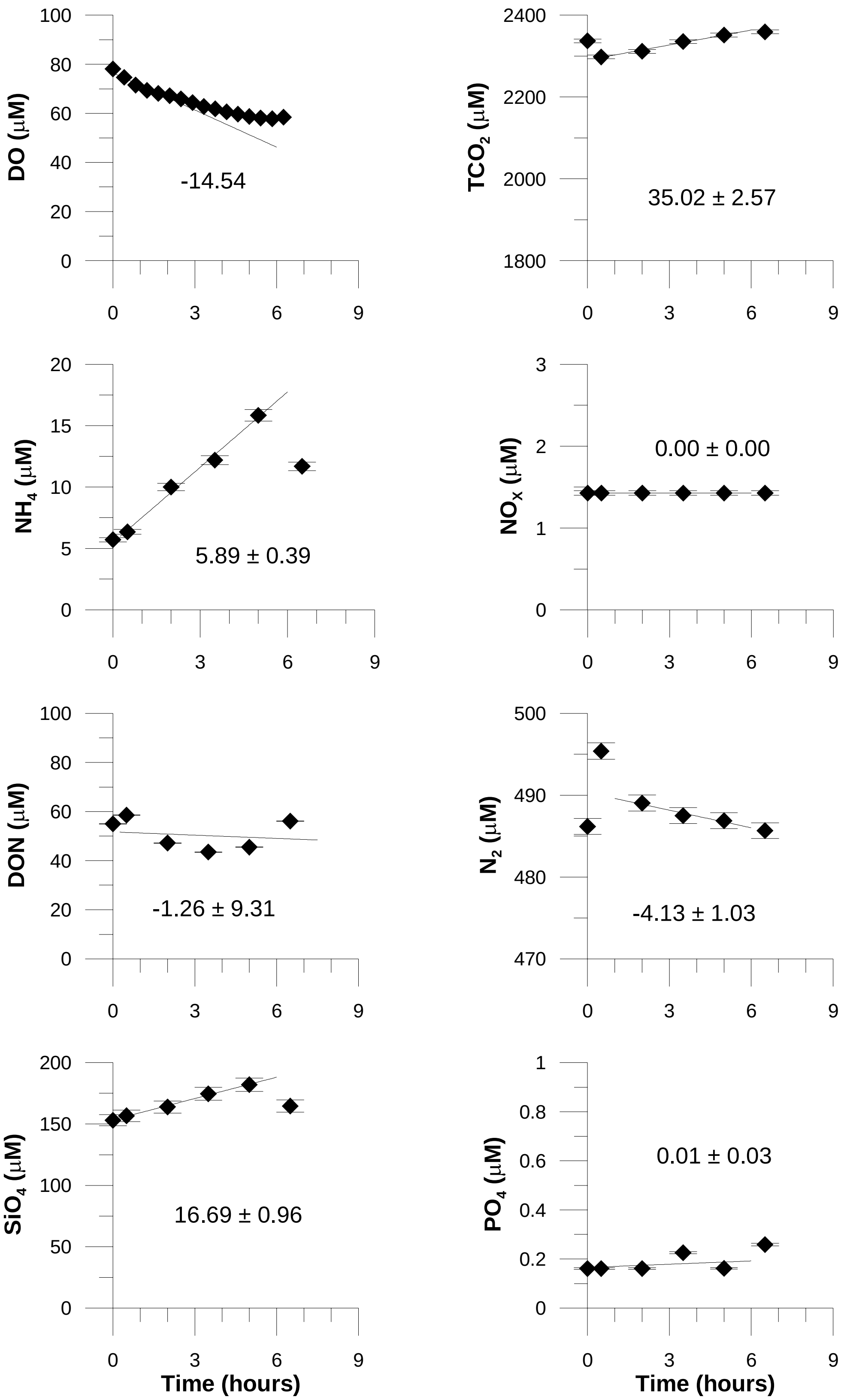
Light

SR33A_1



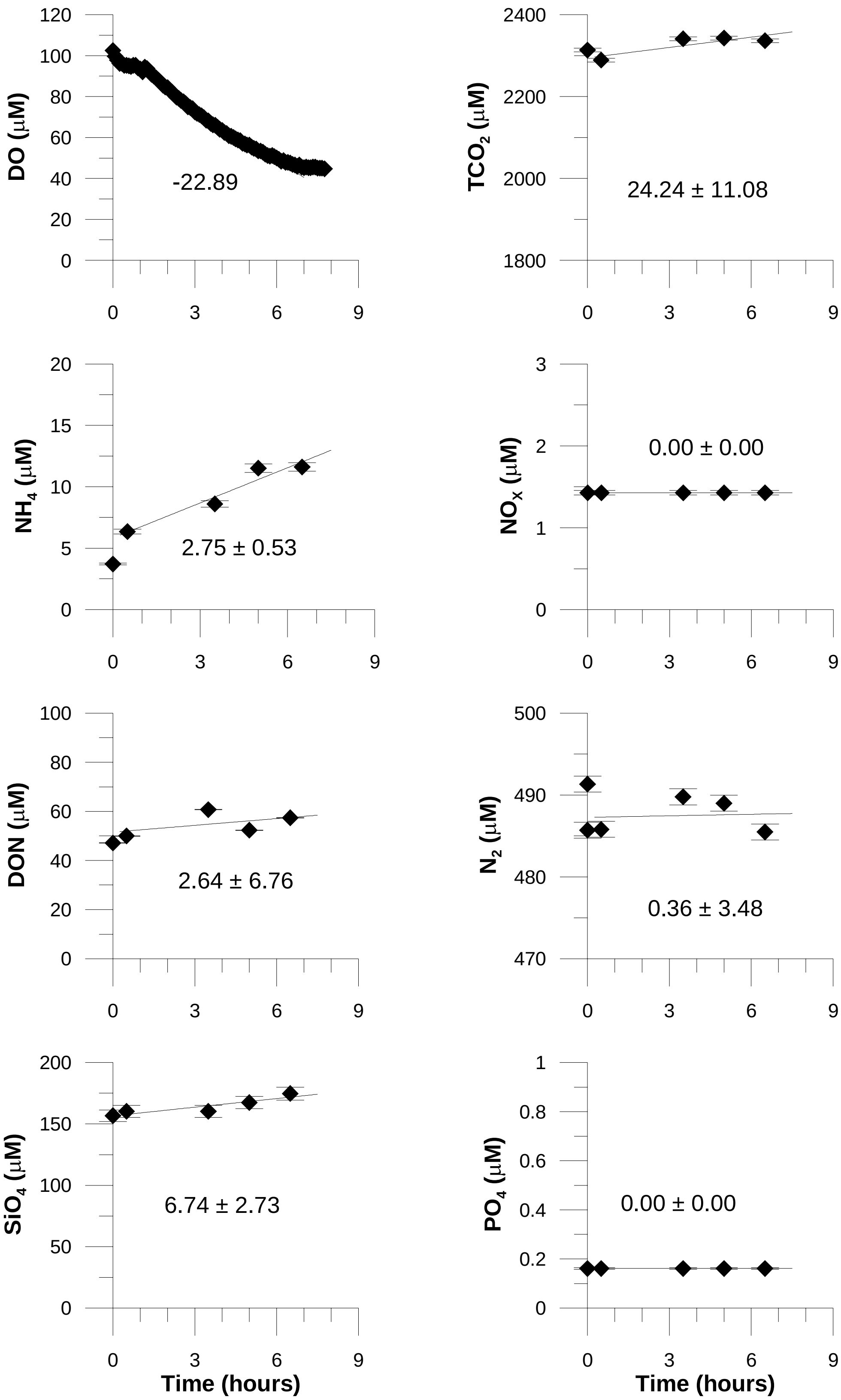
Light

SR33A_2



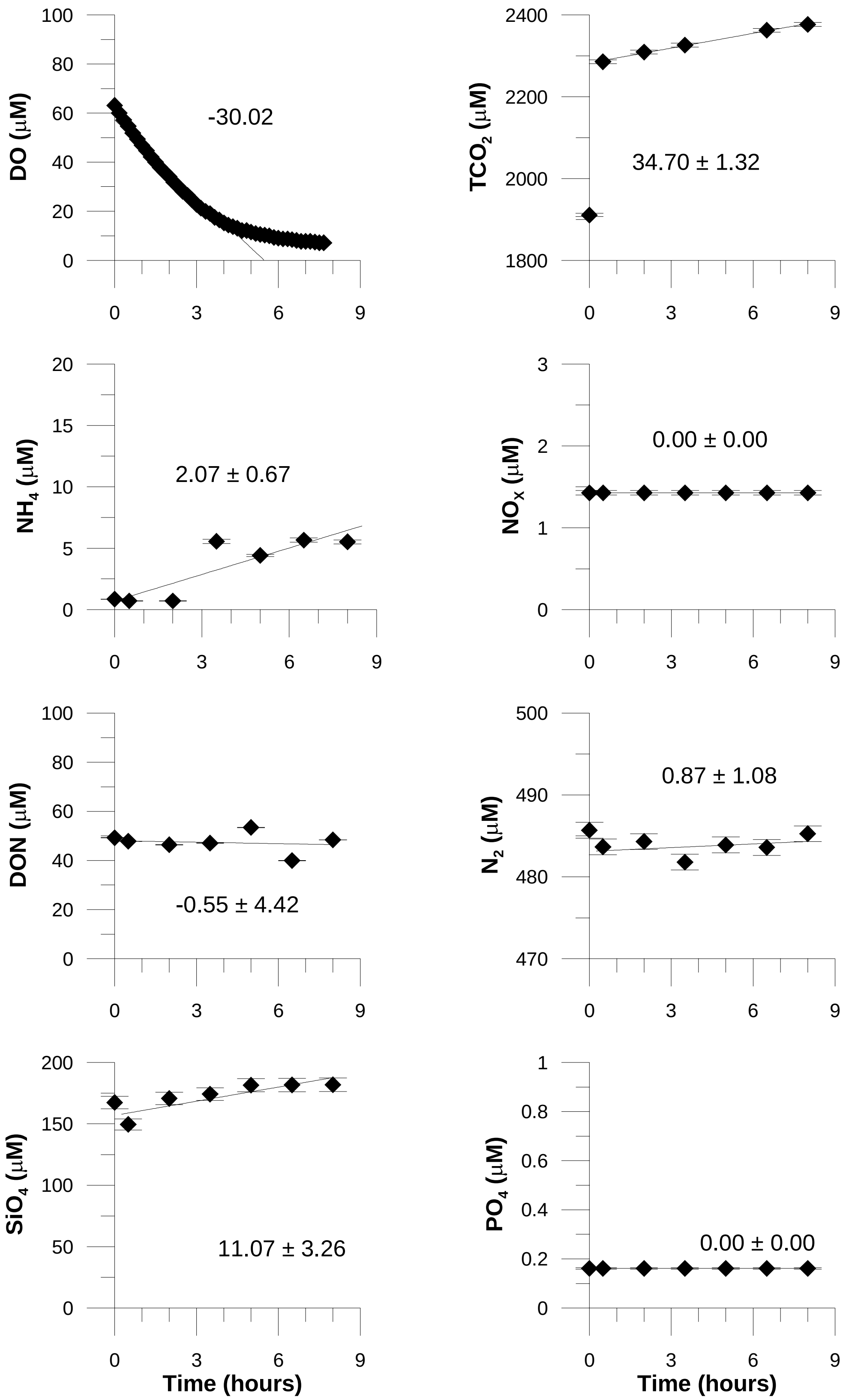
Light

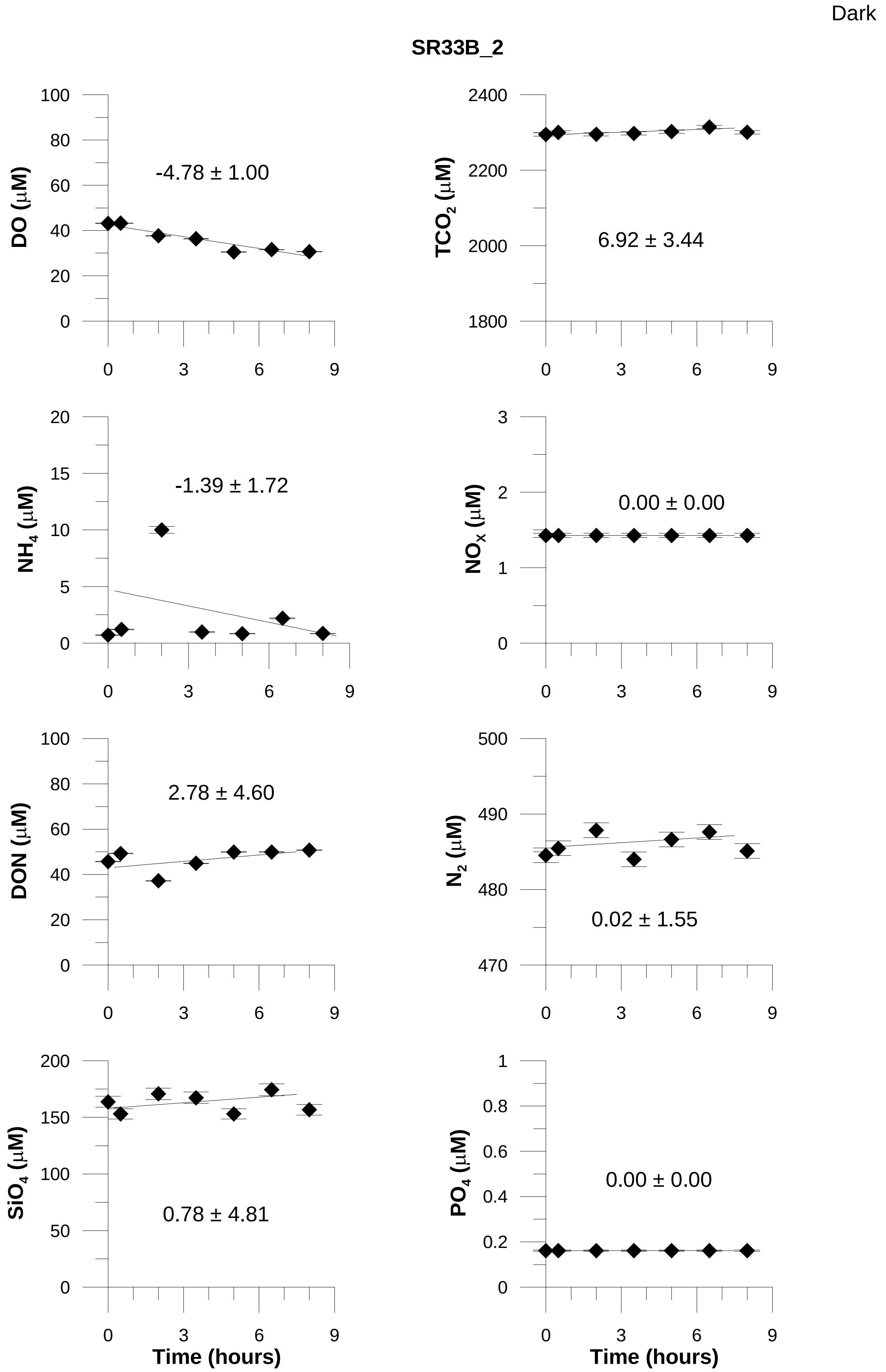
SR33A_3



Dark

SR33B_1

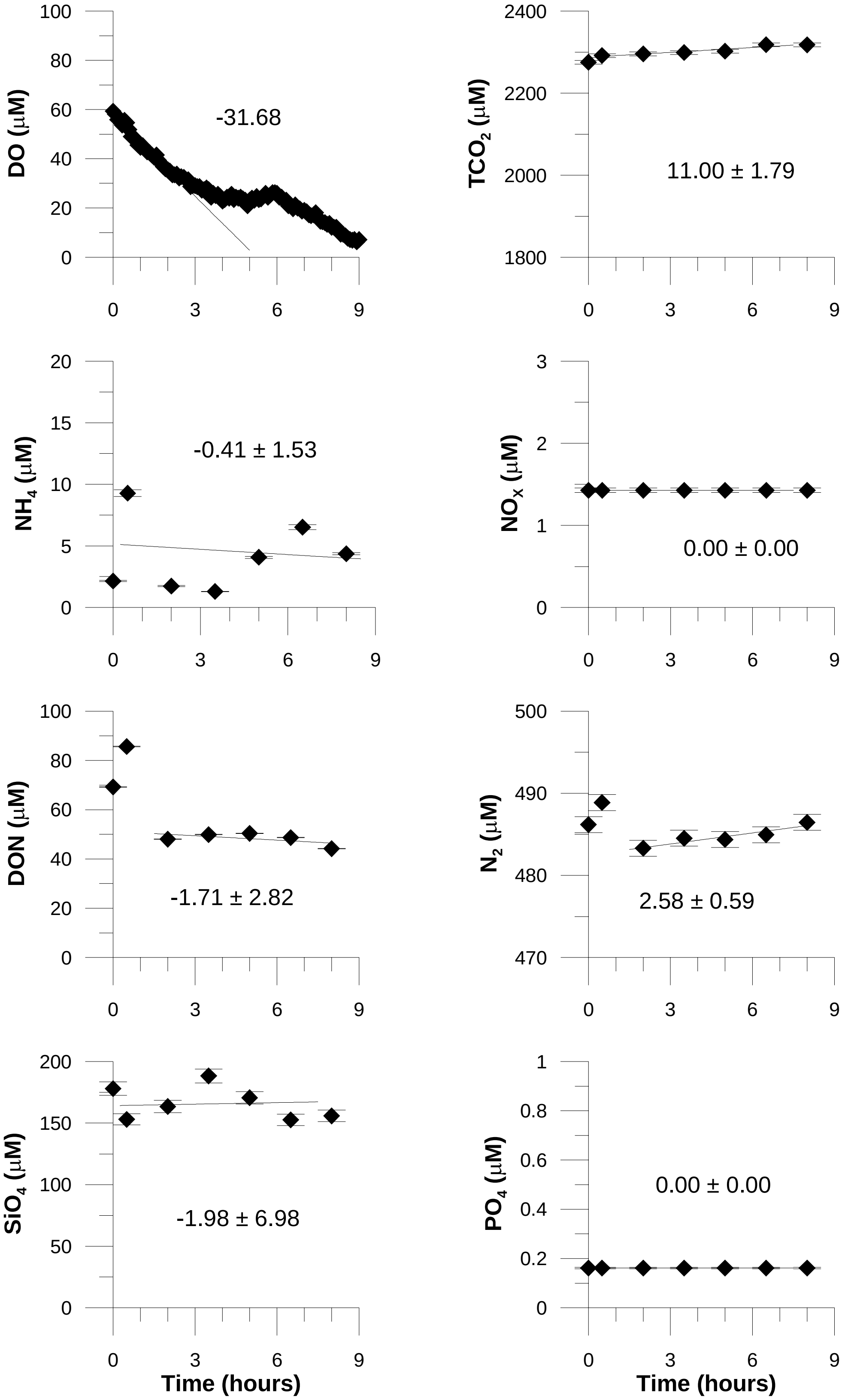

DO (μM)
-30.02
TCO2 (μM)
34.70 ± 1.32
NH4 (μM)
2.07 ± 0.67
NOX (μM)
0.00 ± 0.00
DON (μM)
-0.55 ± 4.42
N2 (μM)
0.87 ± 1.08
SiO4 (μM)
11.07 ± 3.26
PO4 (μM)
0.00 ± 0.00
Time (hours)
Time (hours)



Dark
SR33B_2
DO (μM)
-4.78 ± 1.00
TCO2 (μM)
6.92 ± 3.44
NH4 (μM)
-1.39 ± 1.72
NOx (μM)
0.00 ± 0.00
DON (μM)
2.78 ± 4.60
N2 (μM)
0.02 ± 1.55
SiO4 (μM)
0.78 ± 4.81
PO4 (μM)
0.00 ± 0.00
Time (hours)
Time (hours)

