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PMD – Petroleum & Marine Division,
Geoscience for Coastal Waterway Management Project

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Record
2003/22

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GEOSCIENCE AUSTRALIA

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ISSN: 1448-2177
ISBN: 0 642 46780 3

GeoCat No: 50506

Bibliographic reference: Smith, C.S. and Heggie, D.T. (2003). *Benthic Nutrient Fluxes in Wallis Lake, NSW - Feb 2003*. Geoscience Australia, Record 2003/22.

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EXECUTIVE SUMMARY

Geoscience Australia conducted a survey to measure the benthic nutrient fluxes in Wallis Lake, during February 2003. The objectives of the survey were:

1. To measure the nutrient and other metabolite fluxes across the sediment-water interface at sites in Pipers Creek, Muddy Creek, Wallis Creek and in the Central Basin of Wallis Lake
2. To describe key processes controlling the fluxes of nutrients across the sediment–water interface at each of the four sites.
3. To determine the trophic state and assess the estuarine condition of the four selected sites in Wallis Lake.

The results of this recent summertime survey were compared to the observations made during the winter survey conducted in June, 2000.

The hydrographic data from Pipers Creek and Muddy Creek showed that the water column was stratified and oxygen concentrations were near saturation (100 %) throughout the water column. Similarly, Wallis Creek oxygen concentrations were also near saturation, however, the water column was well mixed. Dissolved oxygen was supersaturated at 4 m depth in the Central Basin site.

The benthic chamber TCO_2 fluxes from Pipers Creek varied between 18 and 36 mmol m^{-2} day^{-1} (average 29 mmol m^{-2} day^{-1}) and represent an oligotrophic-to-mesotrophic state, with a significant proportion of the carbon inputs being diatomaceous. The average denitrification efficiency at this site was about 38 %, indicating that more than half of the N load to the sediments is recycled back into the overlying waters as ammonia and is available for phototrophic growth. Carbon loadings at Pipers Creek were apparently similar for the summer and previous winter surveys, however, denitrification efficiency appears to have been compromised during the warmer summer survey compared to the winter survey. Given the apparently poor flushing at Pipers Creek, and its proximity to nutrient discharge, and the fact that recycled ammonia can be made available for additional phototrophic growth, this site appears prone to eutrophication and we maintain our 'amber' light condition for Pipers Creek.

The benthic chamber TCO_2 fluxes (estimates of carbon loading to the sediments) from Muddy Creek varied between 6 and 60 mmol m^{-2} day^{-1} (average 34 mmol m^{-2} day^{-1}). This represents an oligotrophic-to-mesotrophic state and most of the organic carbon was probably diatomaceous. The average denitrification efficiency was about 51 % and this result indicates that about half of the N input to the sediments is recycled as biologically available N that can subsequently be used for

phototrophic growth. This site is probably poorly flushed and these combinations of factors suggest that Muddy Creek is prone to eutrophication and is probably similar to Pipers Creek in this context.

An average diatomaceous TCO_2 flux of 57 mmol m^{-2} day^{-1} was estimated from a site in the Central basin, and this represents a mesotrophic state. There has been an apparent increase in carbon flux to the sediments (more than twofold) since the winter (June 2000) observation period. The denitrification efficiency during the summer was found to be approximately 73 % based on our estimates of diatomaceous TCO_2 carbon fluxes. This compares to a denitrification efficiency of near 100 % during the winter. Because we could not reconcile all metabolite fluxes according to the Redfield model of organic matter degradation in sediments, there is a note of caution in our interpretation of these data. It is possible that the denitrification efficiencies are lower than those reported based on the estimates of diatomaceous carbon fluxes. Denitrification is undoubtedly occurring in the central basin as evidenced by measured N_2 anomalies. On balance we think that there has been an increase in carbon flux to the sediments of the central basin during the summer months and the denitrification efficiency has only decreased slightly since the winter, and we think this site is in 'good' condition. It is impossible to draw inferences of the trophic state and water quality in the entire central basin part of the lake based on an observation from one station only in the central basin.

The benthic chamber TCO_2 fluxes from Wallis Creek varied between 46 and 110 mmol m^{-2} day^{-1} (average 75 mmol m^{-2} day^{-1}), and this represent a mesotrophic-to-eutrophic state. Diatomaceous organic matter was estimated to represent half-to-most of the carbon input to the sediments at this site. Seagrass was observed growing in the sediments and seagrass detritus probably accounts for another component or organic carbon degrading in these sediments. These results represent about a 50 % increase in carbon loading to the sediments than was observed during the winter months. Despite this increase in loading the site was found to have a denitrification efficiency of near 100 % indicating that most of the N falling to the sediments was recycled as biologically unavailable nitrogen gas. There was no perceived increased risk to water quality under these conditions, and this site is in 'good' condition.

ACKNOWLEDGMENTS

The authors would like to thank the following people for their contribution to this project:

Colin Tindall, Ian Atkinson, David Ryan, Craig Wintle and Emma Murray for their assistance in undertaking the field survey.

Mick from Barkley's for driving the boat and assisting with sampling.

Andy Longmore (Marine and Freshwater Research Institute - VIC), Ian Atkinson, Rachel Davenport, Tony Watson and Alex McLachlan (Geoscience Australia) for sample analysis.

Gerard Tuckerman from the Great Lakes Council for his continued support.

Graham Skyring (Skyring Environment Enterprises) for his invaluable assistance during data interpretation.

Emma Murray and Graham Skyring for their editorial comments.

ABBREVIATIONS AND UNITS

Cl^-	Chloride
DO	Dissolved Oxygen
Fe^{2+}	Iron
GA	Geoscience Australia
GLC	Great Lakes Council
H_2S	Hydrogen Sulphide
ICOLL	Intermittently Closed and Open Lake/Lagoon
mL	milliliter
µg	micrograms
µL	microlitre
mAHD	metres above Australian Height Datum
mM	millimoles per litre
mmol m^{-2} day^{-1}	millimoles per metre squared per day
µM	micromoles per litre
NH_4^+	Ammonium
NO_2^-	Nitrite
NO_3^-	Nitrate
NO_X^-	Nitrate + Nitrite
PO_4^{3-}	Phosphate
SiO_4^{2-}	Silicate
SO_4^{2-}	Sulphate
TCO_2	Total Carbon Dioxide
TOC	Total Organic Carbon
TN	Total Nitrogen
TP	Total Phosphorus
TS	Total Sulfur
TFe	Total Iron

CONTENTS

1. INTRODUCTION

Wallis Lake is a wave-dominated estuary on the NSW Lower North Coast and has a surface area of approximately 90 km^2. The Great Lakes Council has undertaken a variety of studies to assess the environmental resources and assets of the lake and to collect baseline data from which any environmental changes can be assessed. The region is under increasing 'stress' from development pressures.

As part of these studies Geoscience Australia (formally the Australian Geological Survey Organisation) conducted studies of nutrient cycling within the surface sediments at several sites in Wallis Lake to assess the trophic status of those sites and report upon the implications for nutrients cycling and water quality. This survey was undertaken during the winter month of June, 2000.

The key results from that winter survey in 2000 included the following:

1. The water column was reasonably 'well-mixed' at most sites with little evidence of significant stratification in temperature, salinity or dissolved oxygen concentrations. Dissolved oxygen levels were near saturation at most sites. Only Pipers Creek showed some stratification in water temperature and salinity, and dissolved oxygen levels were about 50 % saturation in the bottom waters.
2. The measured carbon dioxide fluxes (estimates of organic carbon loading) to the sediments at all sites was found to vary between 21 and 48 mmol m^{-2} day^{-1}. These results suggested the sites were oligotrophic-to-mesotrophic according to the criteria articulated by Nixon (1995).
3. The denitrification efficiency (the efficiency with which microbial reactions in the sediments convert N fixed in plant organic material into nitrogen gas) was found to be very efficient (near 100 % at all sites). This was an important result because it indicated that there was limited recycling of ammonia from the sediments to the overlying waters, where it could contribute to phototrophic growth. Under these conditions, we suggested there is little risk to eutrophication and deterioration in water quality.

The most recent survey, undertaken during February 2003, represented summer conditions in Wallis Lake. This period coincided with severe drought conditions in eastern Australia, perhaps resulting in atypical summer hydrographic and ecological conditions. We have no previous data to make an assessment of this possibility. This fact should be kept in mind when considering the implications of the results of this survey.

1A. OBJECTIVES

The objectives of the current survey included the following:

1. To measure the nutrient and other metabolite fluxes across the sediment-water interface at sites in Pipers Creek, Muddy Creek, Wallis Creek and the Central Basin of Wallis Lake
2. To describe key processes controlling the fluxes of nutrients across the sediment–water interface at each of the four sites.
3. To determine the trophic state and assess the condition of the four selected sites in Wallis Lake.

To achieve these objectives Geoscience Australia conducted a survey of Wallis Lake during February, 2003. Benthic chambers were deployed at each site to measure fluxes of metabolites across the sediment-water interface. In addition, cores and hydrographic data were collected at each site.

1B. EXPERIMENTAL DESIGN

Four sampling sites were selected within Wallis Lake (Figure 1) in consultation with the Great Lakes Council. Sites 2 (Pipers Creek), 3 (Wallis Creek) and 4 (Central Basin) were chosen due to their risk of deteriorating water quality (identified in a previous survey by Smith, *et al.* (2000)). Site 10 (Muddy Creek) was chosen due to its resemblance to Pipers Creek (i.e. canal estate with low water exchange). Four benthic chambers were deployed (1 clear and 3 dark) and two sediment cores collected at each site.

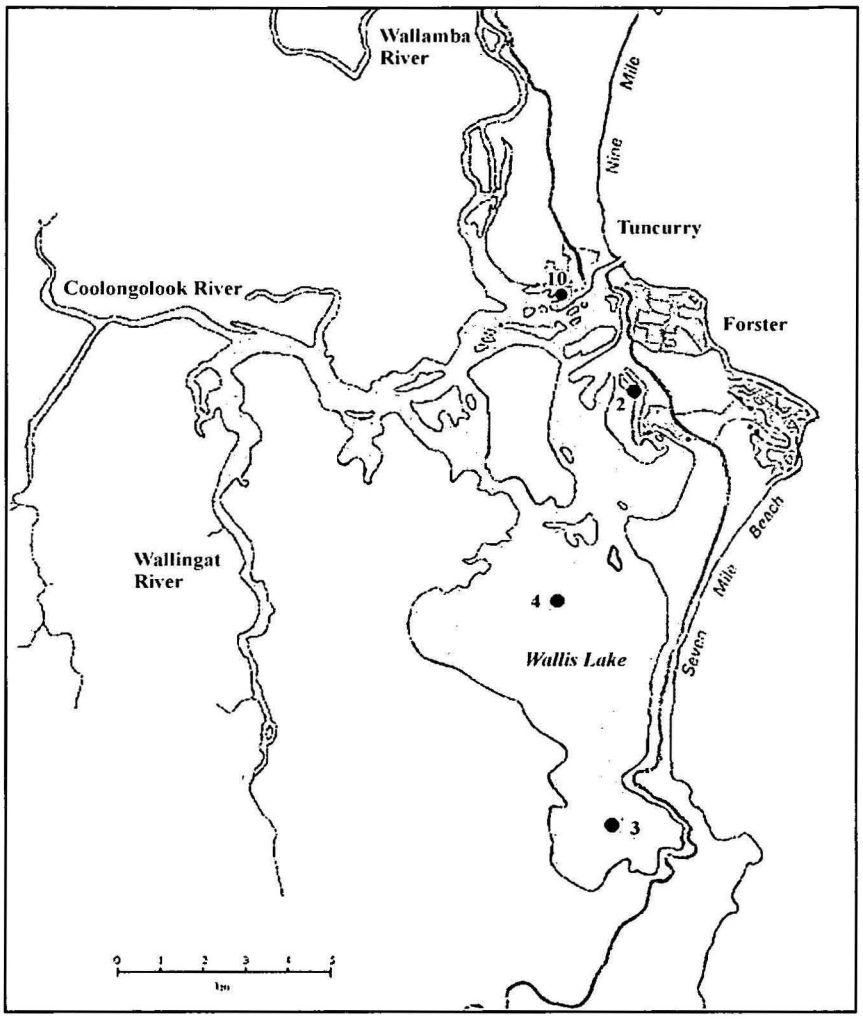

Figure 1 *Wallis Lake sample locations*

2. METHODS

Nutrient and metabolite fluxes between the sediments and overlying water were measured using benthic chambers, following the method described by Berelson *et al.* (1997). Ambient bottom waters and samples drawn from the chambers were analysed for dissolved inorganic nutrients (NH_4^+, NO_2^-, NO_3^-, PO_4^{3-}, SiO_4^{2-}), N_2 gas, alkalinity and pH. The fluxes of nutrients and metabolites (O_2 and TCO_2) were then calculated from the rate of change in concentration measured within the chambers.

Two sediment cores were collected at each site and split into 5 - 10 mm increments for analyses. Each sediment increment was centrifuged and the porewaters collected and analysed for dissolved inorganic nutrients (NH_4^+, NO_2^-, NO_3^-, PO_4^{3-}, SiO_4^{2-}), SO_4^{2-}, Cl^- and Fe^{2+}. TOC (total organic carbon), TN (total nitrogen), TP (total phosphorus), TS (total sulfur), grain size and major elements were measured on the freeze-dried sediment samples from each depth increment.

2A. BENTHIC FLUX MEASUREMENTS

Two types of benthic chambers were used: (i) manually sampled chambers; and (ii) automatically sampled chambers.

Both chamber types consisted of simple plexiglass cylinders that isolated approximately 10 litres of water in contact with 0.066 m^2 of bottom sediment. A data logger recorded dissolved oxygen concentrations, salinity and temperature within the confined waters and in external bottom waters. One transparent (light) chamber and three opaque (dark) chambers were deployed at each site. The light chambers recorded net oxygen consumption and nutrient release (balance of respiration and photosynthesis) during daylight hours, while the dark chambers recorded oxygen consumption and nutrient release during respiration.

A caesium chloride (CsCl) spike was injected into the chambers shortly after lid closure and the observed dilution of this spike in subsequent sample draws was used to calculate chamber volume and verify that the chamber was not leaking.

Manual Chambers

The chambers were placed on the seafloor and allowed to equilibrate with ambient water for about 12 hours prior to lid closure. 100 mL of chamber water were withdrawn from the chamber by syringe via a tube to the surface. Samples were collected at approximately 1 hour, 2.5 hours, 6 hours, 8.5 hours and 24 hours after lid closure. Dissolved inorganic nutrient (NO_x^-, NH_4^+, PO_4^{2-}, SiO_4^{2-}), pH, TCO_2, alkalinity, N_2, and Cs concentrations were measured in each sample. Sub-

samples for nutrient analysis were filtered immediately through 0.45 μM filters, and then frozen for storage prior to analysis at the Geoscience Australia laboratory. The pH of unfiltered samples was measured immediately, whilst alkalinity was determined by Gran titration within 24 hours (on a filtered sample). A 10 mL sample for N_2 gas analysis was transferred into a Quickfit glass vial and preserved with 50 μL of concentrated HgCl solution. The glass vials were stored in a water bath at ambient temperature (~ 20 °C) until analysed.

