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Benthic Nutrient Fluxes in Smiths Lake, NSW

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

Craig S. Smith & David T. Heggie

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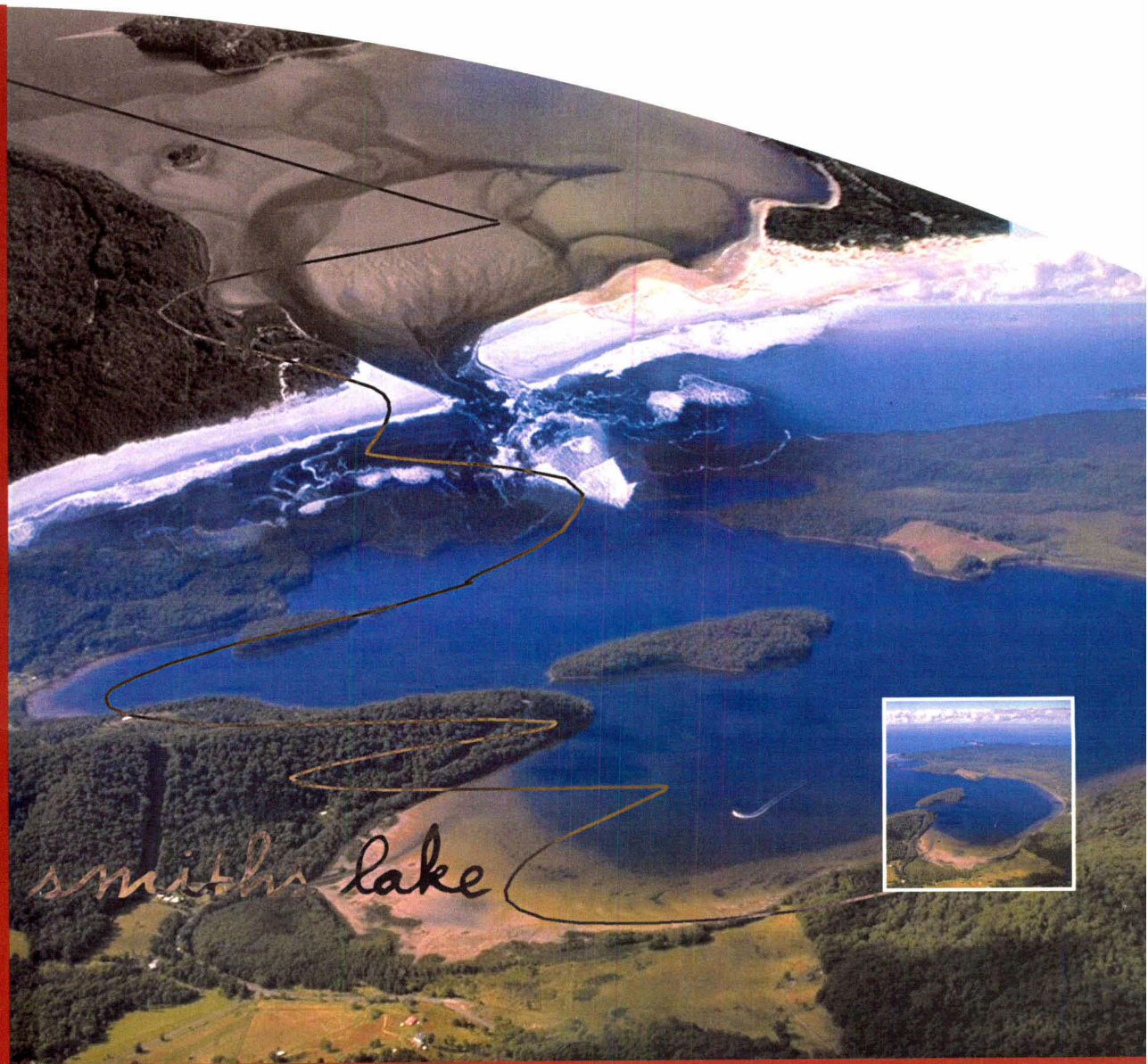

GEOSCIENCE AUSTRALIA RECORD 2003/16

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EXECUTIVE SUMMARY

Geoscience Australia conducted a survey of benthic nutrient fluxes in Smiths Lake, during February 2003, to gather baseline data for the ongoing management of the waterway by the Great Lakes Council. The objectives of the survey were:

1. To measure the nutrient and other metabolite fluxes across the sediment-water interface.
2. To assess the trophic condition of the two selected sites in Smith Lake.
3. To describe key processes controlling the nutrient fluxes across the sediment–water interface at each of the two sites.

Smiths Lake is an ICOLL (Intermittently Closed and Open Lake/Lagoon) on the NSW Lower North Coast approximately 280 km north of Sydney. The lake has a water area of 11 km^2 that is located within a relatively undisturbed catchment. Two sampling sites were selected in Smiths Lake, in consultation with the Great Lakes Council, to correspond with sampling already undertaken by the University of New South Wales. These sites were located in the eastern basin (SL1) and in the larger western basin (SL2). Four benthic chambers were deployed (1 clear and 3 dark) and two sediment cores were collected at each site.