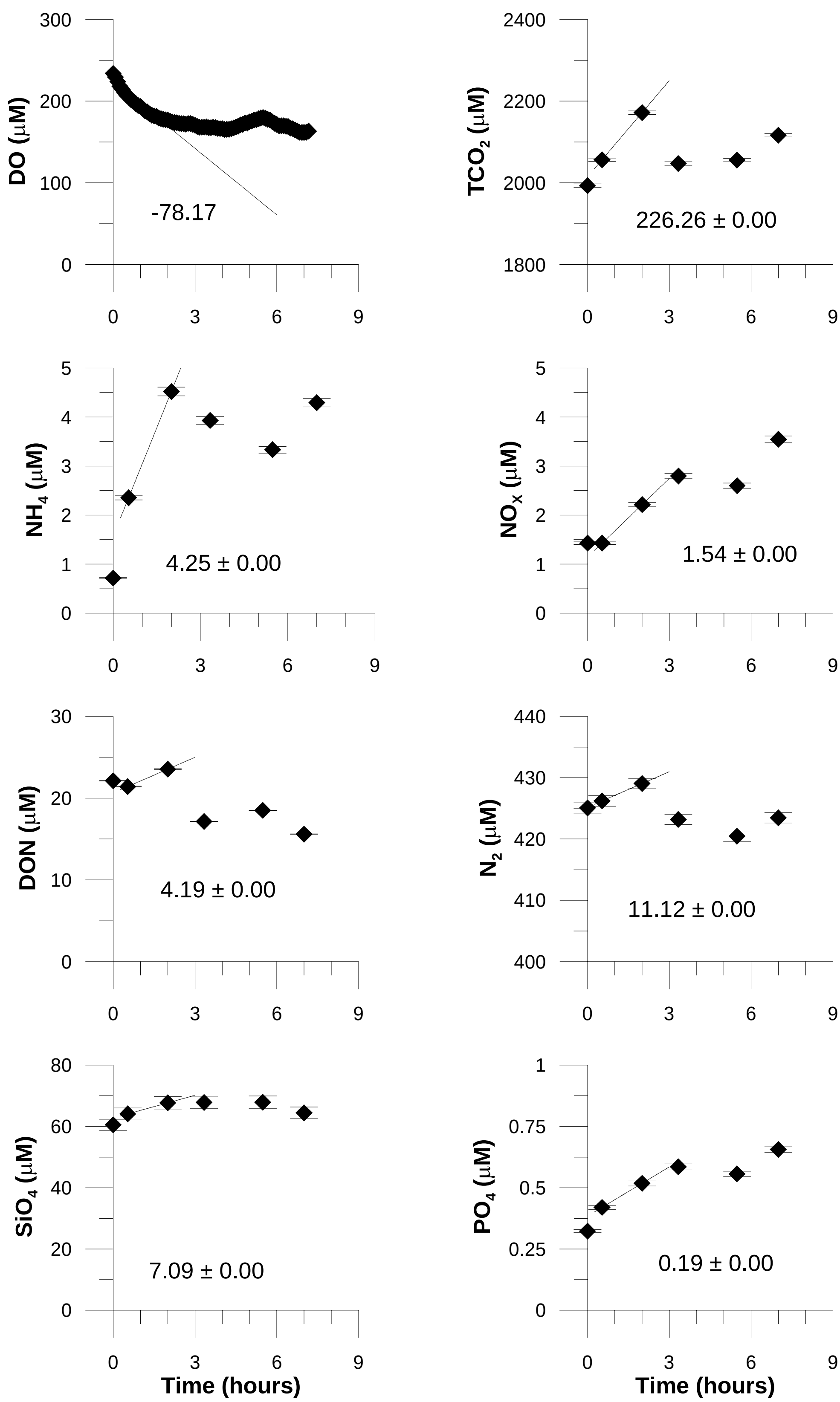
Dark

SR33B_3


DO (μM)
-31.68
TCO_2 (μM)
11.00 ± 1.79
NH_4 (μM)
-0.41 ± 1.53
NO_X (μM)
0.00 ± 0.00
DON (μM)
-1.71 ± 2.82
N_2 (μM)
2.58 ± 0.59
SiO_4 (μM)
-1.98 ± 6.98
PO_4 (μM)
0.00 ± 0.00
Time (hours)
Time (hours)

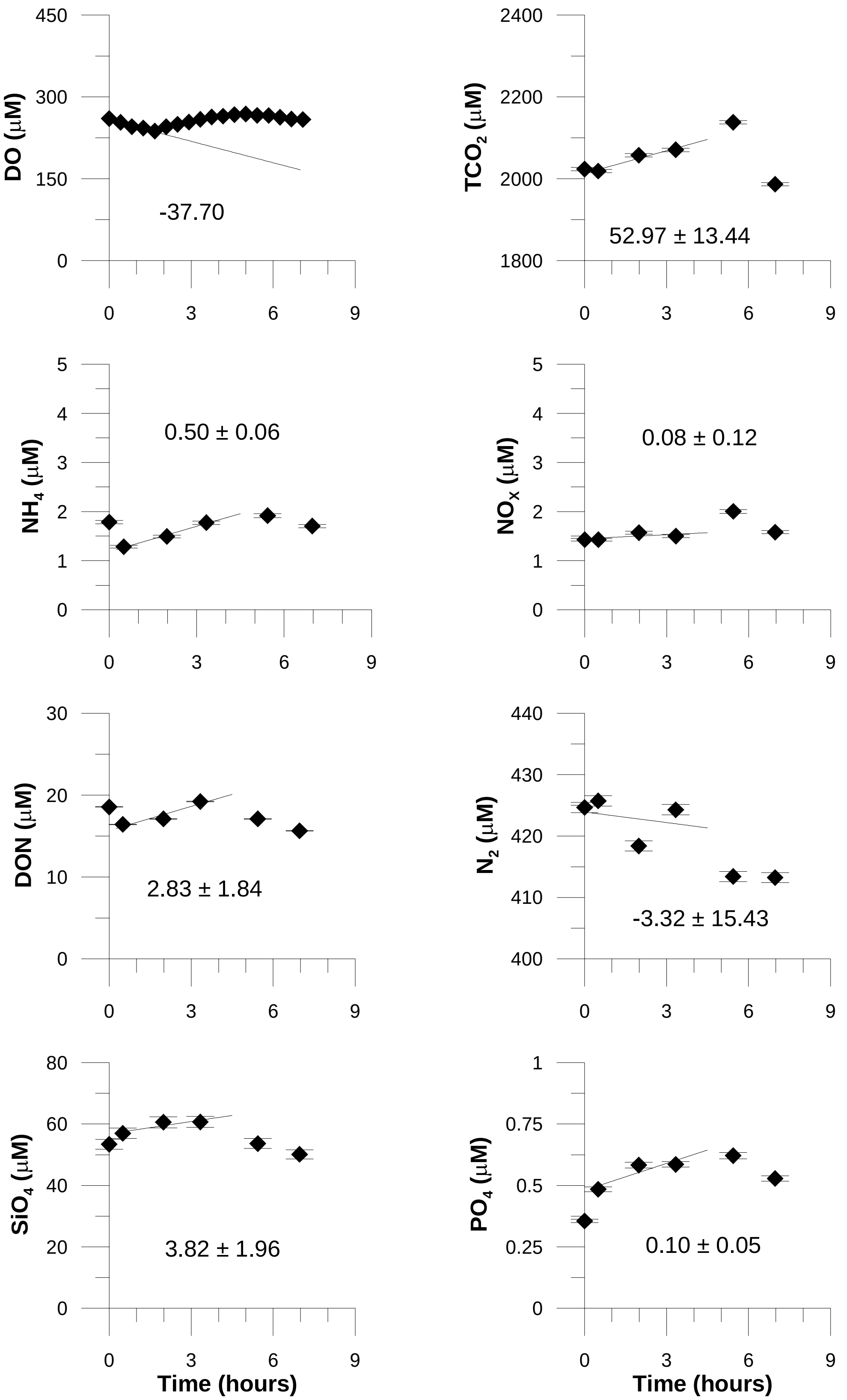
Dark

SR34A_5


DO (μM)
-78.17
TCO_2 (μM)
226.26 ± 0.00
NH_4 (μM)
4.25 ± 0.00
NO_X (μM)
1.54 ± 0.00
DON (μM)
4.19 ± 0.00
N_2 (μM)
11.12 ± 0.00
SiO_4 (μM)
7.09 ± 0.00
PO_4 (μM)
0.19 ± 0.00
Time (hours)
Time (hours)