Automatic Chambers

The automated Geoscience Australia chambers consist of a plexiglass cylinder (of the same design as the manual) with a spring-loaded trap door on the upper surface, a spring-loaded syringe for injecting the tracer, and seven spring-loaded syringes for multiple in-situ sampling and storage. The chamber is housed within an aluminium frame containing an electronics module, which record data from each YSI probe. The module also controls lid closure, spike injection, and sample withdrawal by applying a current across burn wires on each of the spring-loaded devices.

Each chamber was pre-programmed so that it would remain inactive on the sea floor with the lid open following deployment. This allows the water within the chamber to equilibrate with ambient water and ensures a good seal between the sediments and chamber wall. Prior to lid closure a sample was drawn from the chamber to represent ambient conditions. Subsequently the lid was closed and a spike of CsCl tracer was injected. Six samples were withdrawn from each chamber during each deployment at 0.5 hours, 3.5 hours, 6.5 hours, 9.5 hours, 12.5 hours and 24 hours. All chamber samples were stored in situ until the chamber was recovered. All nutrient sub-samples were filtered immediately upon retrieval. Samples drawn from the automatic chambers included an additional in-line 20mL glass sample bulb designed to contain and preserve the N_2 gas and pH samples.

Chamber volumes (V_{ch}) and heights (H_{ch}) were calculated using the following formula:

$$V_{ch} = V_{sp} \frac{(C_{sp} - C_b)}{(C_{\max} - C_b)}$$

where V_{sp} and C_{sp} are the spike volume and concentration, C_b is the background (ambient) chamber concentration, C_{max} is the maximum concentration of the spike in the chamber and A_{ch} is the area of sediment covered by the chamber (0.066 m^2).

Benthic fluxes of nutrients and metabolites (mmol $m^{-2}.day^{-1}$) were calculated from the rate of change of concentration within the chamber (corrected for the intake of ambient water).

$$Flux = \frac{\delta c}{\delta t} * H_{ch}$$

$\delta c/\delta t$ was estimated by least squares regression of concentration against time for the initial linear portion of the plot of concentration vs time. The uncertainty of the flux estimate was chosen to be equal to the standard error of the slope of the regression.

2B. SEDIMENT CORES

Two sediment cores were collected at each site using a manually operated corer with an internal piston to minimise sediment compression. The cores were stored at near in-situ temperatures before processing. The sediments were extruded from the core barrel inside a nitrogen filled 'glove-bag' at 5 - 10 mm increments. The extruded sediments were placed into centrifuge tubes and centrifuged at 11 000 rpm for five minutes; the supernatant was decanted and filtered through 0.45 μm disposable filters. Each sample was purged with N_2 gas immediately following filtration to remove any H_2S, and to prevent oxidation of dissolved Fe^{2+} and the co-precipitation of P. Samples were frozen and stored with N_2 filling the headspace of the sample bottles. Porewaters were analysed for dissolved inorganic nutrients (NH_4^+, NO_2^-, NO_3^-, PO_4^{3-} and SiO_4^{2-}) by Geoscience Australia upon return from the survey.

The solid phase of the sediment cores were also frozen for transportation to the laboratory. Samples were then freeze-dried and analysed for stable isotopes and major elements using XRF.

The TOC determination involves pyrolysis followed by oxidation of 100 mg of dry sample using Rock-Eval 6 instrumentation. The pyrolysis step involves incrementally heating the sample from 300 °C to 650 °C in a stream of nitrogen gas, and detecting the evolved hydrocarbons. The oxidation process involves gradually heating the sample to 800 °C in a stream of air and detecting the evolved oxides of carbon. The detected hydrocarbons and the oxides of carbon were then quantified in terms of carbon and the sum equals the Total Organic Carbon.

We determined TS and TFe in the dry sediments by X-ray fluorescence spectrometry using a Phillips PW2404 sequential X-ray spectrometer. Iron and Sulfur were measured (as oxides Fe_2O_3 and SO_3) on glass fusion discs. Oxides were calibrated using United States Geological Survey and Geoscience Australia rock standards.

3. RESULTS

3A. HYDROGRAPHIC CONDITIONS

Water column dissolved oxygen, temperature and salinity conditions were recorded at each site at the time of chamber deployment (Table 1).

Table 1 *Water Column Profiles in Wallis Lake (numbers in brackets are from the 2000 winter survey)*

	Depth (m)	Temperature (°C)	Salinity	DO (%)
Site 2 Pipers Creek	0	27.21 (13.8)	21.23 (30.36)	126.4 (90.0)
	0.8	26.00 (15.1)	27.39 (34.60)	112.2 (86.6)
	1.4	27.67 (15.1)	32.47 (34.52)	107.9 (43.5)
Site 10 Muddy Creek	0	26.17	30.56	106.1
	1.0	25.58	32.59	115.8
	2.0	23.37	33.92	107.5
Site 3 Wallis Creek	0	25.94 (14.7)	32.31 (33.84)	103.7 (93.5)
	0.8	25.84 (15.1)	32.32 (34.40)	97.4 (95.6)
	1.5	25.86 (15.2)	32.32 (34.35)	96.7 (95.5)
Site 4 Central Basin	0			
	4.0	23.64 (14.8)	33.51 (31.30)	111.6 (75.1)

Pipers Creek (Site 2) was moderately stratified at the time of this survey, with significant salinity differences between surface and bottom waters (21.23 to 32.47). Dissolved oxygen was supersaturated and temperature was consistent throughout the water column.

Muddy Creek (Site 10) showed evidence of temperature and salinity stratification between surface and bottom waters. However, dissolved oxygen was relatively constant throughout the water column and was slightly supersaturated.

The Wallis Creek site (Site 3) appeared 'well-mixed' with only small differences between surface and bottom water temperatures and salinities. Dissolved oxygen levels were close to saturation.

Hydrographic data were not recorded in surface waters at Site 4 (Central Basin). The bottom water sample showed a near marine salinity, a temperature of 23.64 °C and surprisingly, dissolved oxygen levels were supersaturated (116 %).

Water column conditions differed considerably between the summer survey and the winter 2000 survey (Smith *et al.*, 2000). Water column temperatures were approximately 10 °C warmer and dissolved oxygen was up to 60 % higher in summer 2003 compared to winter 2000.

Table 2 *Average Bottom Water Nutrient Concentrations for Wallis Lake (2000 and 2003)*

Site	NH_4	PO_4	NO_X	SiO_4	Date
Pipers Creek (2)	6.67	0.22	0.36	40.9	Feb 2003
Wallis Creek (3)	0.34	0.35	0.06	6.3	Feb 2003
Central Basin (4)	0.87	0.37	0.07	4.4	Feb 2003
Muddy Creek (10)	2.12	0.34	0.31	10.0	Feb 2003
Pipers Creek (2)	0.58	0.02	0.06	1.02	June 2000
Wallis Creek (3)	0.53	0.04	0.08	0.8	June 2000
Central Basin (4)	0.39	0.02	0.20	0.3	June 2000

Average bottom water nutrient concentrations for both the 2000 and 2003 surveys are presented in Table 2. NO_X (nitrate + nitrite) concentrations in bottom waters were significantly higher at Pipers Creek during the summer months, but were comparable between seasons at the other sites. P concentrations were significantly higher at all sites during the summer months. SiO_4 concentrations were also higher at all sites during summer, especially at Pipers Creek.

3B. SEDIMENT CORES

Sediment core descriptions for each site are presented in Table 3. Sediment cores from all sites comprised mainly mud in the upper 0 -7 cm, often with shell fragments. Sites 2 (Pipers Creek) and 10 (Muddy Creek) contained muddy-sand to sand in the lower cores. Seagrasses were identified at Sites 2 (Pipers Creek) and 3 (Wallis Creek). A noticeable H_2S odour was identified (in varying degrees) in the lower sediments of all sites, except Site 2 (Pipers Creek) Site 3 (Wallis Creek) had a noticeable odour throughout the core.

Table 3 *Sediment Core Descriptions*

	Depth	Description
Site 2 Pipers Creek	Surface	Halophila seagrass and rhizomes
	0 - 20 cm	Fine black mud, isoloated shell fragments, gastropods
	20 - 25 cm	Sandy layer
	25 - 33 cm	Gravelly-sandy mud, many shell fragments
	33 - 45 cm	Muddy-sand on sand layer, No noticeable H_2S odour
Site 10 Muddy Creek	Surface	Very fine fluid mud with no seagrass
	0 - 18 cm	Olive grey mud
	18 - 58 cm	Uniform greyish black mud
	58 - 64 cm	Course grey sand with shell fragments, slight H_2S odour
Site 3 Wallis Creek	Surface	Algal covered seagrass, free floating algae
	0 - 9 cm	Olive black silt, shell fragments, slight H_2S odour
	9 - 28 cm	Brown-black mud, shell fragments, moderate H_2S odour
	28 - 50 cm	Brown-black mud, few shell fragments, strong H_2S odour
	50 - 60 cm	Black mud, little or no shell fragments, slight H_2S odour
Site 4 Central Basin	Surface	Olive-grey mud, burrows identified
	0 - 8 cm	Olive-grey mud, organic matter
	8 - 20 cm	Fine grey-black mud, small shell fragments
	20 - 50 cm	Fine grey-black mud, slight H_2S odour
	50 - 60 cm	Fine grey-black mud, moderate H_2S odour

3C. PORE WATERS

Down-core porewater profiles for Wallis Lake are shown in Figures 2 to 5.