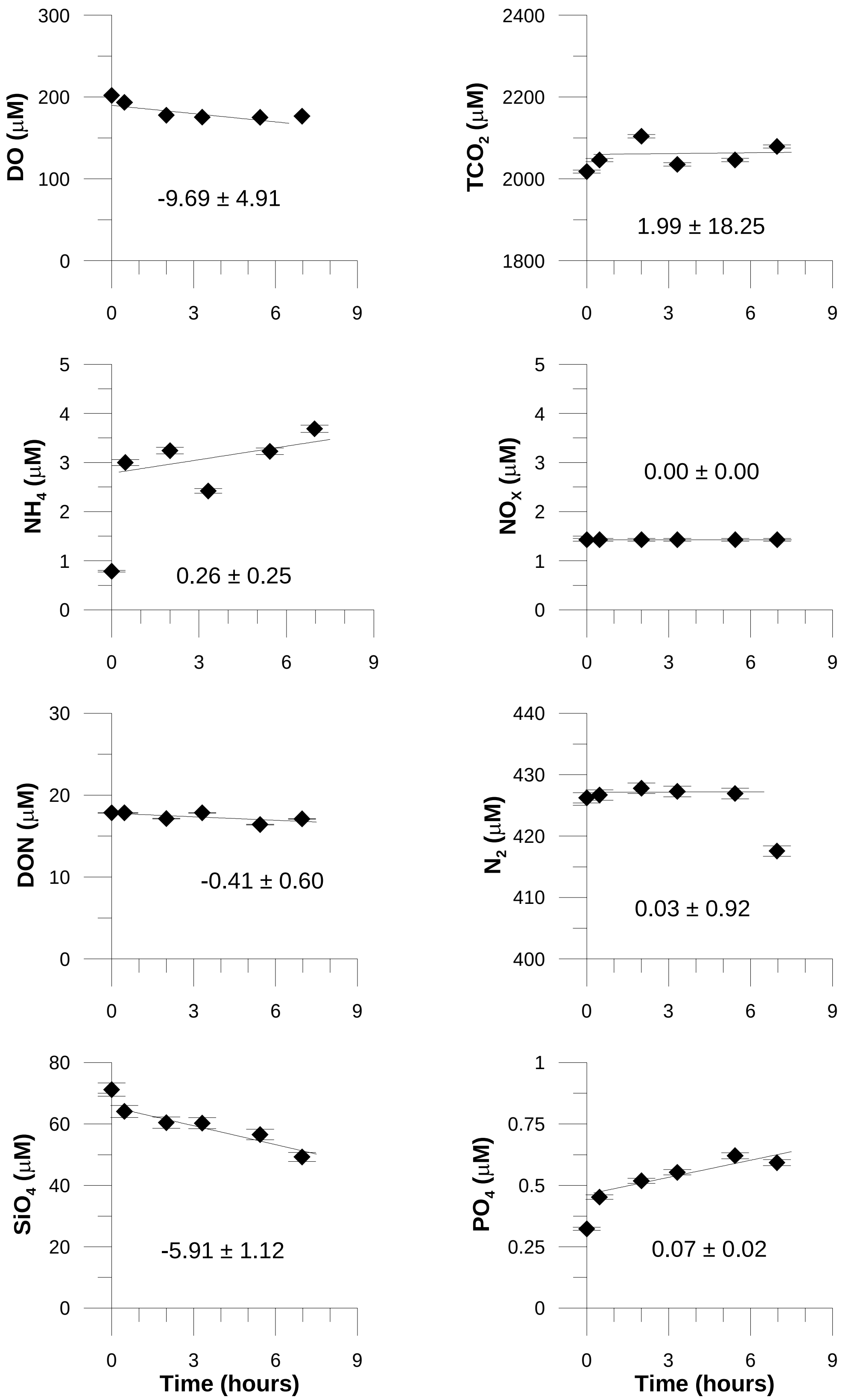
Light

SR34A_6



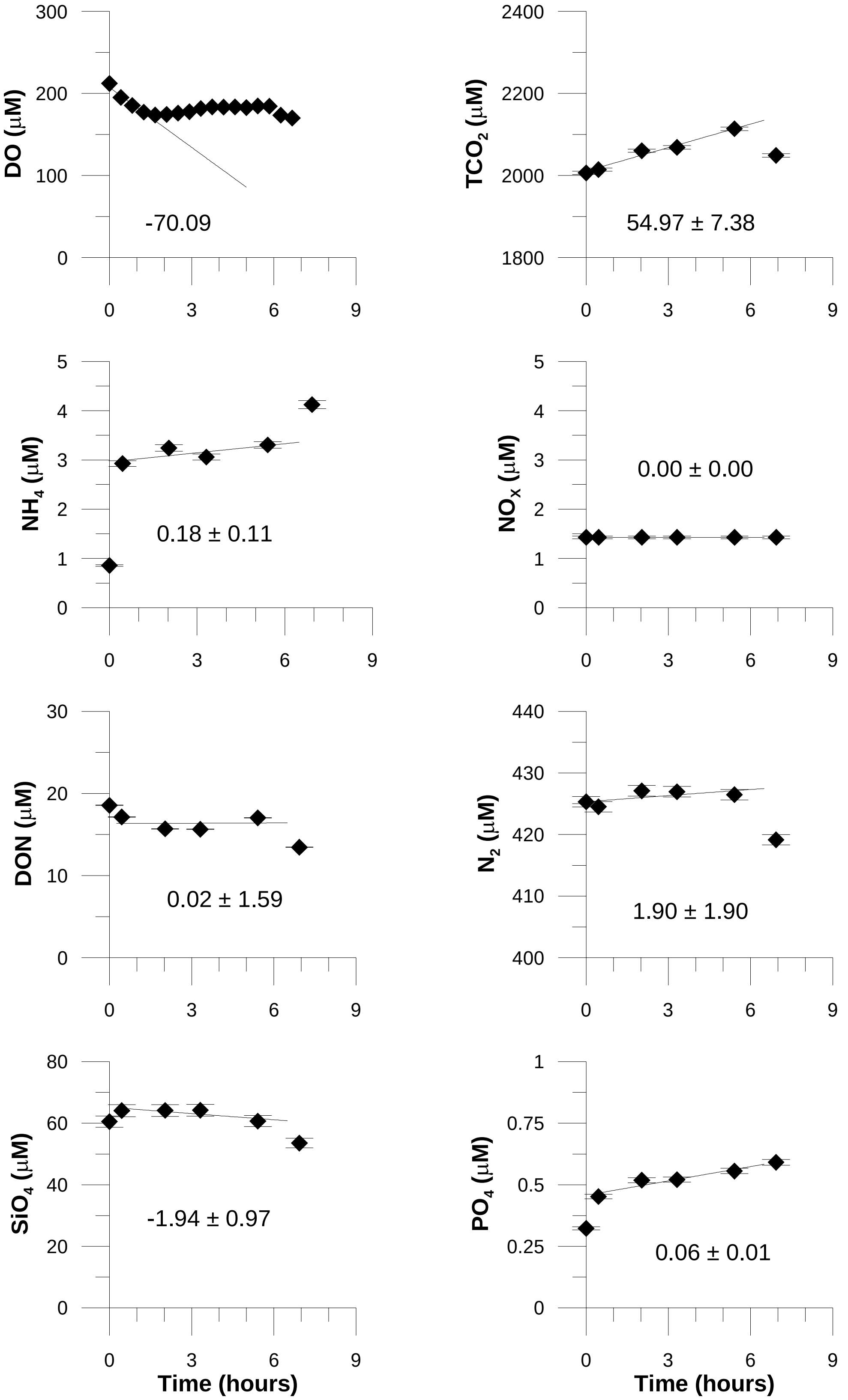
Dark

SR34A_7


DO (μM)
-9.69 ± 4.91
TCO2 (μM)
1.99 ± 18.25
NH4 (μM)
0.26 ± 0.25
NOX (μM)
0.00 ± 0.00
DON (μM)
-0.41 ± 0.60
N2 (μM)
0.03 ± 0.92
SiO4 (μM)
-5.91 ± 1.12
PO4 (μM)
0.07 ± 0.02
Time (hours)
Time (hours)

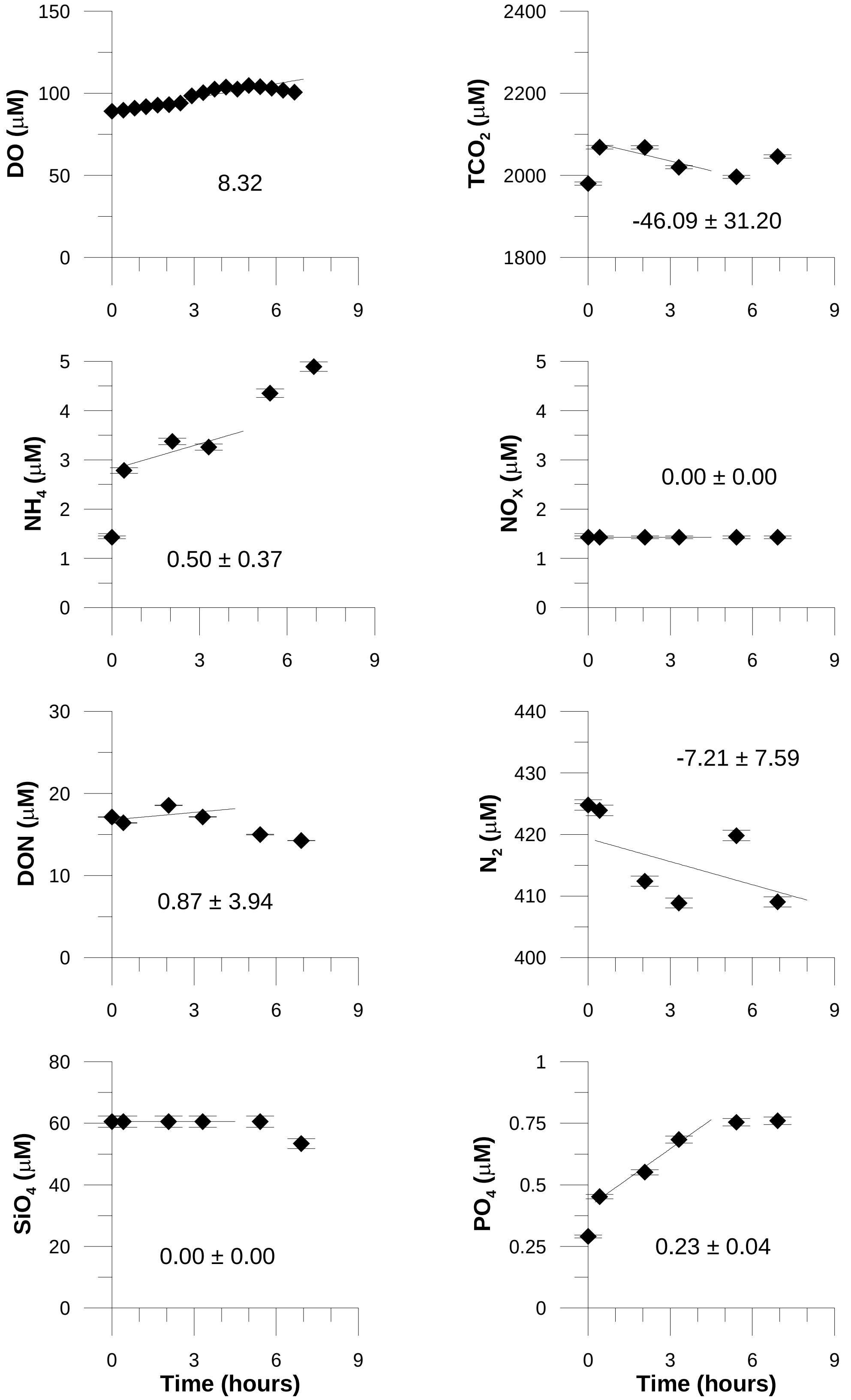
Dark

SR34A_8


DO (μM)
-70.09
TCO2 (μM)
54.97 ± 7.38
NH4 (μM)
0.18 ± 0.11
NOx (μM)
0.00 ± 0.00
DON (μM)
0.02 ± 1.59
N2 (μM)
1.90 ± 1.90
SiO4 (μM)
-1.94 ± 0.97
PO4 (μM)
0.06 ± 0.01
Time (hours)
Time (hours)

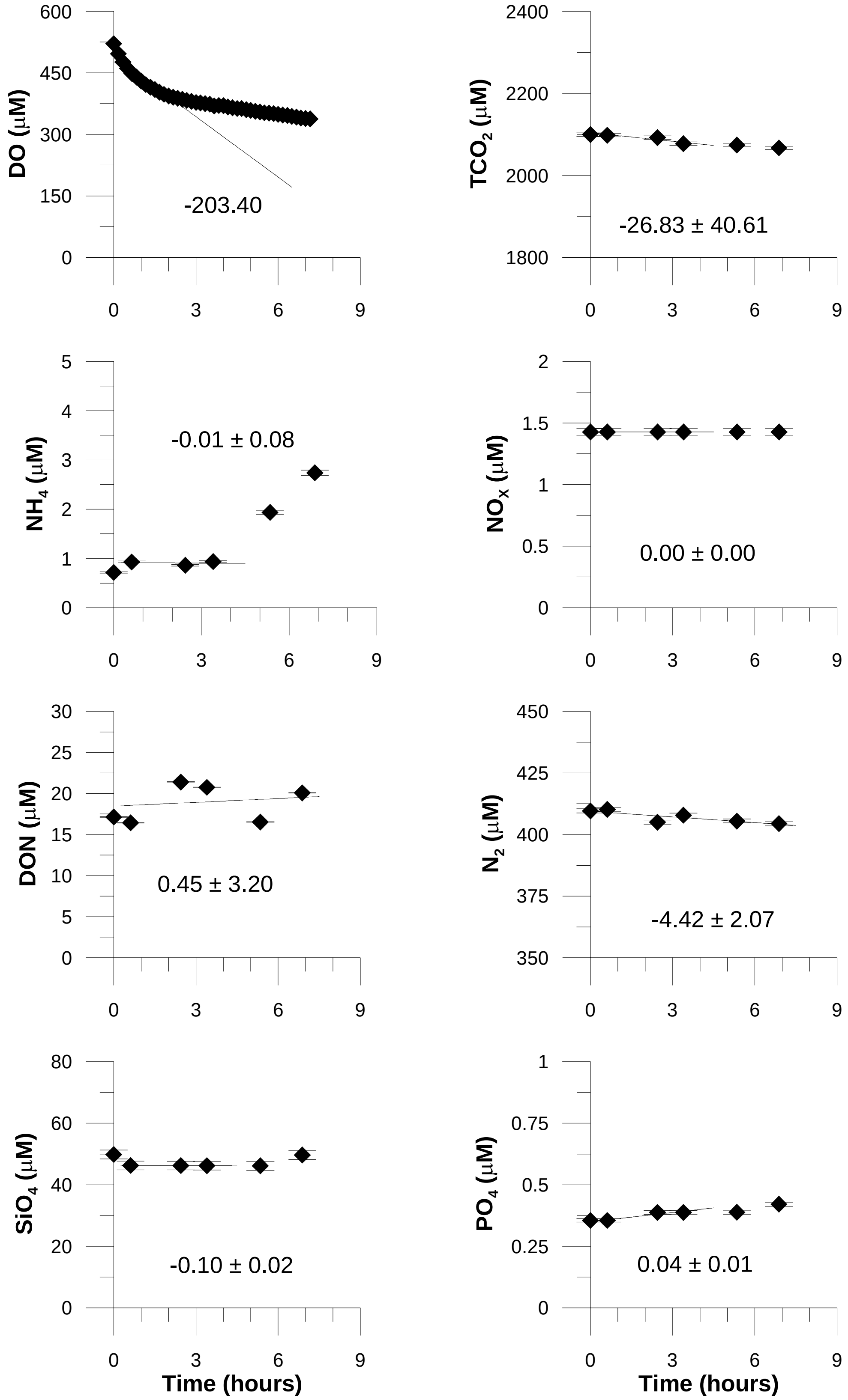
Light

SR34A_9



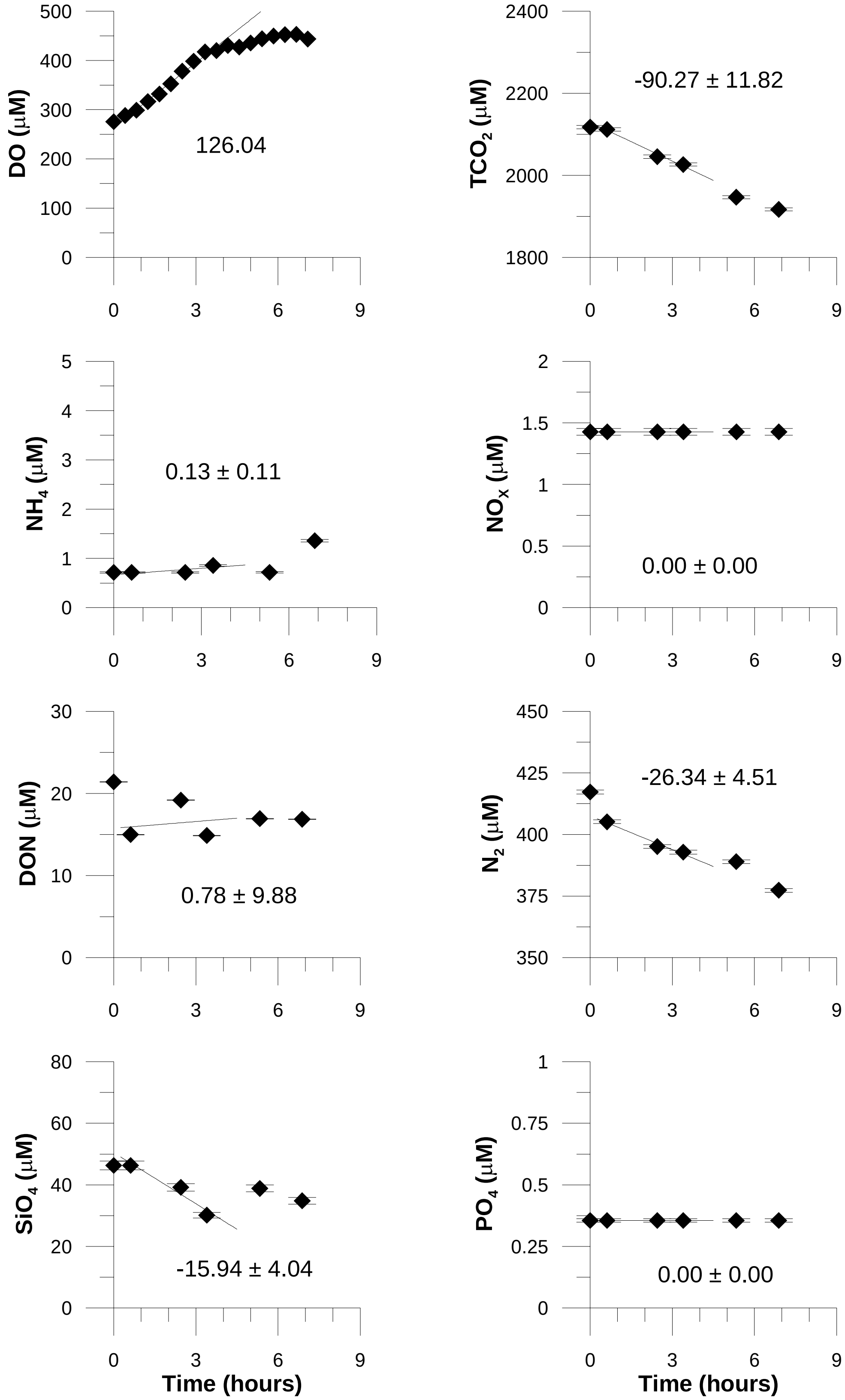
Dark

SR6F_5


DO (µM)
-203.40
TCO2 (µM)
-26.83 ± 40.61
NH4 (µM)
-0.01 ± 0.08
NOX (µM)
0.00 ± 0.00
DON (µM)
0.45 ± 3.20
N2 (µM)
-4.42 ± 2.07
SiO4 (µM)
-0.10 ± 0.02
PO4 (µM)
0.04 ± 0.01
Time (hours)
Time (hours)