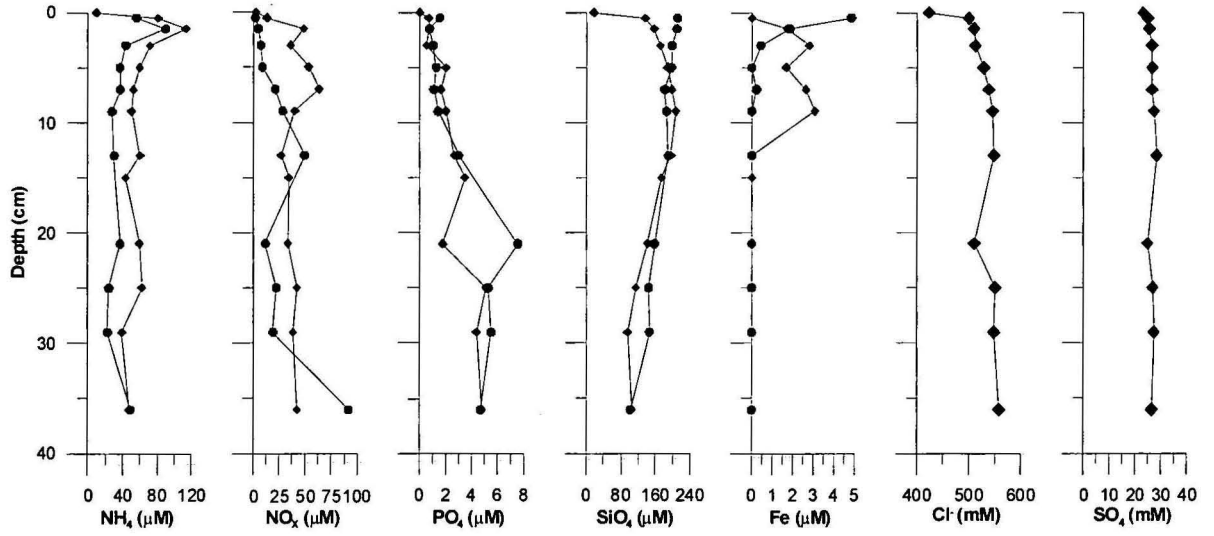

Figure 2 *Pore Water Profiles for Site 2 (Pipers Creek)*

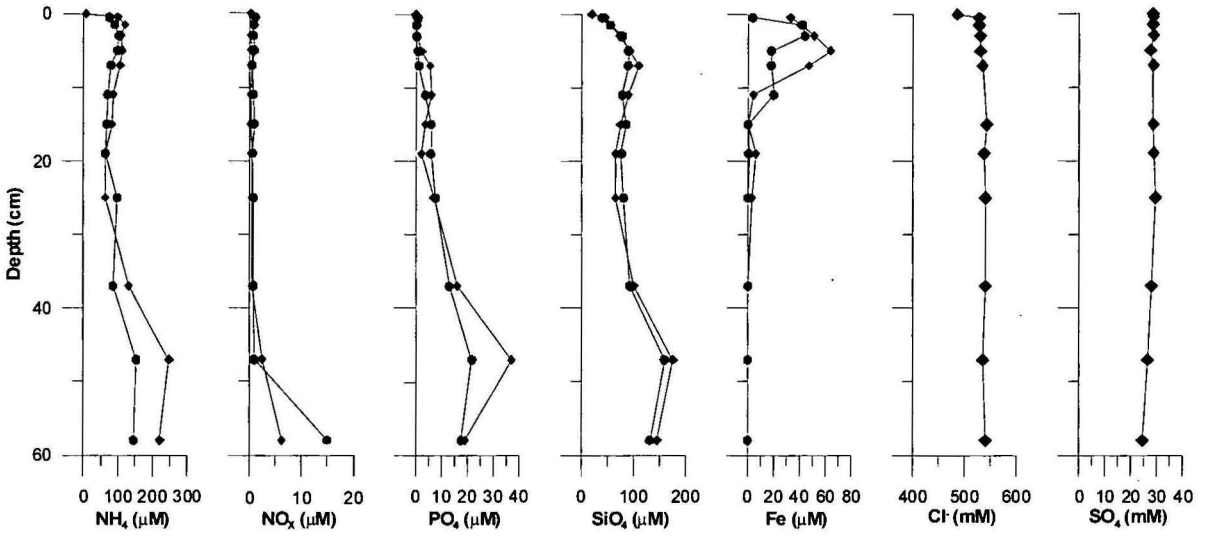

Figure 3 *Pore Water Profiles for Site 10 (Muddy Creek)*

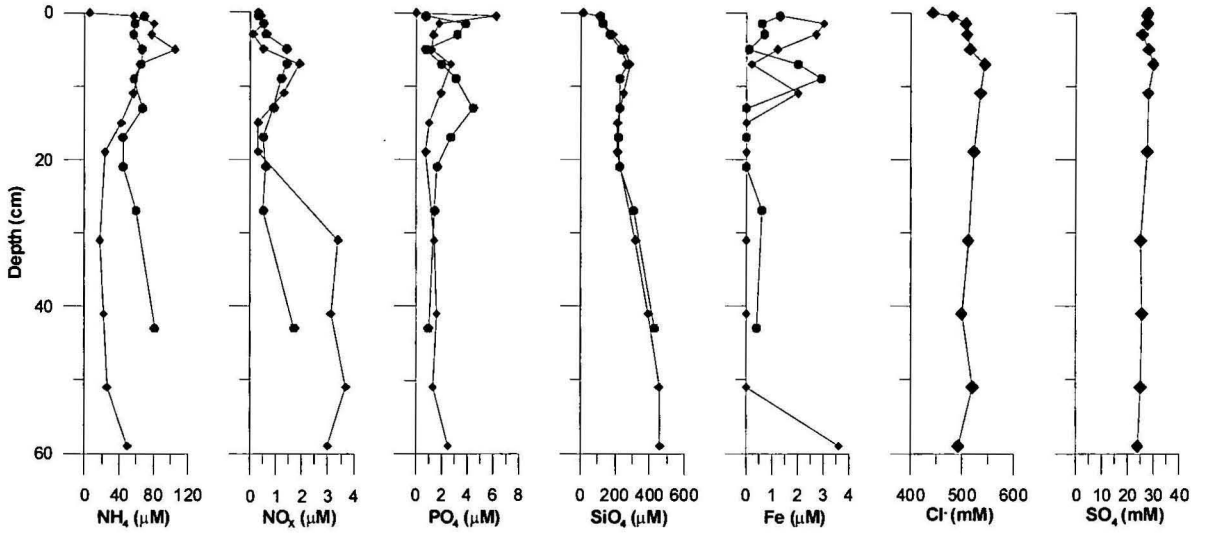

Figure 4 *Pore Water Profiles for Site 3 (Wallis Creek)*

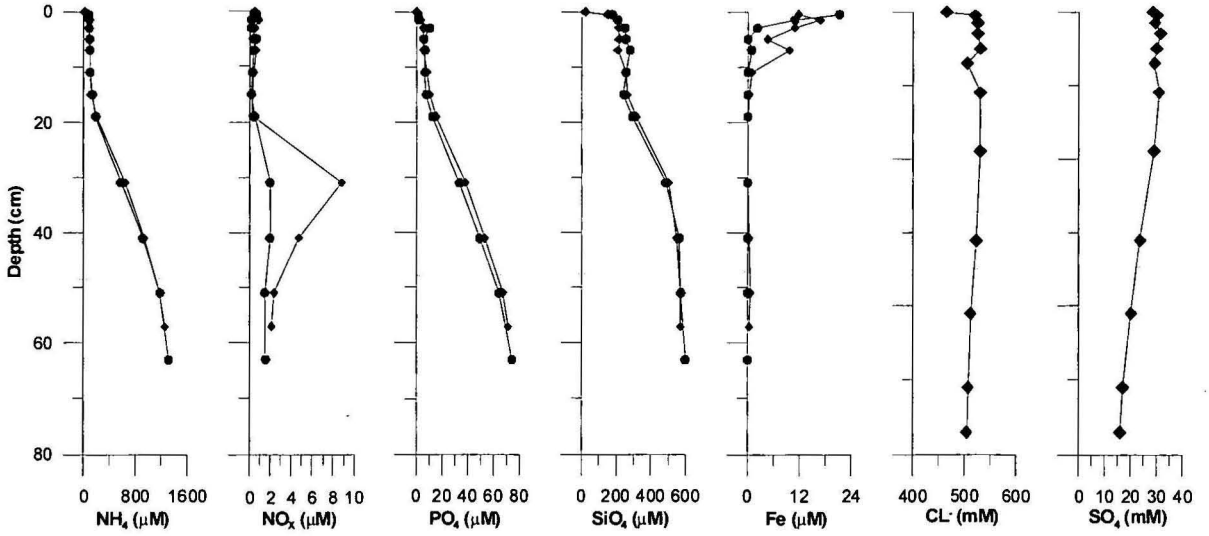

Figure 5 *Pore Water Profiles for Site 4 (Central Basin)*

Concentrations of the key nutrients (N, P and Si) all increased in the porewaters relative to bottom water concentrations. This indicated that nutrients were being released in the sediments as a result of organic carbon oxidation.

The significant quantities of NO_X found in the porewaters of the Pipers Creek site were unusual, although similar observations were made during the June, 2000 survey. The observation suggests nitrification and oxic sediments, but this observation is not consistent with the presence of reduced iron in the porewaters between depths of 0 - 15 cm; this observation suggested suboxic conditions. Bioirrigation and perhaps groundwater inputs could explain this apparent existence of oxic and anoxic metabolites.

The porewater N data from all other sites show low concentrations of NO_X indicating denitrification in the sediments, although some measurable quantities of NO_X were measured at the Wallis Creek site and at depth in the Central Basin site. The results at Wallis Creek can probably be explained by the presence of vascular plants and the ventilation of the sediments with oxygen to produce NO_X.

Reduced iron was measured in the porewaters from 0 - 10 cm depth in the sediments at all sites indicating of the microbial oxidation of organic carbon. This process results in oxides of iron being reduced and soluble reduced Fe^{2+} liberated to the porewaters.

The porewater profiles of silicate and other metabolites show inflexions in their depth distributions suggesting irrigation processes in the surface sediments. Both ammonia and phosphate do not reach high concentrations in the surface sediments and the observation suggests that organic carbon loadings to the sediments are not excessive.

3D. BENTHIC CHAMBERS AND BENTHIC NUTRIENT FLUXES

We determined the success of a benthic chamber deployment using 3 methods:

1. Examination of tracer loss from the chamber for leaks,
2. Examination of the dissolved oxygen concentrations in the chamber throughout the incubation, and
3. Comparing the chamber condition (temperature, salinity and pH) with the ambient conditions.

Based on these criteria, we were confident that 14 of the 16 benthic chamber deployments within Wallis Lake were successful. However, 3 chambers placed at Site 2 (Pipers Creek) showed dissolved oxygen "draw-down" before the chamber door was closed. This indicates that there was insufficient mixing of chamber and ambient water prior to the start of the incubation. For these chambers, the fluxes were calculated using the bottom water sample and the final sample draw. These fluxes may therefore be indicative of minimum rates. Two chambers (one at Site 3 and one at Site 4) were disturbed during the incubation and no samples were recovered from these chambers. The calculated benthic fluxes are summarised in Table 4 and the data for all chamber deployments is presented in Appendix 1.

Table 4 *Summary of Fluxes from Wallis Lake*

Site	Chamber Type	TCO_2 flux	Error	DO flux	Alk flux	Error	NH_4 flux	Error	NO_x flux	Error	DIN flux	Error	N_2 flux	SiO_4 flux	Error	PO_4 flux	Error
2B_1	Light	-34.97		12.26	-13.75	2.01	-0.85	0.28	-0.14	0.02	-0.99	0.28	2.4	-1.94	0.56	-0.03	0.08
2B_2	Dark	18.85		-38.13	4.04	1.74	1.36	0.26	-0.03	0.01	1.33	0.26	0.4	1.74	0.58	0.22	0.03
2B_3	Dark	31.20		-30.82	23.64	11.55	2.97	0.08	-0.05	0.00	2.92	0.08	-0.7	4.28	0.18	0.13	0.08
2B_4	Dark	36.26		-109	9.60	4.73	4.06	0.08	-0.03	0.04	4.03	0.09	-0.8	2.03	0.52	0.37	0.07
10A_5	Light	47.23	1.39	-88.90	-6.11	2.14	3.17	0.22	-0.02	0.04	3.16	0.22	5.1	6.68	0.53	0.24	0.06
10A_6	Dark	60.48	12.30	-57.88	6.98	13.56	4.21	1.73	0.13	0.08	4.34	1.73	12.8	7.86	2.31	0.20	0.04
10A_7	Dark	5.95	3.89	-49.98	5.97	3.80	0.20	2.55	-0.10	0.15	0.10	2.55	10.4	2.32	3.69	0.06	0.15
10A_8	Dark	23.98	2.99	-71.63	23.78	2.73	3.31	0.23	0.09	0.02	3.40	0.23	25.0	5.44	0.19	0.20	0.08
3B_3	Dark	109.84	33.78	-97.07	59.38	5.62	-0.07	0.03	0.00	0.01	-0.07	0.03	-9.3	6.89	0.58	0.18	0.10
3B_4	Dark	46.32	66.16	-62.68	-5.17	61.13	-0.12	0.14	0.03	0.01	-0.09	0.14	5.0	6.47	0.75	-0.11	0.03
3B_5	Light	No result															
3B_6	Dark	71.52	5.67	-81.95	21.79	1.69	0.00	0.08	0.01	0.00	0.01	0.08	9.5	6.35	0.66	0.05	0.00
4B_1	Light	28.05	6.10	-27.39	-2.72	5.16	2.45	0.41	0.07	0.07	2.52	0.41	3.0	8.06	0.91	-0.03	0.08
4B_2	Dark	No result															
4B_7	Dark	24.84	19.33	-58.91	-5.50	15.89	3.08	0.19	0.12	0.02	3.20	0.19	9.2	12.33	0.14	-0.05	0.04
4B_8	Dark	8.99	5.30	-37.69	10.18	7.07	1.05	0.17	0.12	0.03	1.17	0.18	33.0	6.88	0.08	0.00	0.02

Site 2 = Pipers Creek; Site 10 = Muddy Creek; Site 3 = Wallis Creek; Site 4 = Central Basin

4. DISCUSSION

4A. OXYGEN, CARBON & ALKALINITY FLUXES & CARBON OXIDATION BY OXYGEN AND SULPHATE

Carbon dioxide release and oxygen uptake rates in chambers reflect the rate of decomposition of organic matter in sediments (organic carbon + oxygen → CO_2). Dissolved oxygen flux versus TCO_2 flux is shown in Figure 6. The $1CO_2{:}1O_2$ line represents the mineralization of organic matter by ammonification, while the $1CO_2{:}1.3O_2$ line is the ratio expected from sediment undergoing complete nitrification.

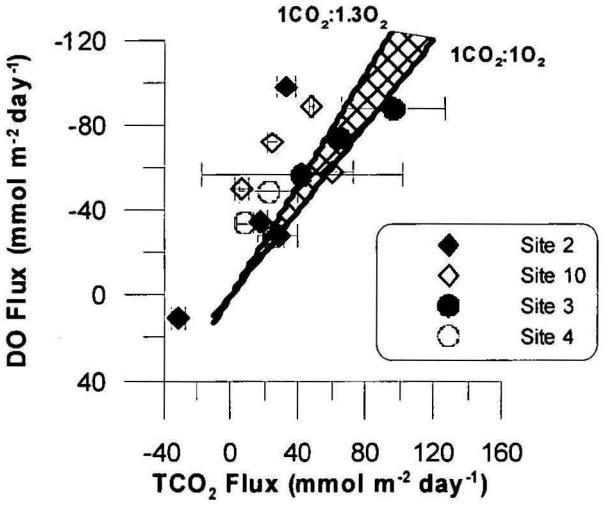

Figure 6 *TCO_2 Flux versus Dissolved Oxygen Flux in Wallis Lake*

Data falling within the envelope marked indicate that aerobic oxidation dominates the degradation of organic matter. Data lying to the left of the envelope indicate that there is an excess of oxygen consumed for the amount of carbon released; oxidation of sulphides (formed during sulphate reduction) in bottom waters or surficial sediments may explain this result. Most data from Site 3 (Wallis Creek) fall within the oxygen reduction envelope while at least some of the chamber data from the other sites suggest oxidation of sulphides produced during sulphate reduction. Observations of the alkalinity flux from chambers, which is produced during sulphate reduction, indicate that sulphate reduction is evident at most sites in the dark chambers. Considering the patchiness in the chamber data and the uncertainties in the alkalinity and TCO_2 fluxes, either way, these observations suggest that sulphate reduction is occurring to some extent at most sites, and sulphides produced are being oxidized.

The alkalinity and TCO_2 results from both Wallis Creek and the Central basin sites are lower than expected. It is not easy to explain these results but acid added to the system by acid sulphate soils in the catchment could be one explanation, although other measurements and observations would be required to examine this possibility. Also, the data from Pipers and Muddy Creeks did not show depleted alkalinity and TCO_2 results and it is not easy to explain why these sites would be buffered against acid release unless they isolated from a free exchange with the central basin lake waters.

A comparison of oxygen consumption and TCO_2 respiration rates for a selection of Australian estuaries is shown in Table 5. These data show that for Smiths Lake, Myall Lakes and Port Philip

Bay the mean oxygen and TCO_2 fluxes are about the same, indicating that oxygen reduction dominates organic carbon oxidation. Within Durras Lake and Wilson Inlet there is an excess of average TCO_2 over average oxygen consumption fluxes, indicating a component of the TCO_2 is contributed to by sulphate reduction. We note that in Wallis Lake during this summer survey that the mean oxygen flux exceeds the mean TCO_2 flux, suggesting net oxidation of sulphides produced during sulphate reduction.

Table 5 *Summary of O_2 and TCO_2 Fluxes from Selected Australian Waterways (1. this study, 2. Smith, et al., 2000, 3. Smith & Heggie, 2003, 4. Palmer, et al., 2000a, 5. Berelson, et al., 1998, 5. AGSO, 1998, 7. Palmer, et al., 2000b, 8. Fredericks, D.J. & Heggie, D.T., 2000.)*

Waterway	O_2 fluxes Range and mean (mmol m^{-2} day^{-1})	TCO_2 fluxes Range & mean (mmol m^{-2} day^{-1})	Season and month
Wallis Lake[1]	-30.8 to -109 mean = -65.4	5.95 to 109.8 mean = 39.5	Summer 2003 (Feb)
Wallis Lake[2]	-21.6 to –64.3 mean = -40.4	20.7 to 69.2 mean = 34.2	Winter 2000 (June)
Smiths Lake[3]	-9.0 to -45.54 mean = -21.2	8.17 to 43.23 mean = 21.9	Summer 2003 (Feb)
Myall Lakes[4]	-11.5 to –40.9 mean = -26.3	3.2 to 47.1 mean = 18.4	Winter 2000 (June)
Port Philip Bay[5]	-21.0 to –86.2 mean = -42.1	18.2 to 119.8 mean = 48.4	Summer 1995 (Jan)
Durras Lake[7]	-17 to –77 mean = -40	39 to 106 mean = 67	Summer 1999 (Dec)
Wilson Inlet[8]	-4.7 to –135.1 mean = -55.4	15 to 275 mean = 73.8	Spring 1998 (May)

4B TROPHIC STATE

We have classified the trophic state of each location using the classification system proposed by Nixon (1995). Nixon (1995) suggested that oligotrophic states had organic carbon supply rates of <23 mmol m^{-2} day^{-1}; mesotrophic states < 70 mmol m^{-2} day^{-1}; eutrophic states <115 mmol m^{-2} day^{-1} and hypertrophic states were characterised by organic carbon supply rates > 115 mmol m^{-2} day^{-1}. Site 4 (Central Basin) has estimated diatomaceous TCO_2 fluxes varying between approximately 43 and 77; average 57 mmol m^{-2} day^{-1} and is considered a mesotrophic site. Note that measured TCO_2 fluxes at site 4 varied between about 9 and 29 mmol m^{-2} day^{-1} but because of some difficulties with the time-course measurements we think these are low, and use the more reliable silicate fluxes to estimate diatomaceous organic carbon fluxes, and thus classify trophic state. Site 2 (Pipers Creek) has measured TCO_2 fluxes varying between 19 and 36; average TCO_2 flux 29 mmol m^{-2} day^{-1}, most of which is diatomaceous organic matter, and is oligotrophic-to-mesotrophic. Site 10 (Muddy Creek) has measured TCO_2 fluxes which vary between 6 and 60; average 34 mmol m^{-2} day^{-1}, most of which is also diatomaceous organic matter and is considered oligotrophic-to-mesotrophic (23 - 68 mmol m^{-2} day^{-1}). Site 3 (Wallis Creek) has measured TCO_2 fluxes which vary between 46 and 109; average 75 mmol m^{-2} day^{-1}, about half-to-most is probably diatomaceous and this site is considered mesotrophic-to-eutrophic (> 68 mmol m^{-2} day^{-1}).