Light

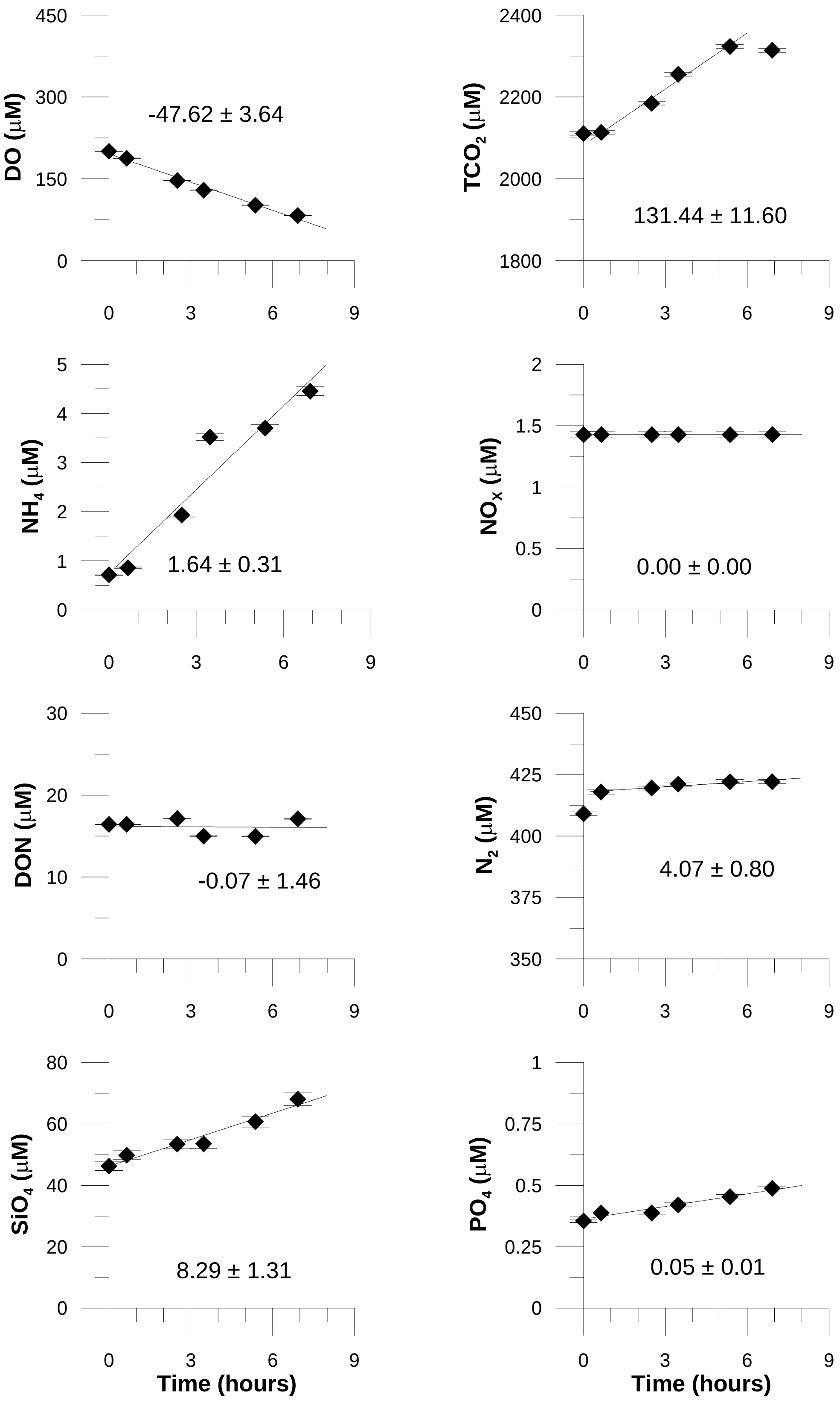
SR6F_6



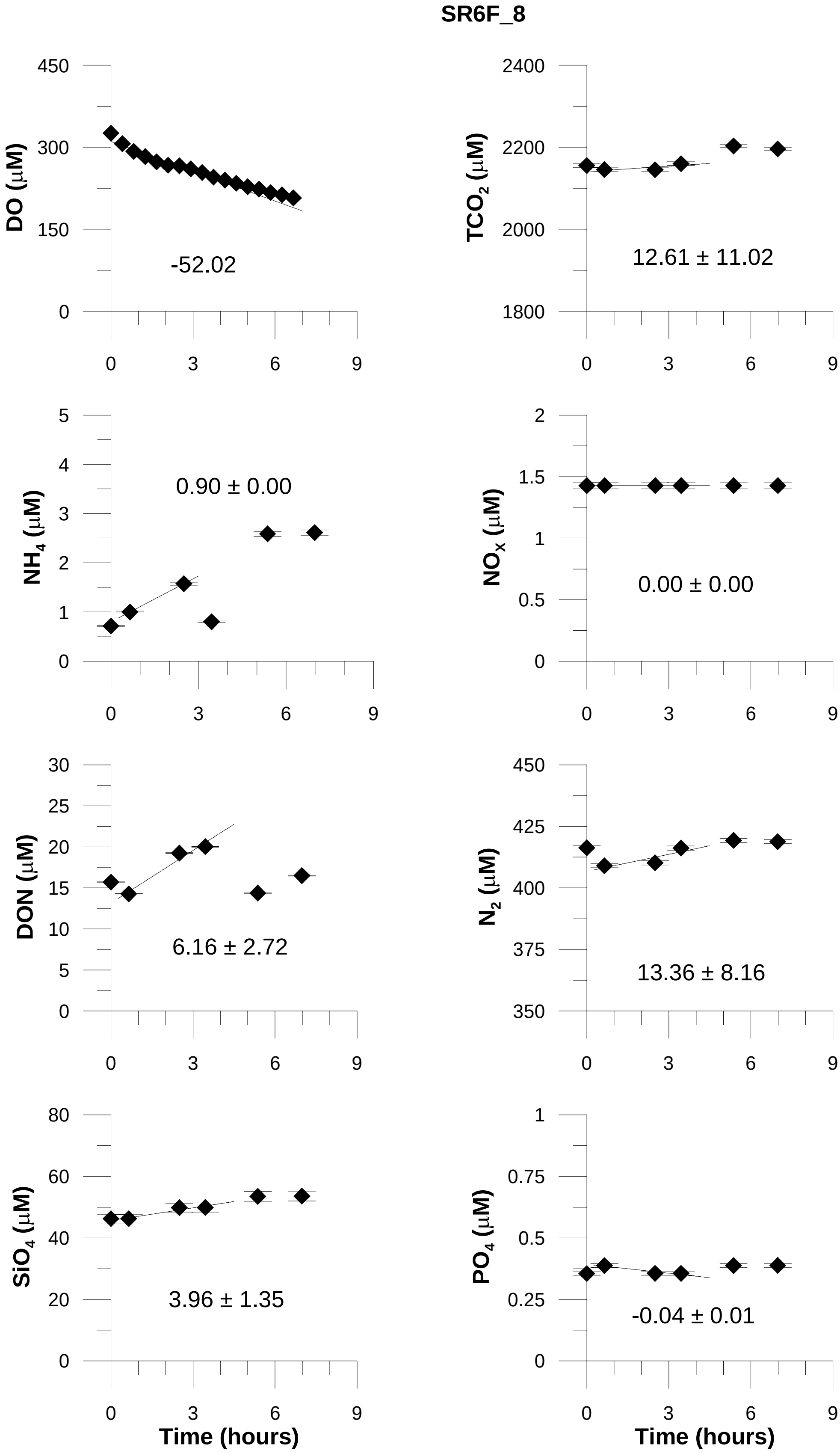
DO (μM)
126.04
TCO2 (μM)
-90.27 ± 11.82
NH4 (μM)
0.13 ± 0.11
NOx (μM)
0.00 ± 0.00
DON (μM)
0.78 ± 9.88
N2 (μM)
-26.34 ± 4.51
SiO4 (μM)
-15.94 ± 4.04
PO4 (μM)
0.00 ± 0.00
Time (hours)
Time (hours)

Dark

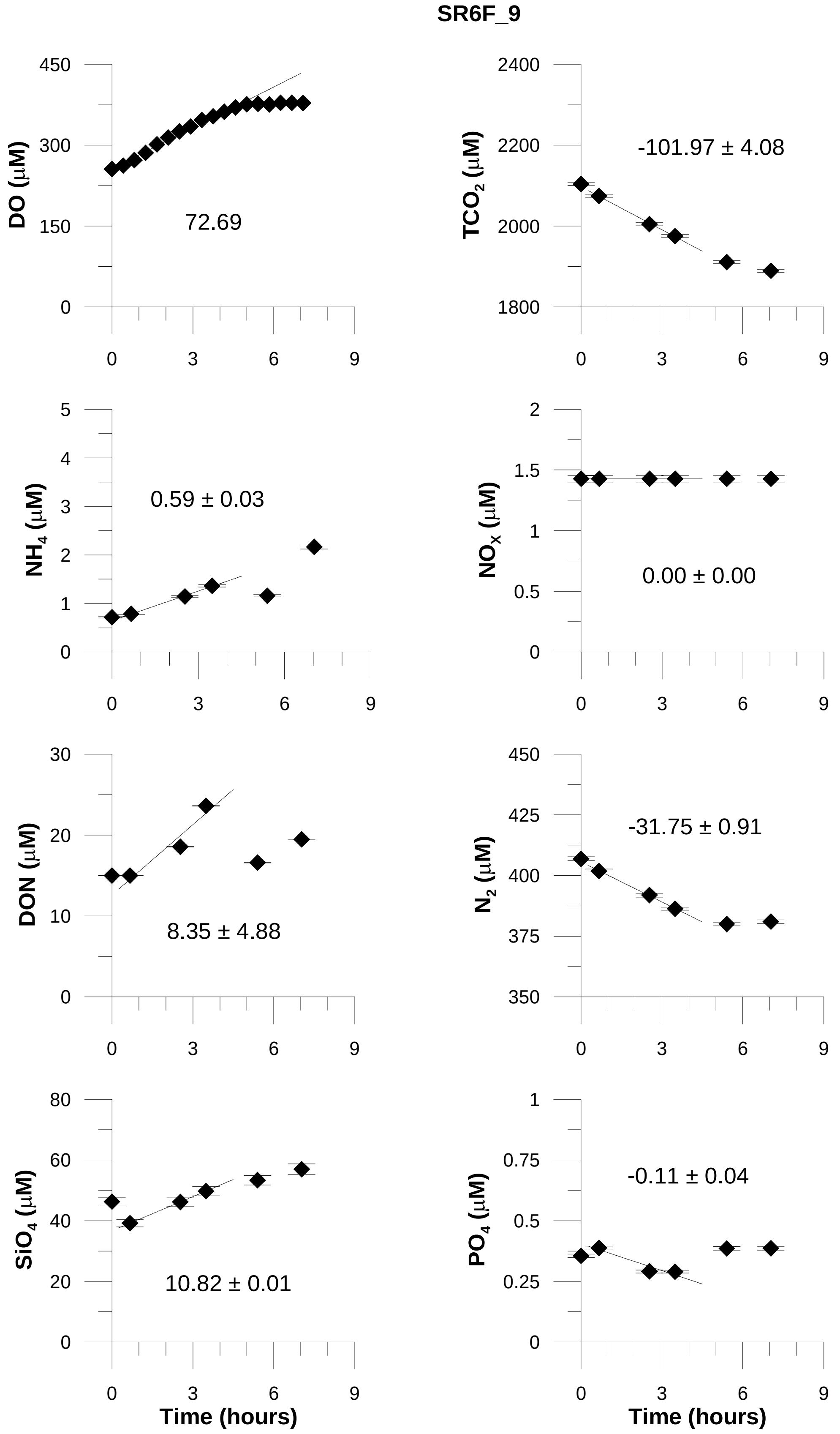
SR6F_7


DO (μM)
-47.62 ± 3.64
TCO2 (μM)
131.44 ± 11.60
NH4 (μM)
1.64 ± 0.31
NOX (μM)
0.00 ± 0.00
DON (μM)
-0.07 ± 1.46
N2 (μM)
4.07 ± 0.80
SiO4 (μM)
8.29 ± 1.31
PO4 (μM)
0.05 ± 0.01
Time (hours)
Time (hours)

Dark

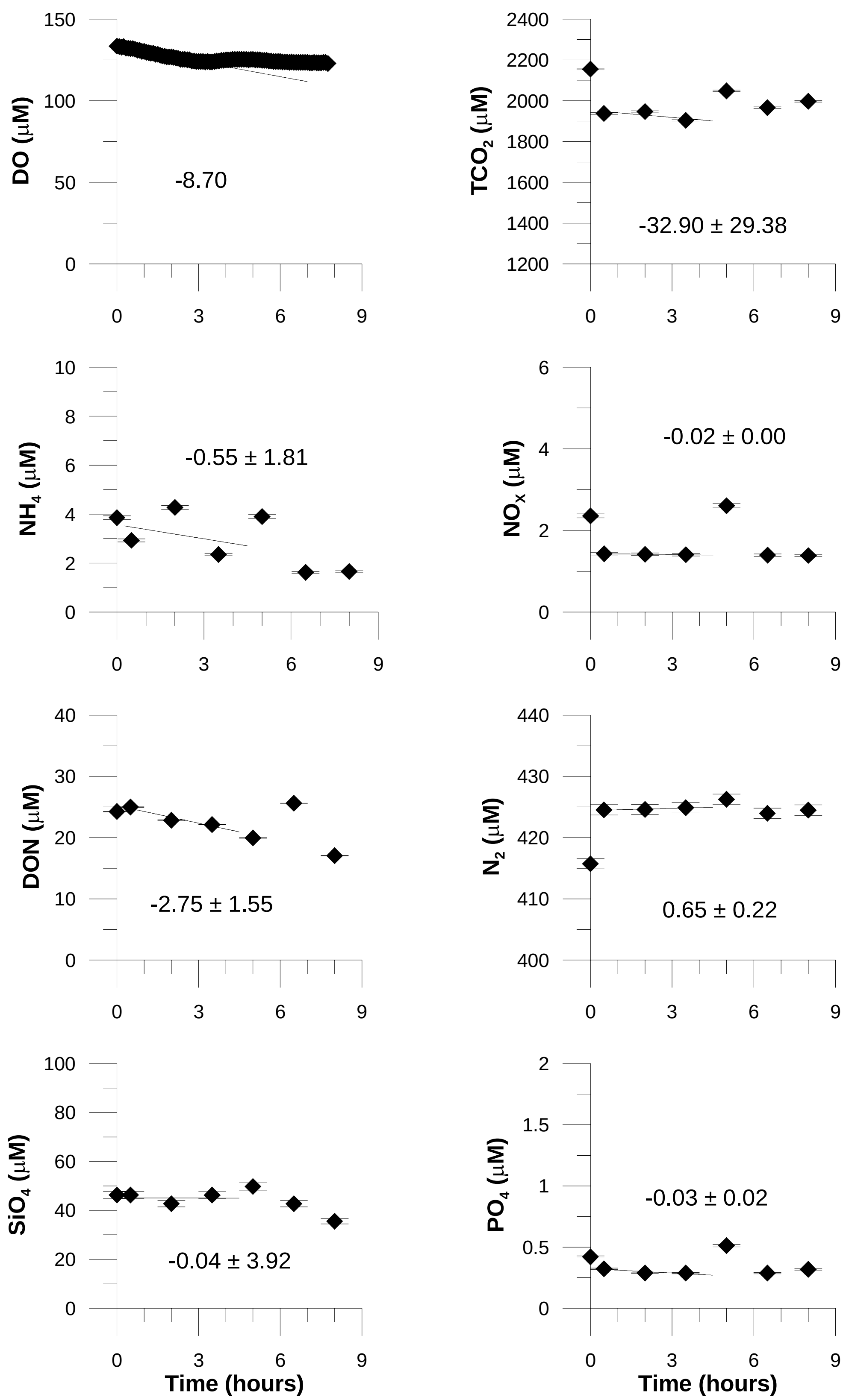

SR6F_8
DO (μM)
-52.02
TCO2 (μM)
12.61 ± 11.02
NH4 (μM)
0.90 ± 0.00
NOX (μM)
0.00 ± 0.00
DON (μM)
6.16 ± 2.72
N2 (μM)
13.36 ± 8.16
SiO4 (μM)
3.96 ± 1.35
PO4 (μM)
-0.04 ± 0.01
Time (hours)
Time (hours)

Light


SR6F_9
DO (μM)
72.69
TCO_2 (μM)
-101.97 ± 4.08
NH_4 (μM)
0.59 ± 0.03
NO_X (μM)
0.00 ± 0.00
DON (μM)
8.35 ± 4.88
N_2 (μM)
-31.75 ± 0.91
SiO_4 (μM)
10.82 ± 0.01
PO_4 (μM)
-0.11 ± 0.04
Time (hours)
Time (hours)

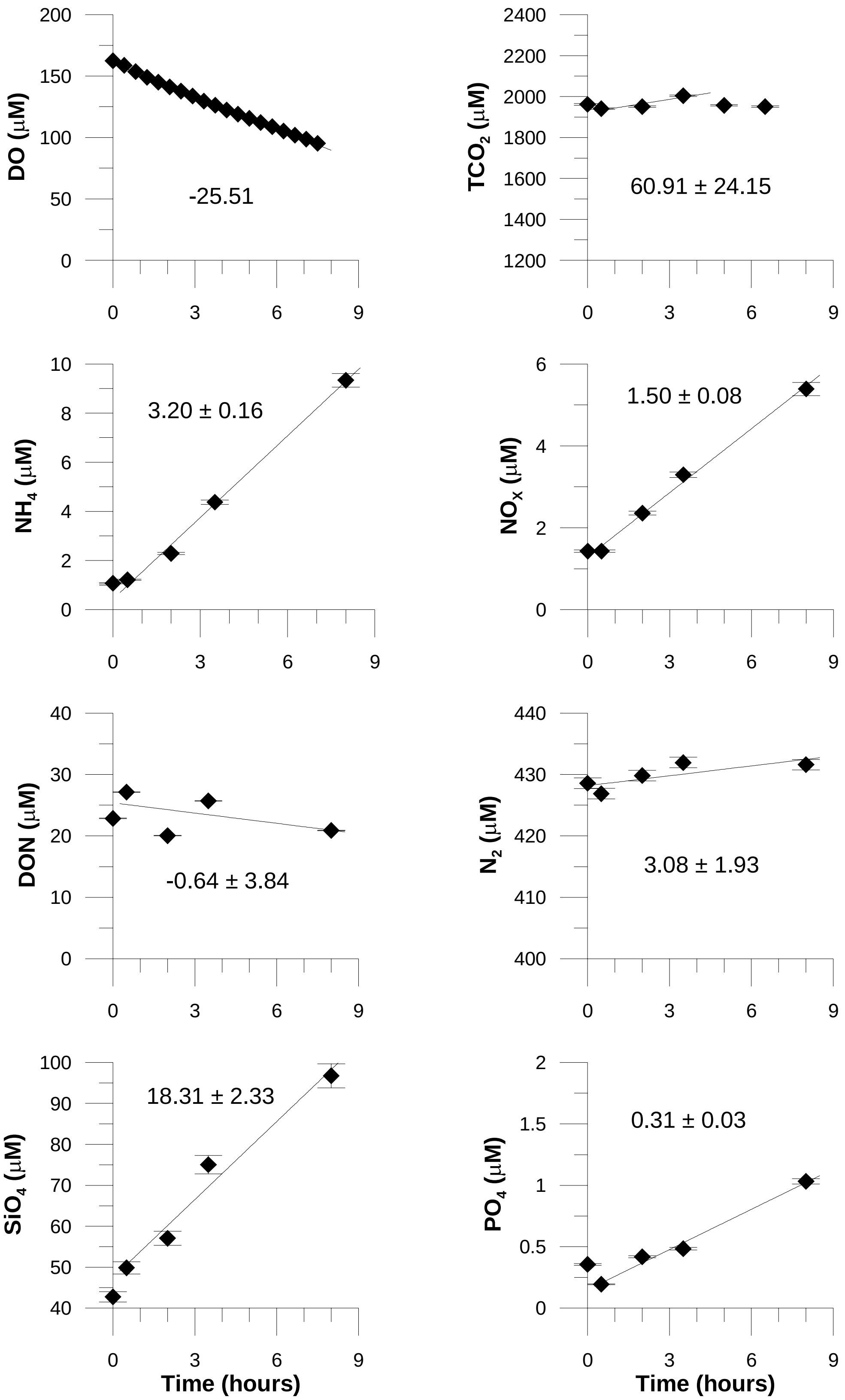
Dark

SR5I_3


DO (μM)
-8.70
TCO2 (μM)
-32.90 ± 29.38
NH4 (μM)
-0.55 ± 1.81
NOx (μM)
-0.02 ± 0.00
DON (μM)
-2.75 ± 1.55
N2 (μM)
0.65 ± 0.22
SiO4 (μM)
-0.04 ± 3.92
PO4 (μM)
-0.03 ± 0.02
Time (hours)
Time (hours)