4C. NITROGEN BIOGEOCHEMISTRY AND DENITRIFICATION

Nitrogen (N) is delivered to coastal lakes in dissolved and particulate forms. This nitrogen is either consumed by primary producers, including diatomaceous phytoplankton, various seagrasses and mangroves, or flushed out to sea. In most Australian barrier estuaries with poor flushing (Smiths Lake, for example) most nitrogen is trapped and recycled within the water body. Denitrification is a process by which the estuary can naturally cleanse itself of anthropogenic nitrogen. This process converts nitrate (NO_3^-) and nitrite (NO_2^-) formed in the sediments from the microbial breakdown of organic matter, into nitrogen gas (N_2), which is subsequently lost to the atmosphere.

The denitrification rate in the sediments can be estimated using two methods:

1. from the rate of organic carbon diagenesis, assuming a Redfield stoichiometric relationship of C:N:P = 106:16:1 (Froelich *et al.*, 1979), or
2. from the direct measurement of N_2 evolving from the sediments.

Figure 7 shows the flux of dissolved inorganic nitrogen (DIN) plotted against the TCO_2 flux. The expected nitrogen flux based on the TCO_2 flux rate, assuming a C:N of 106:16, is also shown. Most data fall close to the Redfield line except Site 3 (Wallis Creek) which showed little, or no, DIN flux. These results indicate that denitrification was occurring in the sediments of the Wallis Creek site to a much larger degree than any other site in Wallis Lake.

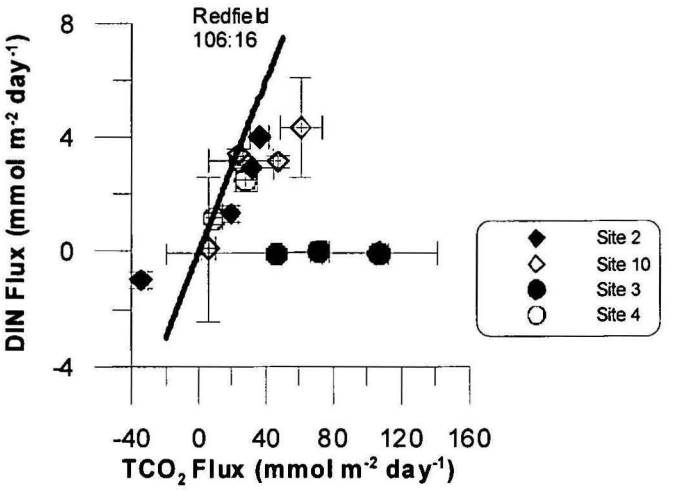

Figure 7 *TCO_2 Flux versus Dissolved Inorganic Nitrogen (DIN) Flux in Wallis Lake*

Observations of N_2 data, N_2 fluxes and comparisons of the TIN (total inorganic nitrogen) predicted from TCO_2 (according to the model of Redfield organic matter being the main source of organic carbon undergoing degradation in the sediments), with the measured TIN results indicates that the two could not always be reconciled. This comparison suggests that during this survey perhaps

some of the measured N_2 flux data are unreliable for some unknown reason (or the Redfield model of organic matter degradation in the sediments is not completely applicable), and we have generally calculated the denitrification efficiency based upon the measured DIN data and the result shown in Figure 7. Denitrification efficiency (expressed as a percentage) is the proportion of total nitrogen released within the sediments as N_2 gas. It is calculated as:

$$DenitrificationEffieiency = \frac{(DIN_{Predicted} - DIN_{Measured})}{DIN_{Predicted}} * 100$$

where $DIN_{Predicted}$ is the calculated flux of DIN from the measured TCO_2 flux assuming Redfield stoichiometry.

There is one exception to the above, where for Site 4 (Central basin) we think that the measured TCO_2 fluxes are low, perhaps by a factor of about three, and we have calculated the denitrification efficiency based on the TCO_2 estimated from the measured silicate fluxes which are very reliable.

Figure 8 shows the denitrification efficiency plotted against TCO_2 flux for the Wallis Lake sites. Site 4 (Central Basin) was found to have a denitrification efficiency of about 23% at the measured (probably) low carbon flux of 21 mmol m^{-2} day^{-1}. As noted above we think this measured carbon flux is low and we have used the measured silicate flux to estimate an average diatomaceous organic carbon flux to the sediments at Site 4 of 57 mmol m^{-2} day^{-1}. Using these data, and the measured DIN data, we calculated the average denitrification efficiency at site 4 of approximately 73 %. We also note that the N_2 fluxes were positive, confirming the presence of active denitrification. Sites 2 (Pipers Creek) and 10 (Muddy Creek) have similar carbon loadings (average TCO_2 fluxes of 29 and 34 mmol m^{-2} day^{-1} respectively) and both had comparatively low average denitrification efficiencies of 38% and 50 % respectively. The data from Pipers Creek are also different from the winter data with decreased denitrification efficiencies in the summer survey. Site 3 (Wallis Creek), despite having comparatively high carbon loadings (of about 75 mmol m^{-2} day^{-1}), clearly shows that this site maintains high denitrification efficiencies and this is indicative of a 'healthy' capability of the biota to accommodate comparably high N loadings. In this case little of the N being assimilated is recycled back into the overlying waters to be available for phototrophic growth.

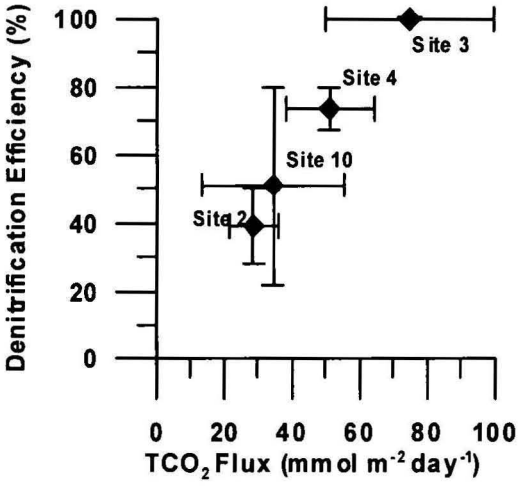

Figure 8 *TCO_2 Flux versus Denitrification Efficiency in Wallis Lake*

4D. PHOSPHORUS DYNAMICS

Phosphate fluxes from the sediments of Pipers Creek and Muddy Creek (Site 2 & 10) were close to those predicted from the degradation of a phytoplankton source of organic matter (Redfield C:P 106:1). The central basin (Site 4) had little or no PO_4 flux and Wallis Creek (Site 3) had less than predicted from a Redfield-like source of organic matter. This indicates that PO_4 is being trapped in the sediments. PO_4 adsorption to Fe-oxyhydroxide is controlled, in part, by redox conditions at the

sediment-water interface. P release from the sediments can occur when either the P adsorption properties of the sediment are exhausted or when, under anoxic conditions, Fe-oxyhydroxides at the sediment-water interface dissolve. Also, the formation of FeS displaces P from iron phosphate in a simple double decomposition reaction (Heggie, *et al.*, 1990).

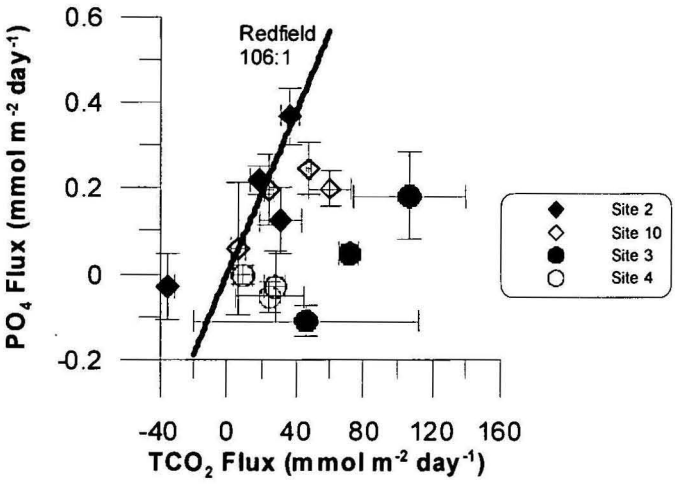

Figure 9 *TCO_2 Flux versus PO_4 Flux in Wallis Lake*

4E. SILICATE DYNAMICS

The silicate fluxes in Wallis Lake (Figure 10) show that most data, particularly from the Pipers and Muddy Creek sites fall close to the line representing a diatomaceous source of organic matter (Brzezinski, 1985). Two of the three chambers at Site 3 (Wallis Creek) showed less SiO_4 than predicted if diatomaceous organic matter predominated; this probably indicates a mixed source of organic matter. Rooted benthic plants were observed on the sediments at this site. Site 4 (Central Basin) data lie above the line, indicating that there is generally more silicate than can be attributed to diatomaceous organic matter alone. We found a similar result in Moreton Bay and ascribed the silicate enrichment to smectite dissolution in the sediments during the warm summer months. This is a possibility in Wallis Lake although we would expect an enrichment of silicate at all sites and not only the central basin site, if smectite dissolution were occurring. To investigate this possibility further we examined the silicate/chloride ratio in the pore waters between the summer (this survey) and winter months (June 2000) and found no significant change between these two observation periods; pore water silicate/chloride ratios would be higher during summer if smectite dissolution was occurring in the sediments. While we cannot unequivocally rule-out the possibility of some smectite dissolution during the summer months we cannot find any evidence for it in the pore water data during summer over winter periods. These considerations suggest that the TCO_2 fluxes at the central basin site measured from alkalinity and pH are low.

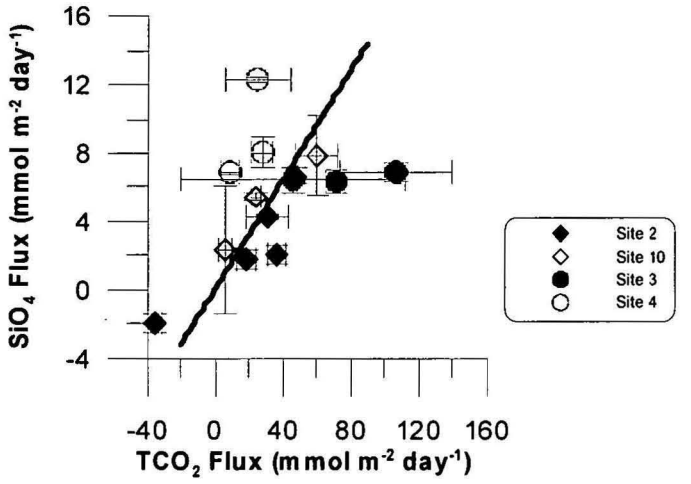

Figure 10 *TCO_2 Flux versus SiO_4 Flux in Wallis Lake (line represents C:Si of 106:17 as per Brzezinski, 1985)*

We note that the TCO_2 fluxes were not easily determined from the time course experiments and these have large uncertainties. The individual chamber observations of silicate fluxes are well defined with small errors. We have used these data to calculate a diatomaceous carbon flux to the sediments, and these fluxes are greater than measured TCO_2 fluxes. These silicate-predicted TCO_2 fluxes are also comparable to the TCO_2 predicted from measured oxygen consumption rates. Hence, at this time we cannot reconcile all flux observations according to a simple model of organic matter degradation and are reluctant to argue for smectite dissolution in the sediments. We suspect that measured TCO_2 fluxes at this site underestimate true TCO_2 fluxes, perhaps as much as a factor of three.

5. SURVEY COMPARISON

Table 6 shows the average fluxes in Wallis Lake in both June 2000 and February 2003.

Table 6 *Average Fluxes (mmol m^{-2} day^{-1}) for Wallis Lake (2000 and 2003)*

Site	Date	TCO_2	O_2	NH_4	NO_X	PO_4	SiO_4	Denit. Efficiency
Pipers Creek	Feb 2003	28.7 ± 7.3	-59.3 ± 35	2.8 ± 1.1	-0.04 ± 0.0	0.24 ± 0.10	2.7 ± 1.1	35 %
	Jun 2000	28.0 ± 3.1	-34.2 ± 0.4	0.3 ± 0.2	0.01 ± 0.02	0.01 ± 0.01	1.1 ± 0.2	92 %
Muddy Creek	Feb 2003	34.4 ± 21	60.4 ± 13	2.5 ± 1.3	0.03 ± 0.01	0.16 ± 0.01	5.02 ± 1.9	51 %
	No comparison							
Wallis Creek	Feb 2003	74.9 ± 25	-80.6 ± 14	-0.1 ± 0.1	0.01 ± 0.01	0.04 ± 0.12	6.6 ± 0.2	100%
	Jun 2000	48.0 ± 0.3	-38.1 ± 4.9	0.03 ± 0.04	-0.01 ± 0.01	0.00 ± 0.00	1.0 ± 0.4	100 %
Central Basin	Feb 2003	^20.6 ±8.3	-48.3 ± 11	2.2 ± 0.9	0.10 ± 0.02	-0.03 ± 0.02	9.1 ± 2.3	^23.3 %
		*57		2.2	0.1		9.1	73%
	Jun 2000	21.6 ± 0.9	-24.1 ± 2.5	0.09 ± 0.09	0.00 ± 0.02	-0.01 ± 0.02	2.2 ± 0.2	98 %

* The TCO_2 flux attributed to diatomaceous organic matter was estimated from the average silicate flux multiplied by 6.2.

^ The measured TCO_2 flux is thought to be low, and not representative of the actual flux as noted in the text, resulting in a low denitrification efficiency.

Results for Pipers Creek show that there are comparable carbon loads to the sediments between the summer and winter observations, although we think that the recent observations are probably somewhat low estimates. Nevertheless this is a surprising result given the ten degree increase in temperature between summer and winter. This may have been because of the low nutrient inputs during the drought years. Phosphate and ammonia fluxes from the sediments are both higher than those measured in winter. The higher ammonia fluxes result in a denitrification efficiency of about 35 % (Figure 11) and this is a significant decrease from the winter efficiency of 92 %.

The data from Wallis Creek show that there has been more than a twofold increase in carbon loading to the sediments during these summer months, although there has been no significant increase in ammonia or phosphate fluxes. The insignificant increase in ammonia fluxes indicate that denitrification is still very efficient at this site despite the increase in carbon loading.

The summertime results from the central basin are not easy to compare to the winter data because of the uncertaintity associated with the measured TCO_2 fluxes, but TCO_2 fluxes have probably increased (more than twofold) with a decrease in denitrification efficiency although we think this is still comparatively high at about 73 %.

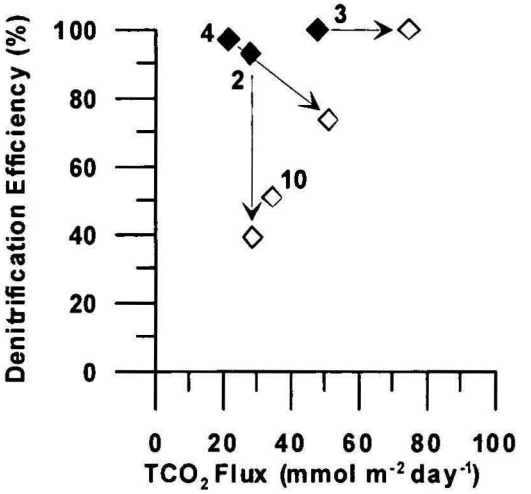

Figure 11 *Changes in TCO_2 flux versus Denitrification Efficiency in Wallis Lake between the 2000 and 2003 Survey (Closed diamonds are the winter 2000 survey, open diamonds are the summer 2003 survey).*

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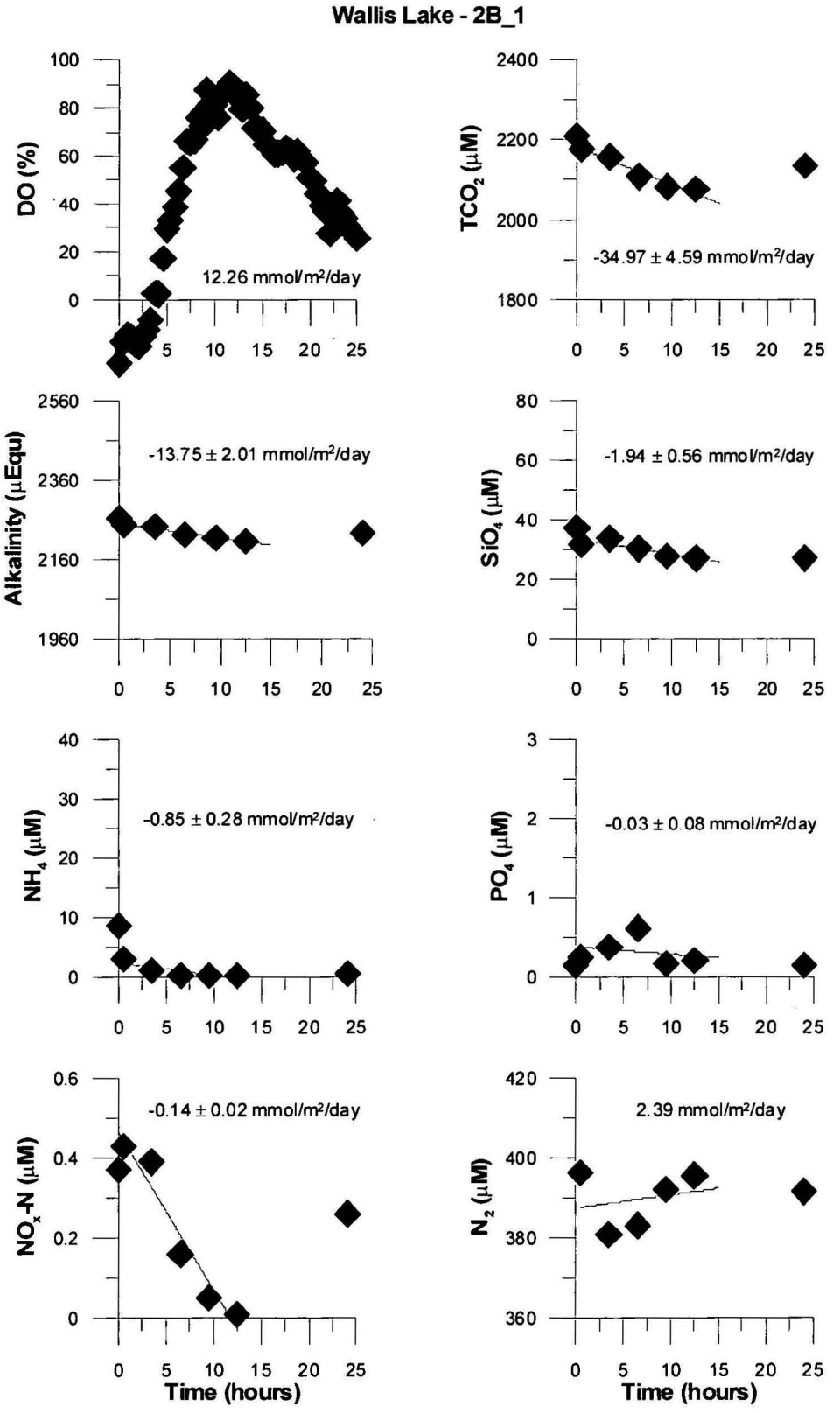
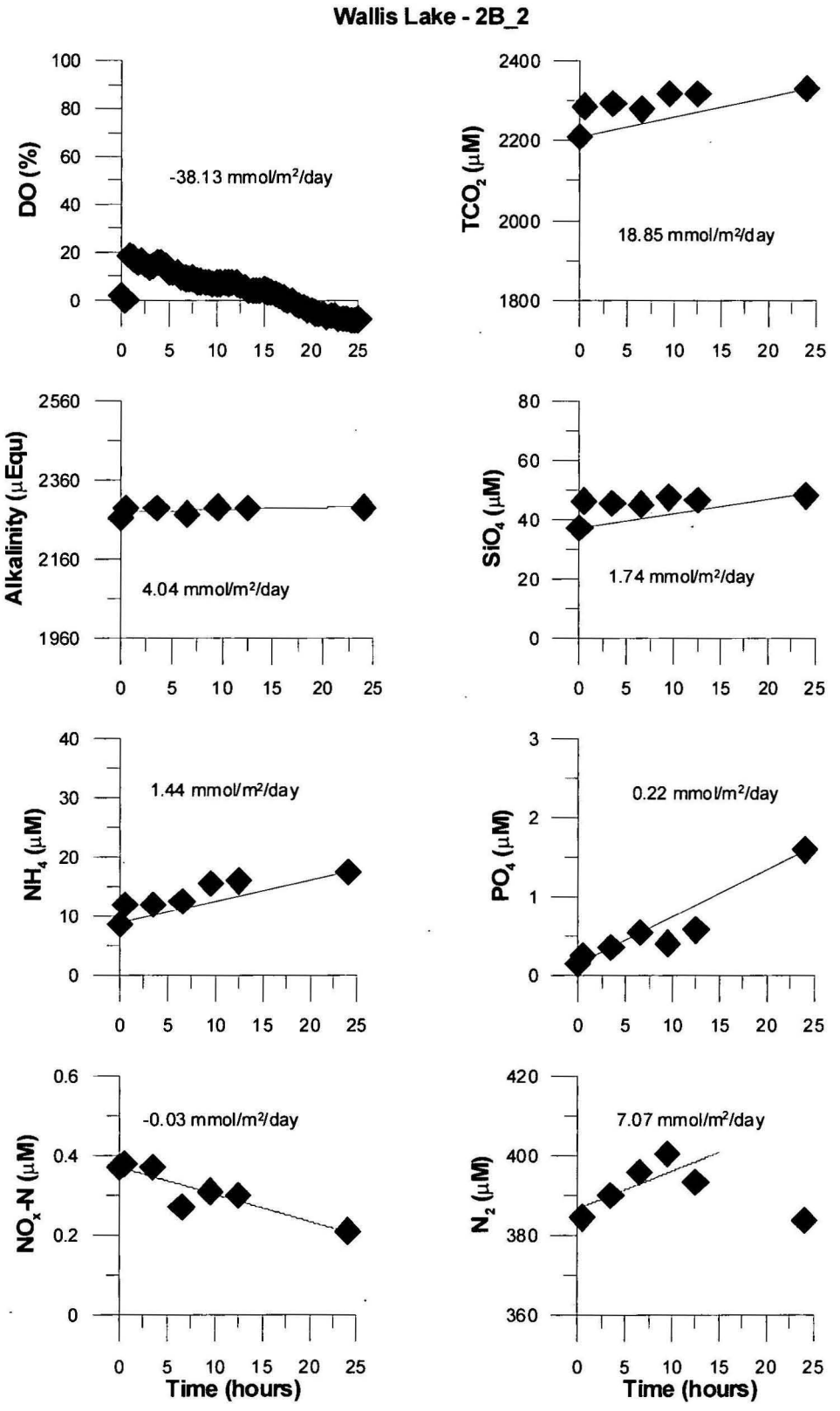
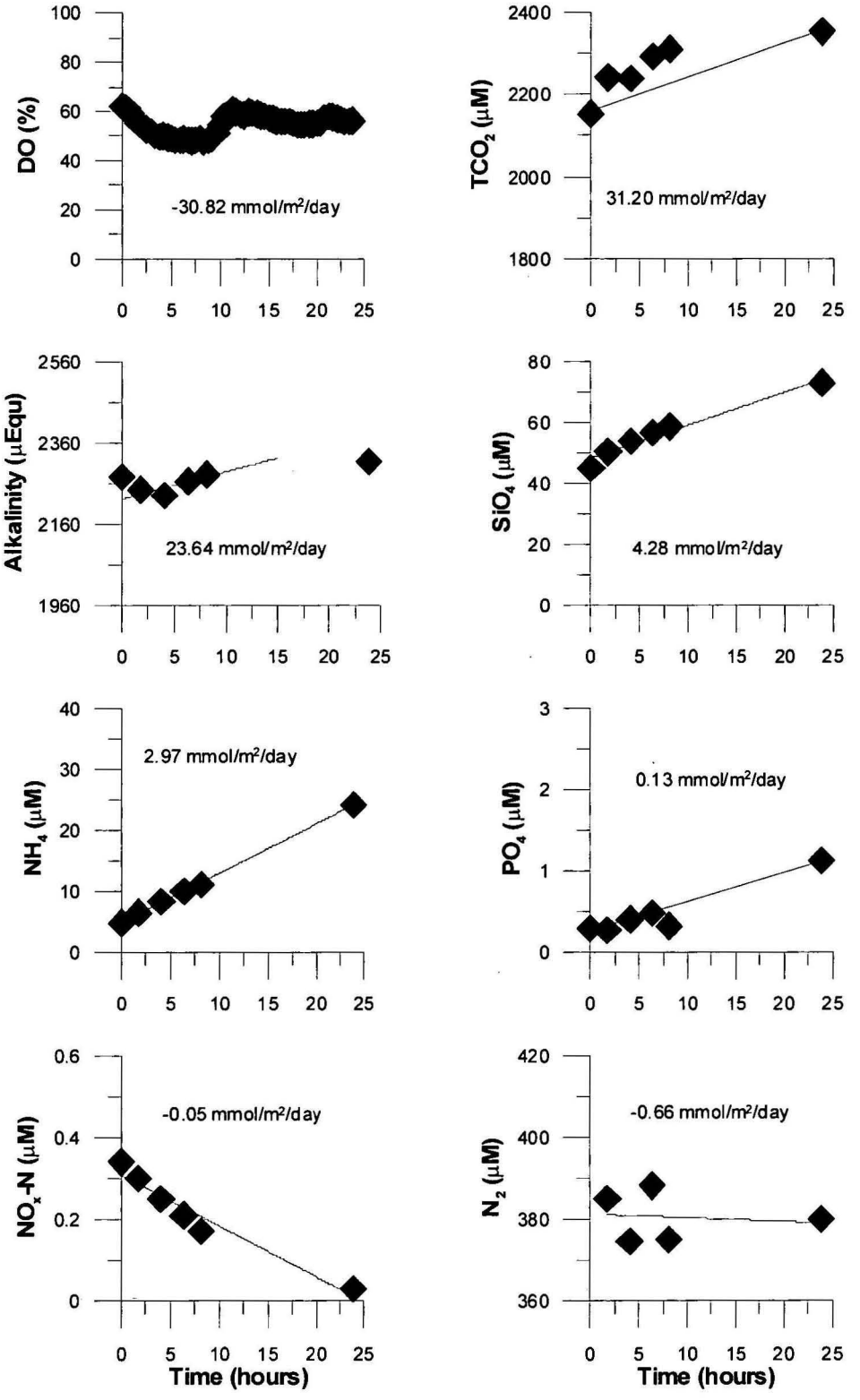
APPENDIX