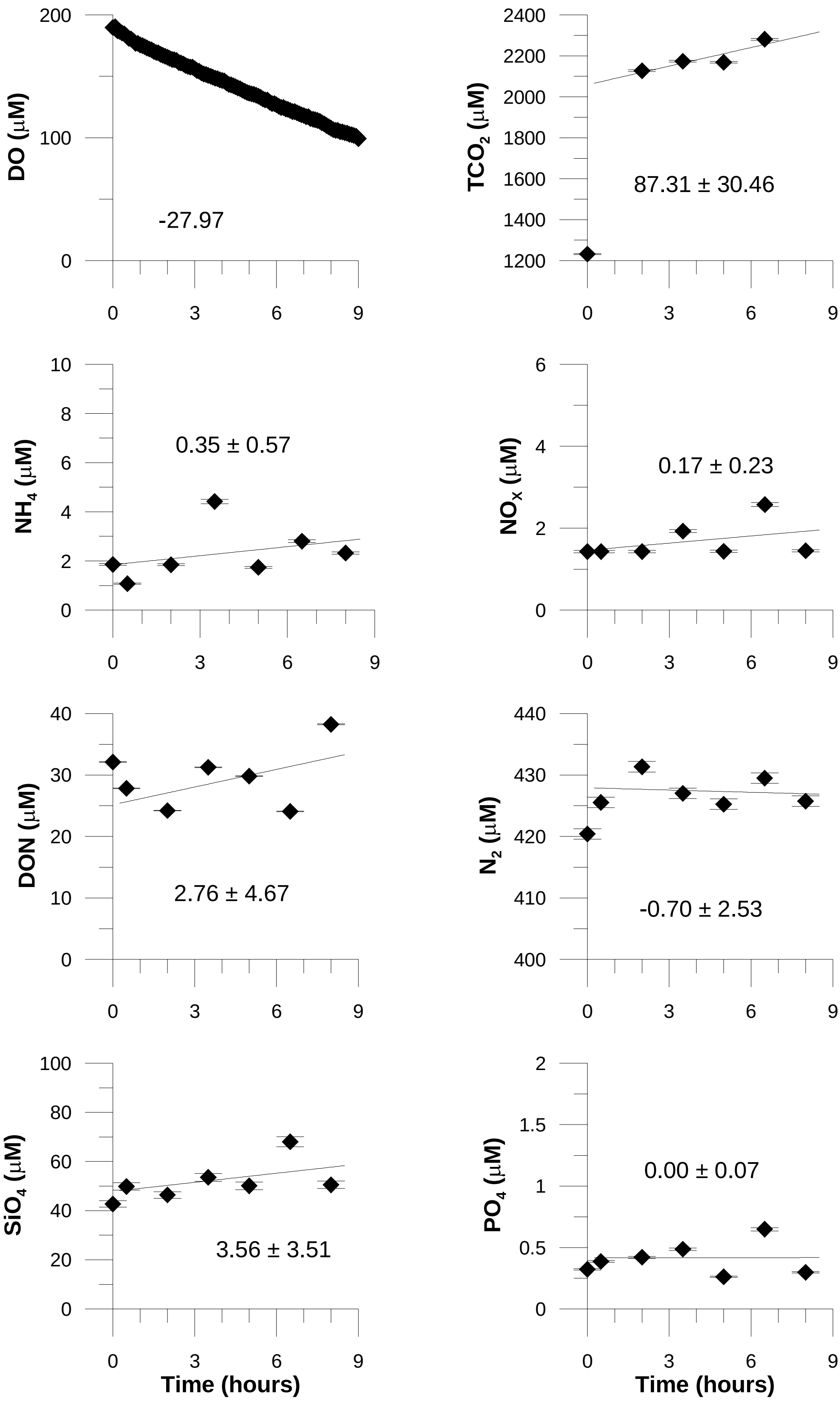
Light

SR5J_1


DO (μM)
-25.51
TCO2 (μM)
60.91 ± 24.15
NH4 (μM)
3.20 ± 0.16
NOx (μM)
1.50 ± 0.08
DON (μM)
-0.64 ± 3.84
N2 (μM)
3.08 ± 1.93
SiO4 (μM)
18.31 ± 2.33
PO4 (μM)
0.31 ± 0.03
Time (hours)
Time (hours)

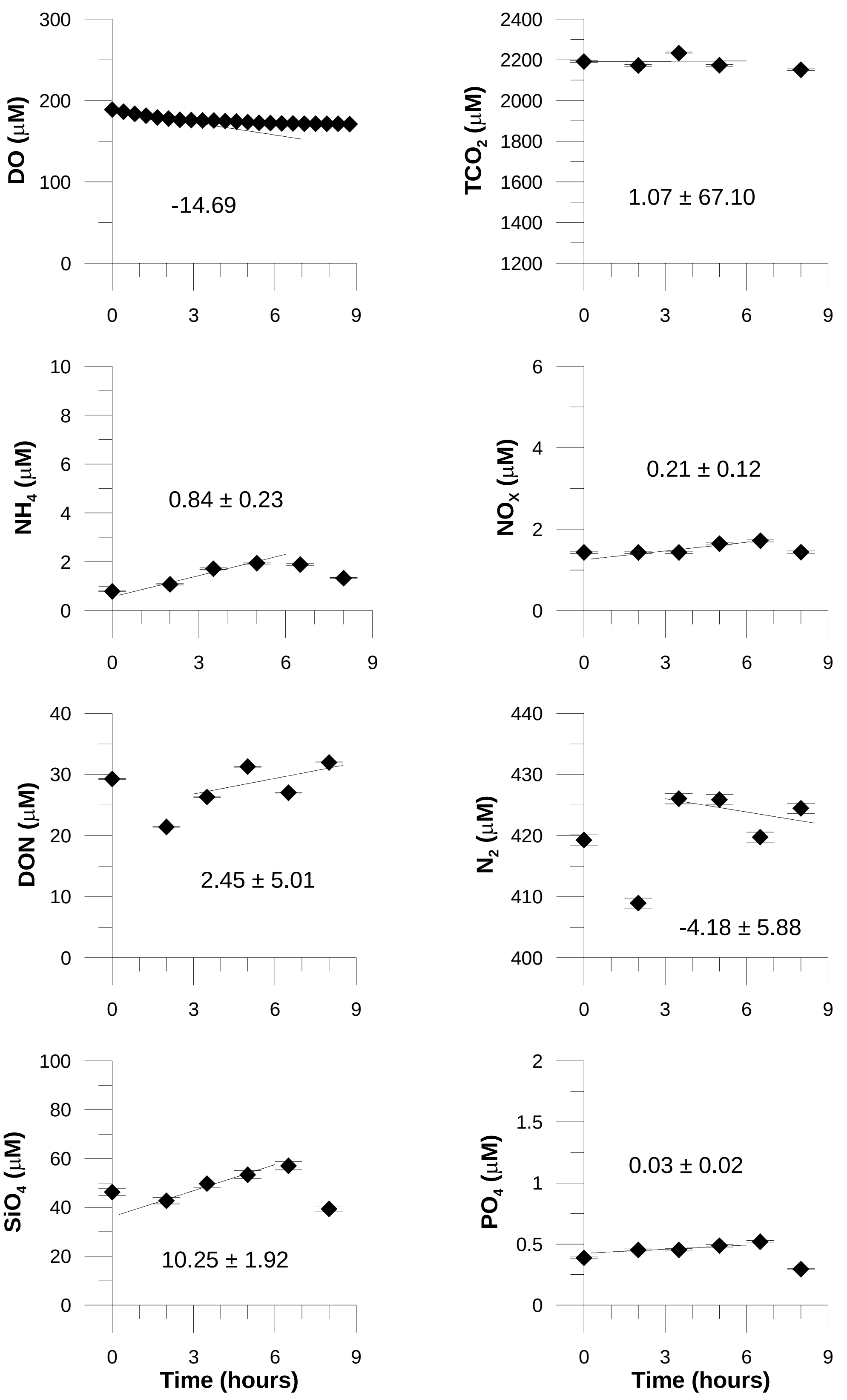
Dark

SR5J_2


DO (μM)
-27.97
TCO2 (μM)
87.31 ± 30.46
NH4 (μM)
0.35 ± 0.57
NOx (μM)
0.17 ± 0.23
DON (μM)
2.76 ± 4.67
N2 (μM)
-0.70 ± 2.53
SiO4 (μM)
3.56 ± 3.51
PO4 (μM)
0.00 ± 0.07
Time (hours)
Time (hours)

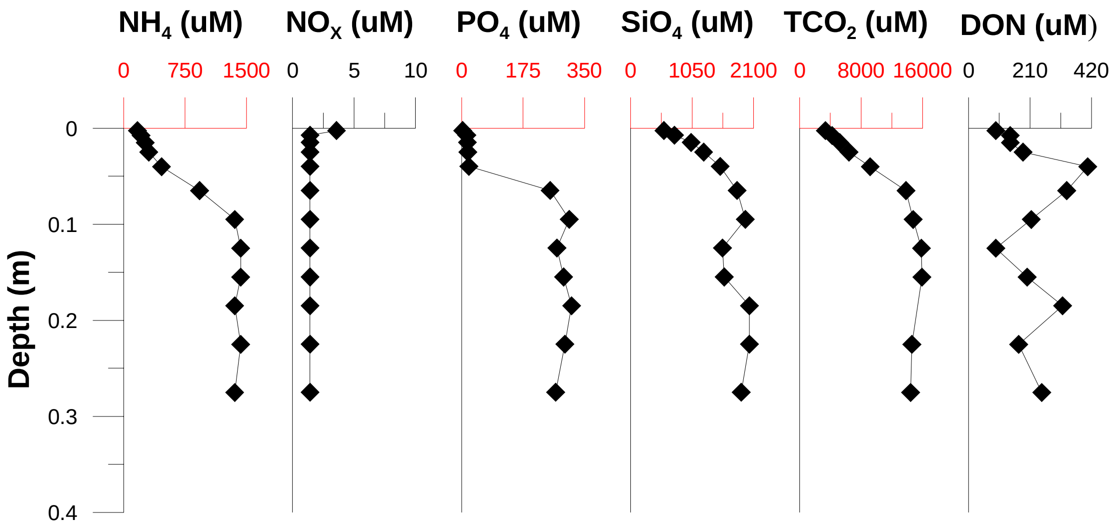
Dark

SR5J_3

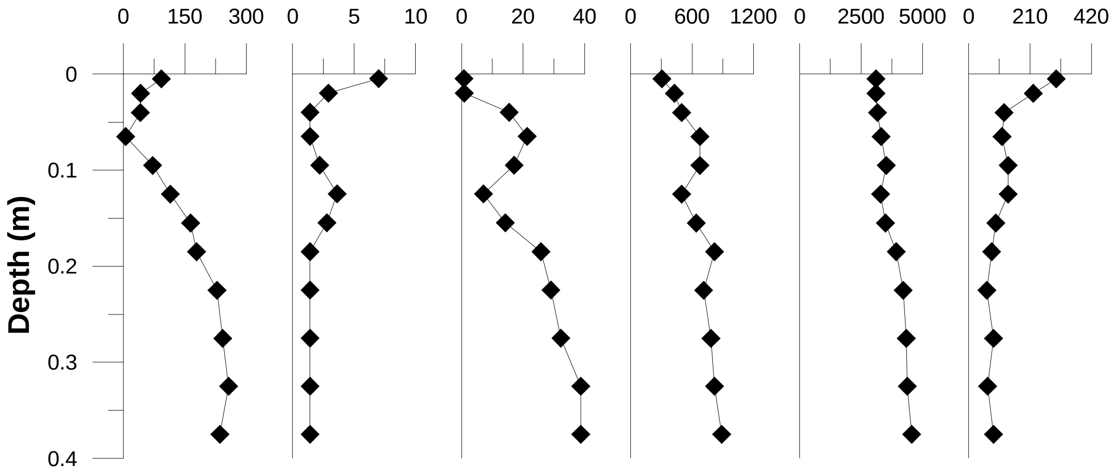

DO (μM)
-14.69
TCO2 (μM)
1.07 ± 67.10
NH4 (μM)
0.84 ± 0.23
NOx (μM)
0.21 ± 0.12
DON (μM)
2.45 ± 5.01
N2 (μM)
-4.18 ± 5.88
SiO4 (μM)
10.25 ± 1.92
PO4 (μM)
0.03 ± 0.02
Time (hours)
Time (hours)

Appendix 4. Down-core profiles

Swan River - Site 32



Swan River - Site 33



Swn River - Site 34