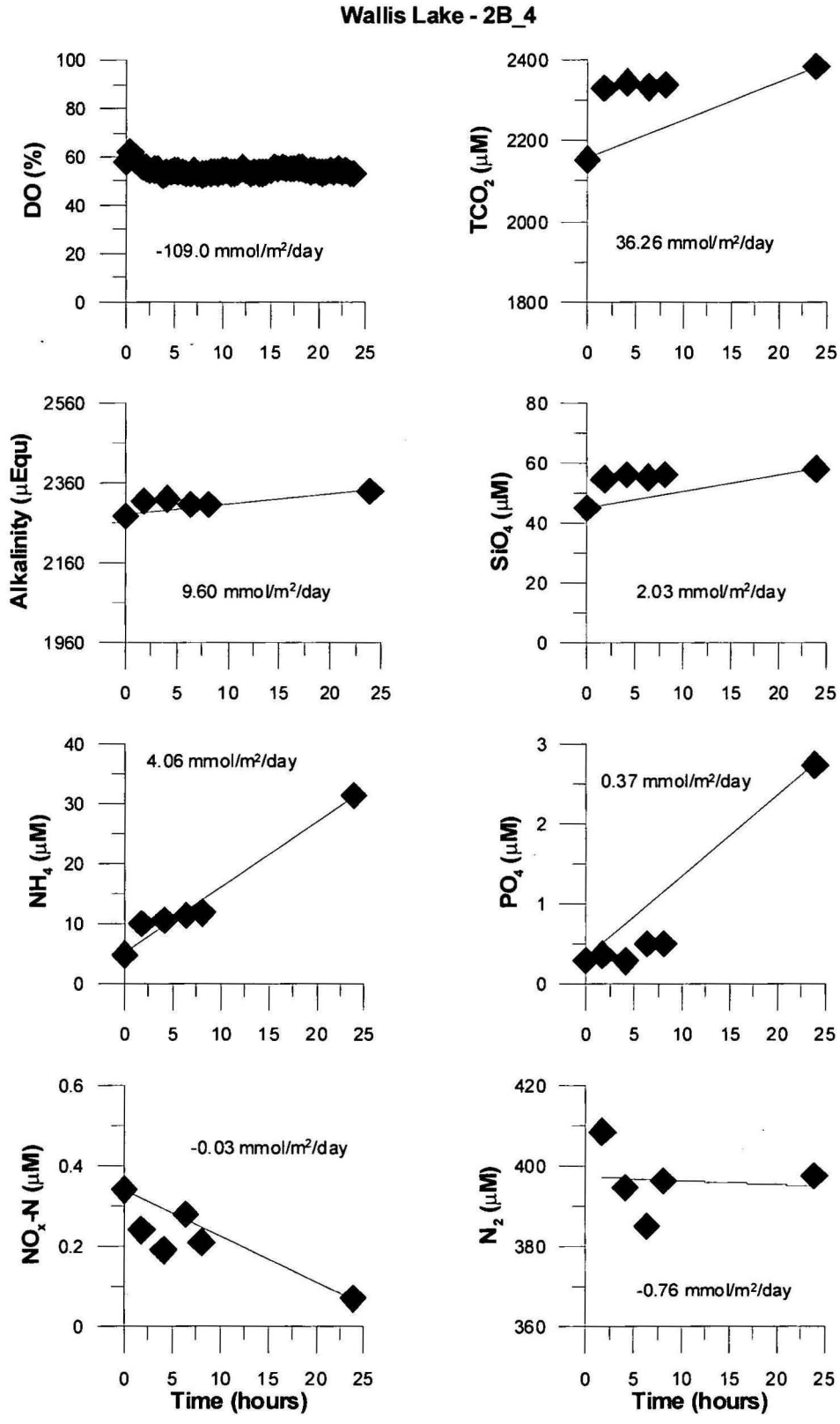
1. CHAMBER METABOLITE CONCENTRATIONS

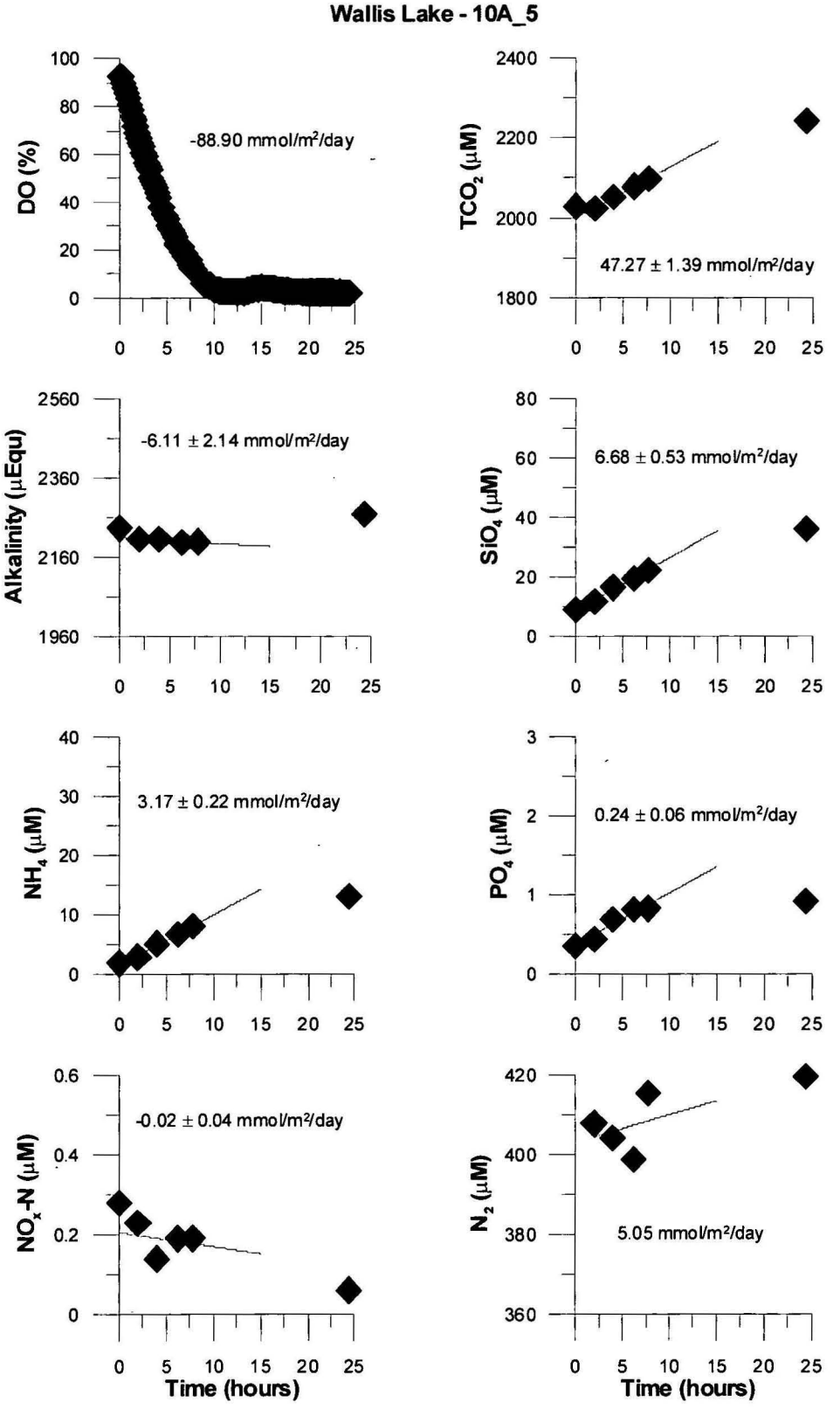

Wallis Lake - 2B_1
DO (%)
12.26 mmol/m²/day
TCO₂ (µM)
-34.97 ± 4.59 mmol/m²/day
Alkalinity (µEqu)
-13.75 ± 2.01 mmol/m²/day
SiO₄ (µM)
-1.94 ± 0.56 mmol/m²/day
NH₄ (µM)
-0.85 ± 0.28 mmol/m²/day
PO₄ (µM)
-0.03 ± 0.08 mmol/m²/day
NOx-N (µM)
-0.14 ± 0.02 mmol/m²/day
N₂ (µM)
2.39 mmol/m²/day
Time (hours)
Time (hours)

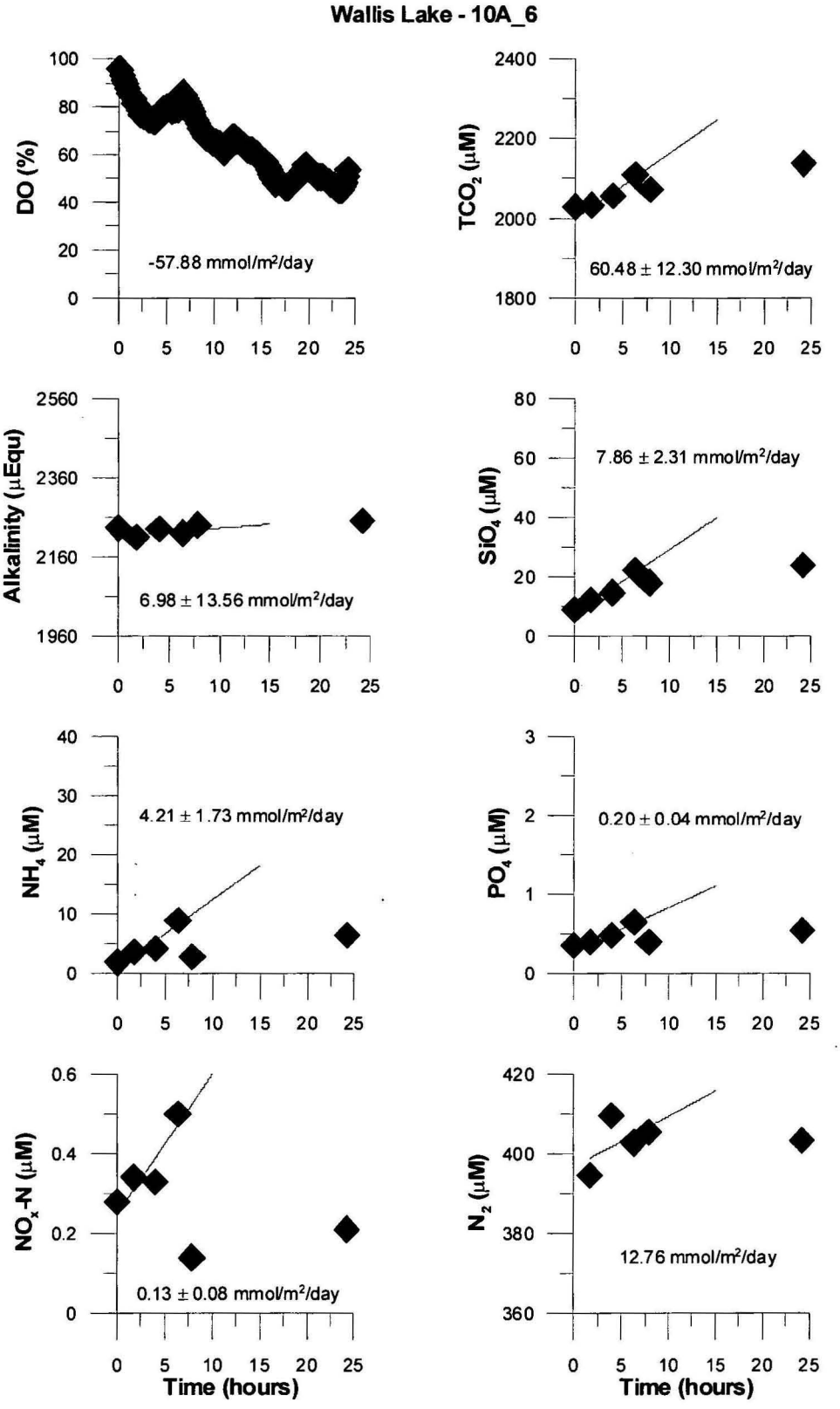

Wallis Lake - 2B_2
DO (%)
-38.13 mmol/m²/day
TCO2 (µM)
18.85 mmol/m²/day
Alkalinity (µEqu)
4.04 mmol/m²/day
SiO4 (µM)
1.74 mmol/m²/day
NH4 (µM)
1.44 mmol/m²/day
PO4 (µM)
0.22 mmol/m²/day
NOx-N (µM)
-0.03 mmol/m²/day
N2 (µM)
7.07 mmol/m²/day
Time (hours)
Time (hours)

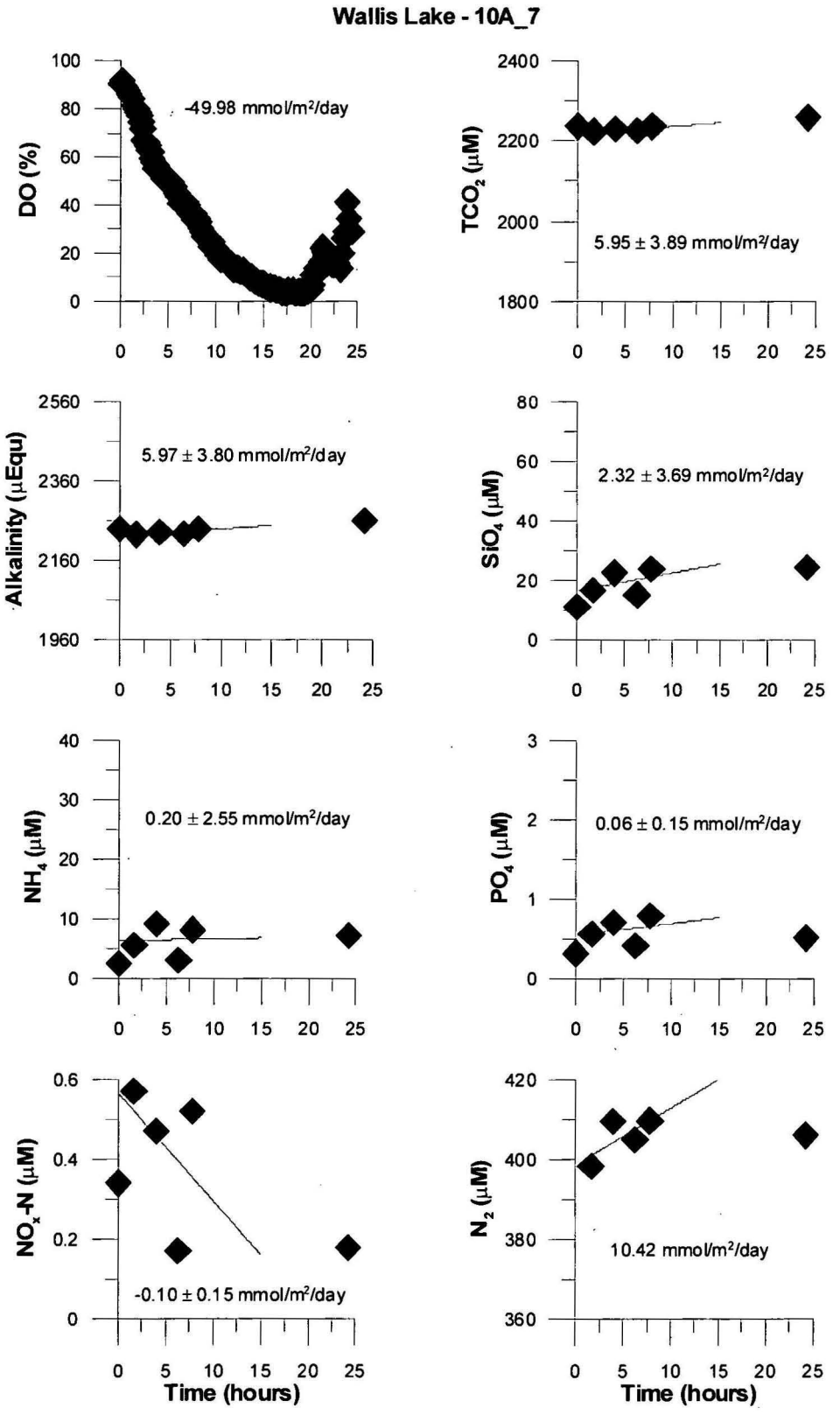
Wallis Lake - 2B_3

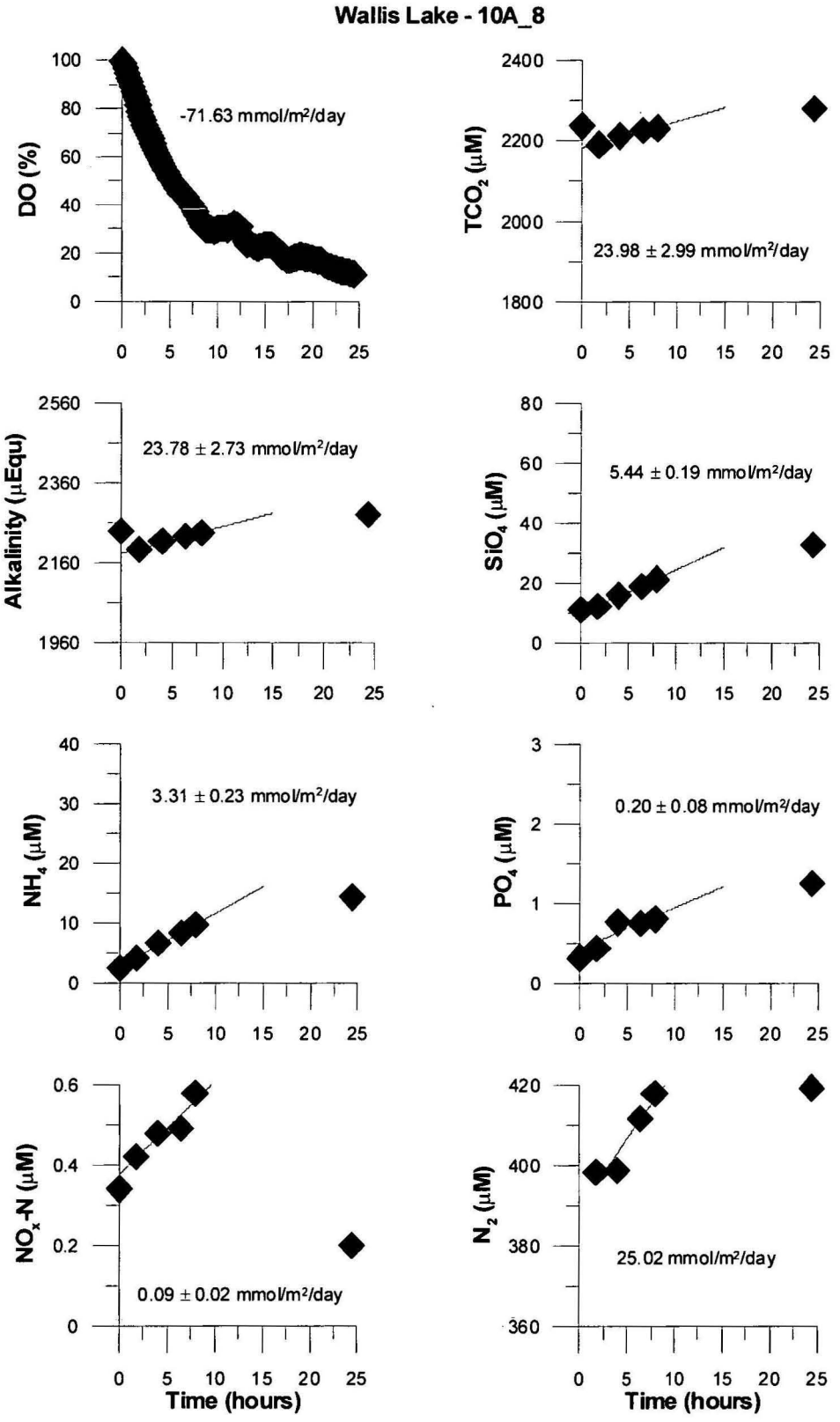


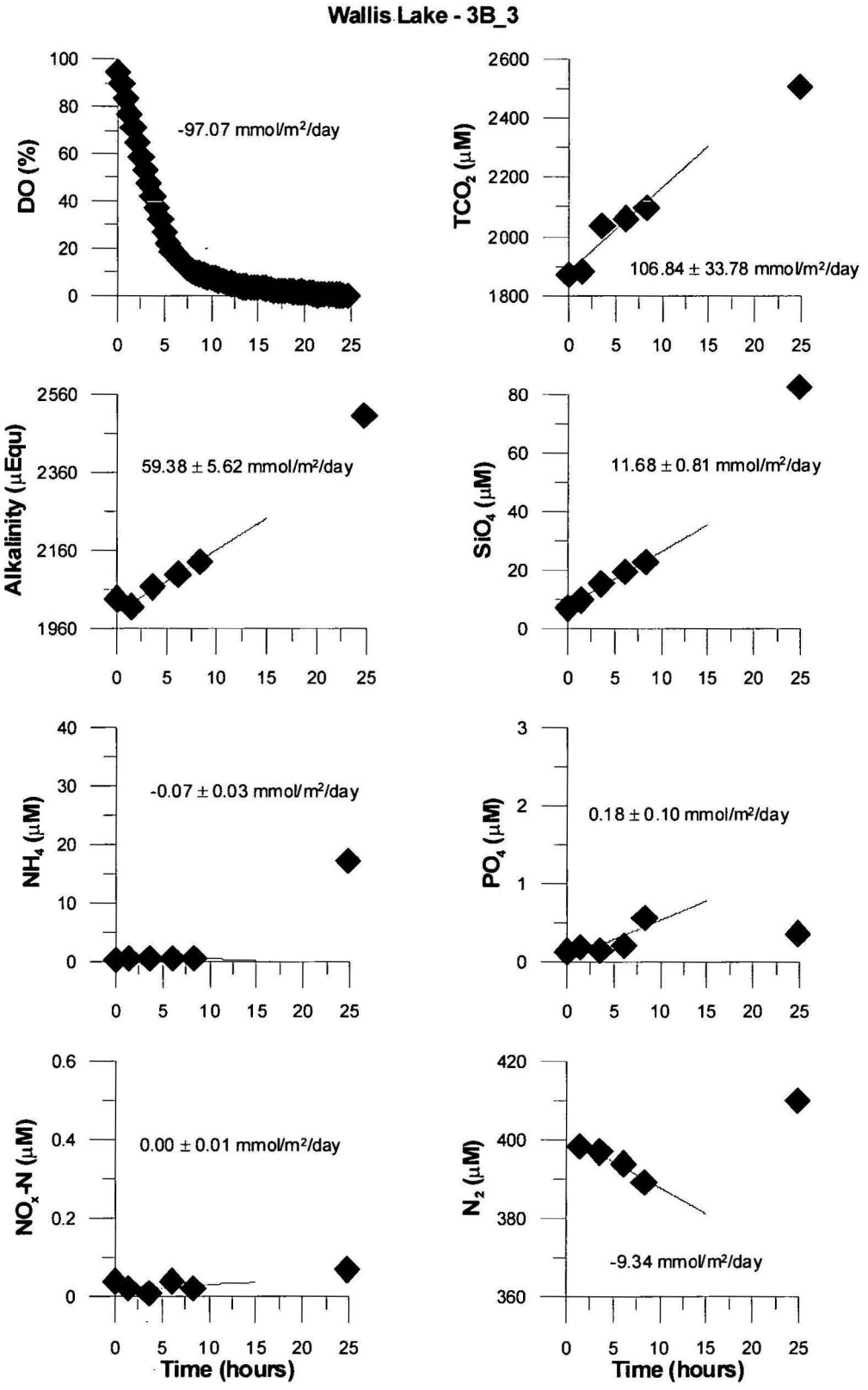

Wallis Lake - 2B_4
DO (%)
-109.0 mmol/m²/day
TCO₂ (µM)
36.26 mmol/m²/day
Alkalinity (µEqu)
9.60 mmol/m²/day
SiO₄ (µM)
2.03 mmol/m²/day
NH₄ (µM)
4.06 mmol/m²/day
PO₄ (µM)
0.37 mmol/m²/day
NOx-N (µM)
-0.03 mmol/m²/day
N₂ (µM)
-0.76 mmol/m²/day
Time (hours)
Time (hours)


Wallis Lake - 10A_5
DO (%)
-88.90 mmol/m²/day
TCO2 (µM)
47.27 ± 1.39 mmol/m²/day
Alkalinity (µEqu)
-6.11 ± 2.14 mmol/m²/day
SiO4 (µM)
6.68 ± 0.53 mmol/m²/day
NH4 (µM)
3.17 ± 0.22 mmol/m²/day
PO4 (µM)
0.24 ± 0.06 mmol/m²/day
NOx-N (µM)
-0.02 ± 0.04 mmol/m²/day
N2 (µM)
5.05 mmol/m²/day
Time (hours)
Time (hours)

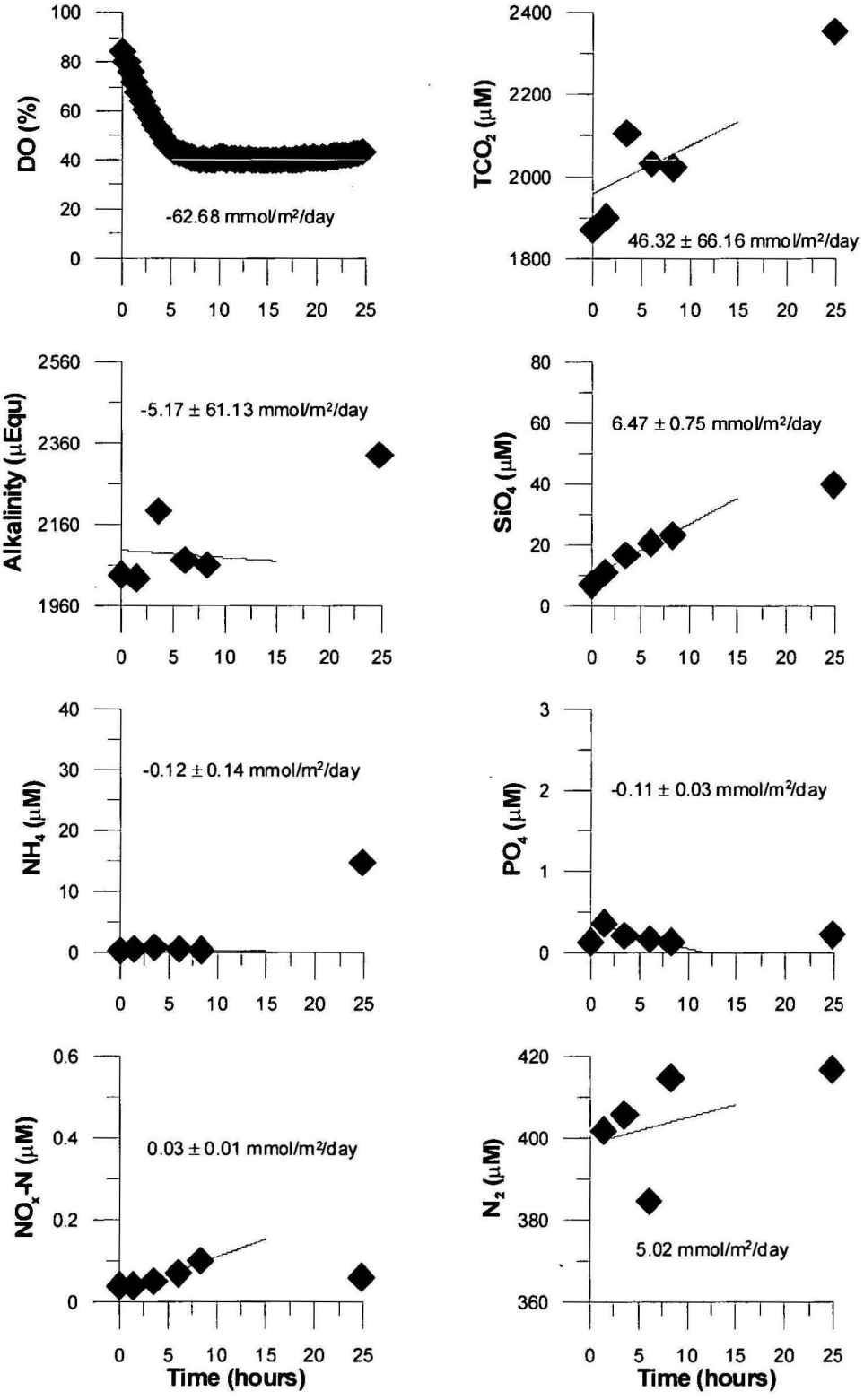

Wallis Lake - 10A_6
DO (%)
-57.88 mmol/m²/day
TCO₂ (µM)
60.48 ± 12.30 mmol/m²/day
Alkalinity (µEqu)
6.98 ± 13.56 mmol/m²/day
SiO₄ (µM)
7.86 ± 2.31 mmol/m²/day
NH₄ (µM)
4.21 ± 1.73 mmol/m²/day
PO₄ (µM)
0.20 ± 0.04 mmol/m²/day
NOx-N (µM)
0.13 ± 0.08 mmol/m²/day
N₂ (µM)
12.76 mmol/m²/day
Time (hours)
Time (hours)


Wallis Lake - 10A_7
DO (%)
-49.98 mmol/m²/day
TCO₂ (µM)
5.95 ± 3.89 mmol/m²/day
Alkalinity (µEqu)
5.97 ± 3.80 mmol/m²/day
SiO₄ (µM)
2.32 ± 3.69 mmol/m²/day
NH₄ (µM)
0.20 ± 2.55 mmol/m²/day
PO₄ (µM)
0.06 ± 0.15 mmol/m²/day
NOx-N (µM)
-0.10 ± 0.15 mmol/m²/day
N₂ (µM)
10.42 mmol/m²/day
Time (hours)
Time (hours)

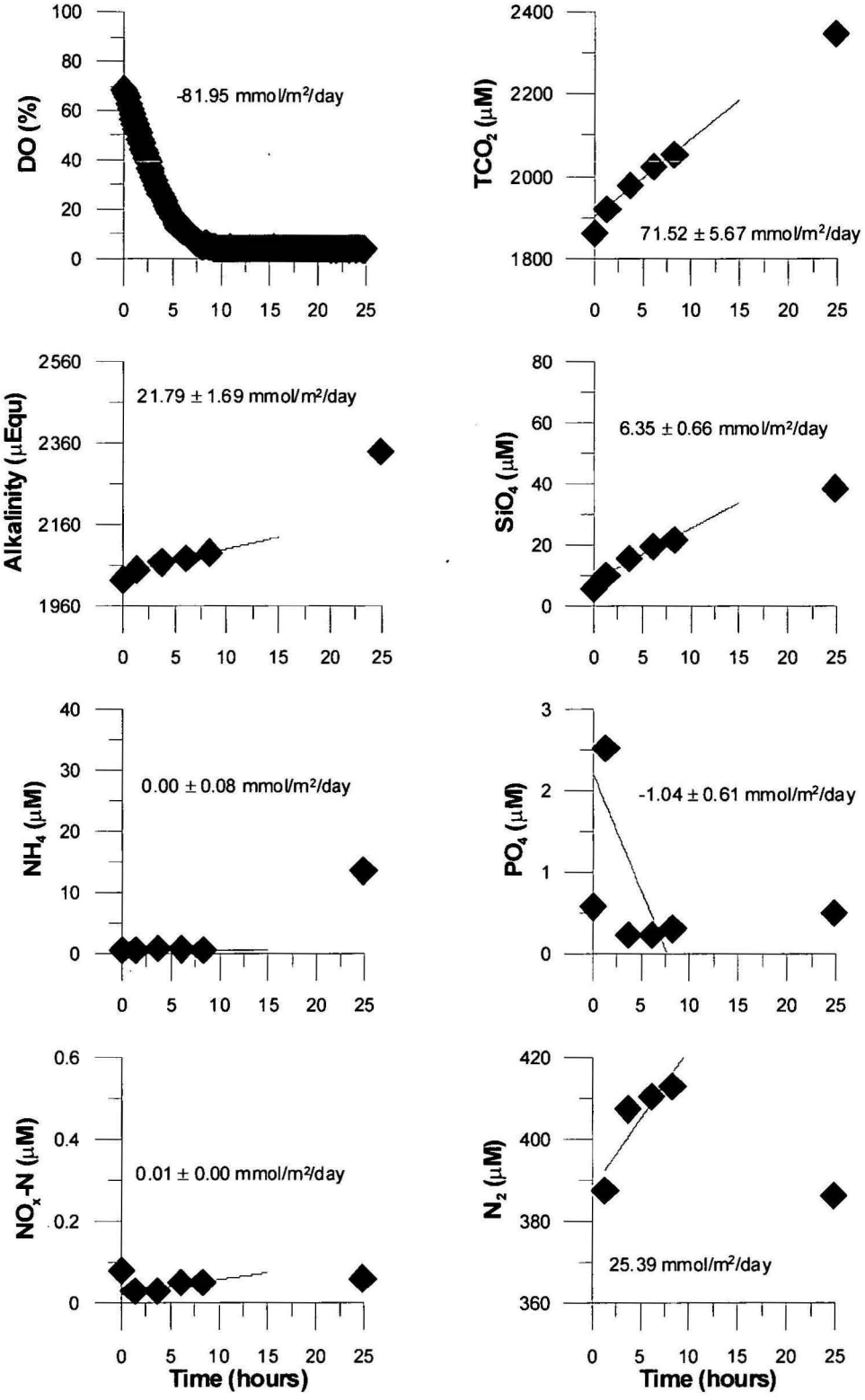

Wallis Lake - 10A_8
DO (%)
-71.63 mmol/m²/day
TCO₂ (µM)
23.98 ± 2.99 mmol/m²/day
Alkalinity (µEqu)
23.78 ± 2.73 mmol/m²/day
SiO₄ (µM)
5.44 ± 0.19 mmol/m²/day
NH₄ (µM)
3.31 ± 0.23 mmol/m²/day
PO₄ (µM)
0.20 ± 0.08 mmol/m²/day
NOx-N (µM)
0.09 ± 0.02 mmol/m²/day
N₂ (µM)
25.02 mmol/m²/day
Time (hours)
Time (hours)

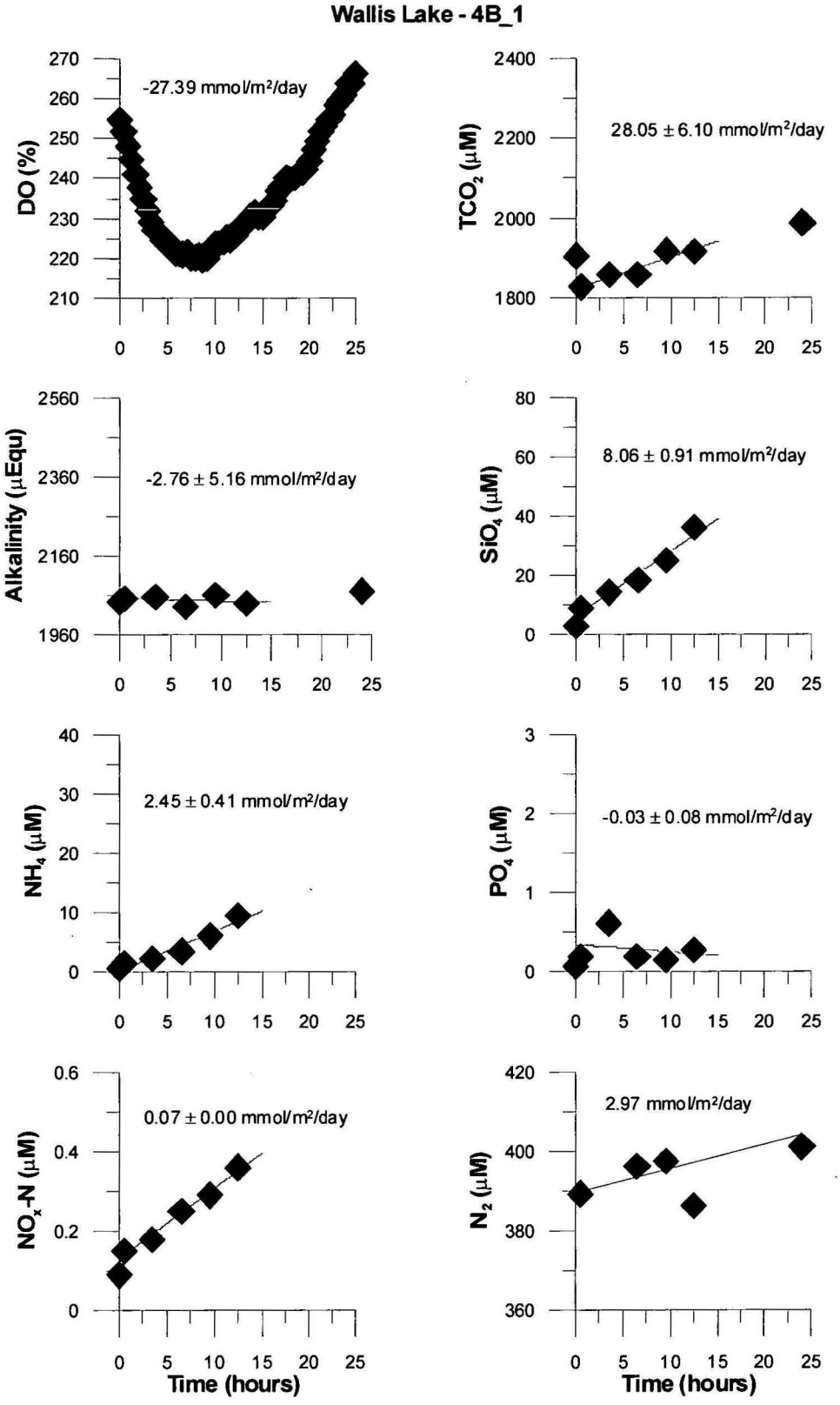

Wallis Lake - 3B_3
DO (%)
-97.07 mmol/m²/day
TCO2 (µM)
106.84 ± 33.78 mmol/m²/day
Alkalinity (µEqu)
59.38 ± 5.62 mmol/m²/day
SiO4 (µM)
11.68 ± 0.81 mmol/m²/day
NH4 (µM)
-0.07 ± 0.03 mmol/m²/day
PO4 (µM)
0.18 ± 0.10 mmol/m²/day
NOx-N (µM)
0.00 ± 0.01 mmol/m²/day
N2 (µM)
-9.34 mmol/m²/day
Time (hours)
Time (hours)

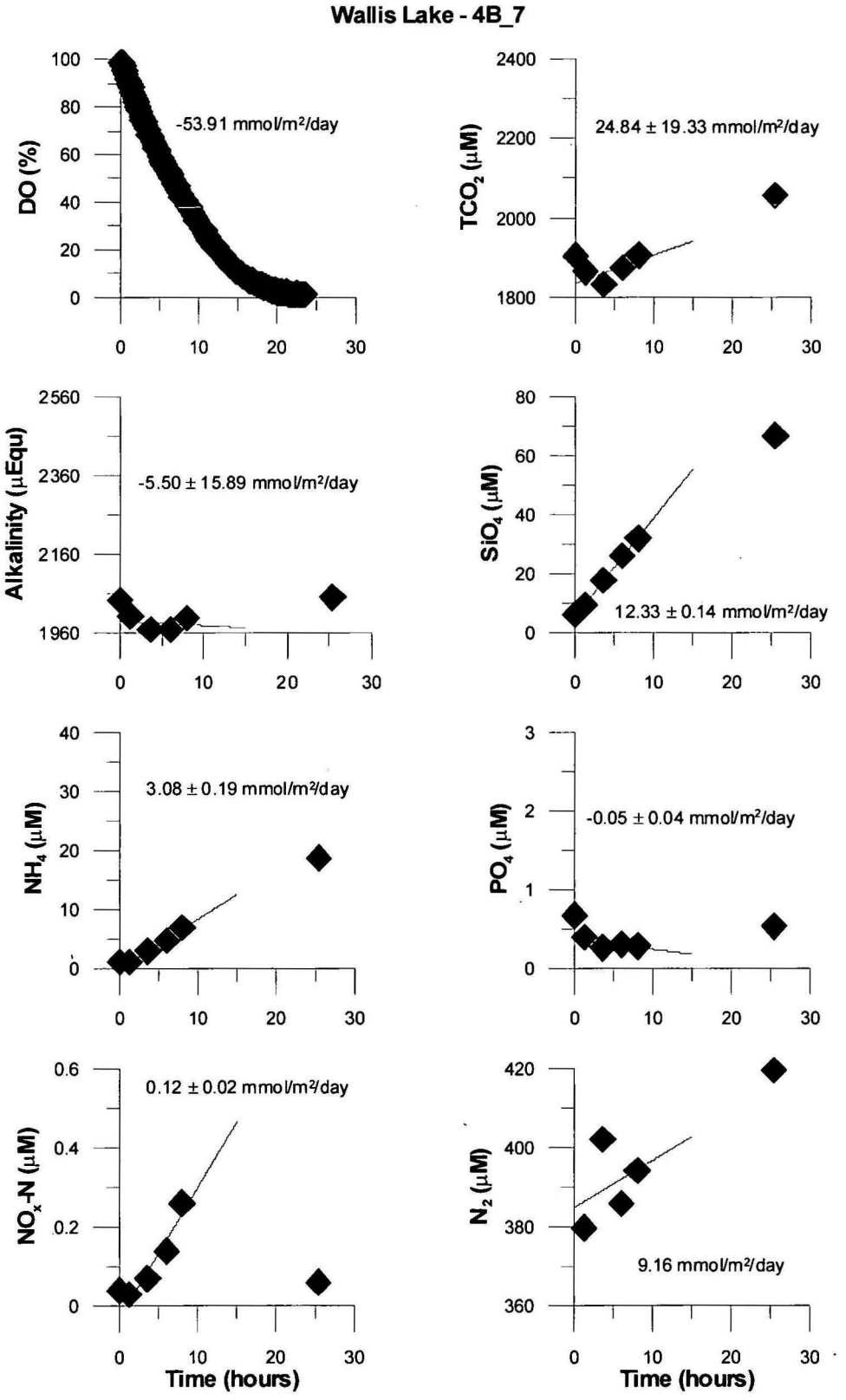
Wallis Lake - 3B_4

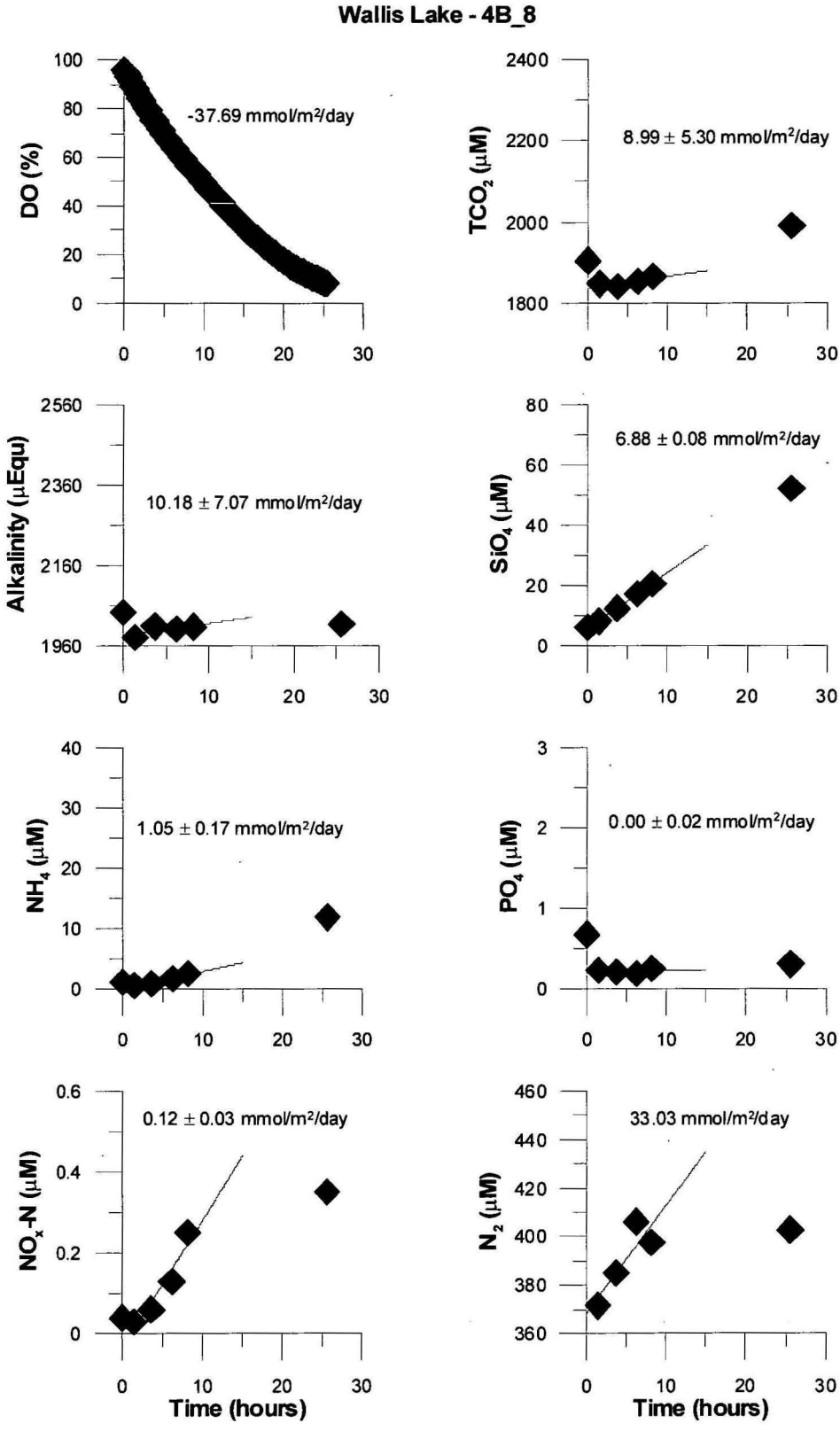


Wallis Lake - 3B_6




Wallis Lake - 4B_1
DO (%)
-27.39 mmol/m²/day
TCO2 (µM)
28.05 ± 6.10 mmol/m²/day
Alkalinity (µEqu)
-2.76 ± 5.16 mmol/m²/day
SiO4 (µM)
8.06 ± 0.91 mmol/m²/day
NH4 (µM)
2.45 ± 0.41 mmol/m²/day
PO4 (µM)
-0.03 ± 0.08 mmol/m²/day
NOx-N (µM)
0.07 ± 0.00 mmol/m²/day
N2 (µM)
2.97 mmol/m²/day
Time (hours)
Time (hours)


Wallis Lake - 4B_7
DO (%)
-53.91 mmol/m²/day
TCO2 (µM)
24.84 ± 19.33 mmol/m²/day
Alkalinity (µEqu)
-5.50 ± 15.89 mmol/m²/day
SiO4 (µM)
12.33 ± 0.14 mmol/m²/day
NH4 (µM)
3.08 ± 0.19 mmol/m²/day
PO4 (µM)
-0.05 ± 0.04 mmol/m²/day
NOx-N (µM)
0.12 ± 0.02 mmol/m²/day
N2 (µM)
9.16 mmol/m²/day
Time (hours)
Time (hours)


Wallis Lake - 4B_8
DO (%)
-37.69 mmol/m²/day
TCO2 (µM)
8.99 ± 5.30 mmol/m²/day
Alkalinity (µEqu)
10.18 ± 7.07 mmol/m²/day
SiO4 (µM)
6.88 ± 0.08 mmol/m²/day
NH4 (µM)
1.05 ± 0.17 mmol/m²/day
PO4 (µM)
0.00 ± 0.02 mmol/m²/day
NOx-N (µM)
0.12 ± 0.03 mmol/m²/day
N2 (µM)
33.03 mmol/m²/day
Time (hours)
Time (hours)