We have compared measured benthic respiration rates, which approximate the carbon loading to the site, and compared those to carbon loads reported in Nixon (1995). Nixon (1995) identified the trophic status of different environments based on carbon loading. TCO_2 respiration rates at Site 1 (14.6 mmol m^{-2} day^{-1}) indicate that the trophic status of these waters were oligotrophic (< 23 mmol m^{-2} day^{-1}) while Site 2 (29.2 mmol m^{-2} day^{-1}) is considered oligotrophic to mesotrophic (23 - 68 mmol m^{-2} day^{-1}).

We found that denitrification efficiency at Site 1 was 71 % ± 14 %, while that at Site 2 was 36 % ± 8 %. The lower denitrification efficiencies resulted in the majority of nitrogen, recycled from the degradation of organic matter, being returned to the water column as ammonia. This was reflected in the high NH_4 concentrations (5.5 – 6.8 μM) in Smith Lake ambient water samples.

We have used the combined results of carbon loading and denitrification efficiency to rank the 2 sites with respect to 'risk' of deteriorating water quality and report a low risk at Site 1 and a low-to-moderate risk at Site 2.

Low PO_4 fluxes at both sites in Smiths Lake (average 0.02 mmol m^{-2} day^{-1}) indicated that phosphorus was being trapped in the sediments, probably by adsorption to Fe-oxyhydroxides. This process has been identified in many coastal waterways studied in Australia.

SiO_4 fluxes are generally higher than would be predicted from the degradation of a phytoplankton source of organic matter. Excess silicate could result from the dissolution of some silicate-rich clays, probably smectite, in the warm (25 °C) waters of Smiths Lake.

We recommend continued monitoring at these sites, particularly Site 2 and elsewhere in the western basin. The results found at Site 2, if they are characteristic of the whole of the western basin of Smiths Lake, are not encouraging for good water quality.

Monitoring should include:

1. water column parameters such as nutrients and chlorophyll (as per the ANZEC guidelines),
2. the carbon and nitrogen loadings and denitrification efficiencies, and
3. identification of nutrient inputs from the catchment (including urban inputs).

Given the long residence time of waters (up to 1 ½ years), Smiths Lake is at threat of deteriorating water quality if nutrient inputs from the catchment are increasingly recycled as biologically available N, such that N continues to accumulate within the biota, sediments and water column.

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

ABBREVIATIONS AND UNITS

ANZECC	Australian and New Zealand Environment and Conservation Council
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

Smiths Lake is an ICOLL (Intermittently Closed and Open Lake/Lagoon) on the NSW Lower North Coast, approximately 280 km north of Sydney. The lake has a water area of 11 km^2 that is located within a relatively undisturbed catchment. Around 25 % of the catchment lies in either the Myall Lakes National Park or Wallingat State Forest; much of the remainder is forested or waterway (Webb, McKeown & Assoc., 2001). The only developed areas are the Village of Smiths Lake and several smaller settlements. The lake entrance is generally closed to the sea, but is opened mechanically on average about every 1½ years by the Council when the lake level reaches around 1.7 mAHD.

Geoscience Australia conducted a benthic nutrient survey in February, 2003, to gain baseline data for the ongoing management of Smiths Lake.

1A. OBJECTIVES

The objectives of the survey included the following:

1. To measure the fluxes of nutrients and other metabolites across the sediment-water interface.
2. To assess the estuarine condition of the two selected sites within Smiths Lake.
3. To describe key processes controlling the fluxes of nutrients across the sediment–water interface at each of the two sites.

1B. BACKGROUND

The University of New South Wales found that ammonia concentrations, in Smiths Lake in April 2002, were up to 4 times greater than the recommended trigger value specified in the ANZECC guidelines (2000). Values of 60 μg NH_3-N/L (~ 4.3 μM) were recorded in the eastern part of the lake while the western parts of the lake had values of almost 30 μg NH_3-N/L (~ 2.1 μM).

Trigger values (ANZECC Water Quality Guidelines, 2000), are concentrations of key indicators, above or below which there is a risk of adverse biological effects. Default trigger values for South-east Australian estuaries are shown in Table 1 below.

Table 1 *ANZECC Guidelines Trigger Values for South-east Australian Estuaries*

	NH_3-N	NO_X-N	TN	TP
μg L^{-1}	15	15	300	30
μM L^{-1}	1.07	1.07	21.43	0.97

1C. EXPERIMENTAL DESIGN

Two sampling sites were selected in Smiths Lake in consultation with the Great Lakes Council. The sites were chosen to correspond with sampling already undertaken by the University of New South Wales. These sites were located in the eastern basin (SL1) and in the main western basin (SL2) (Figure 1). Four benthic chambers were deployed (1 clear and 3 dark) and two sediment cores were collected at each site.

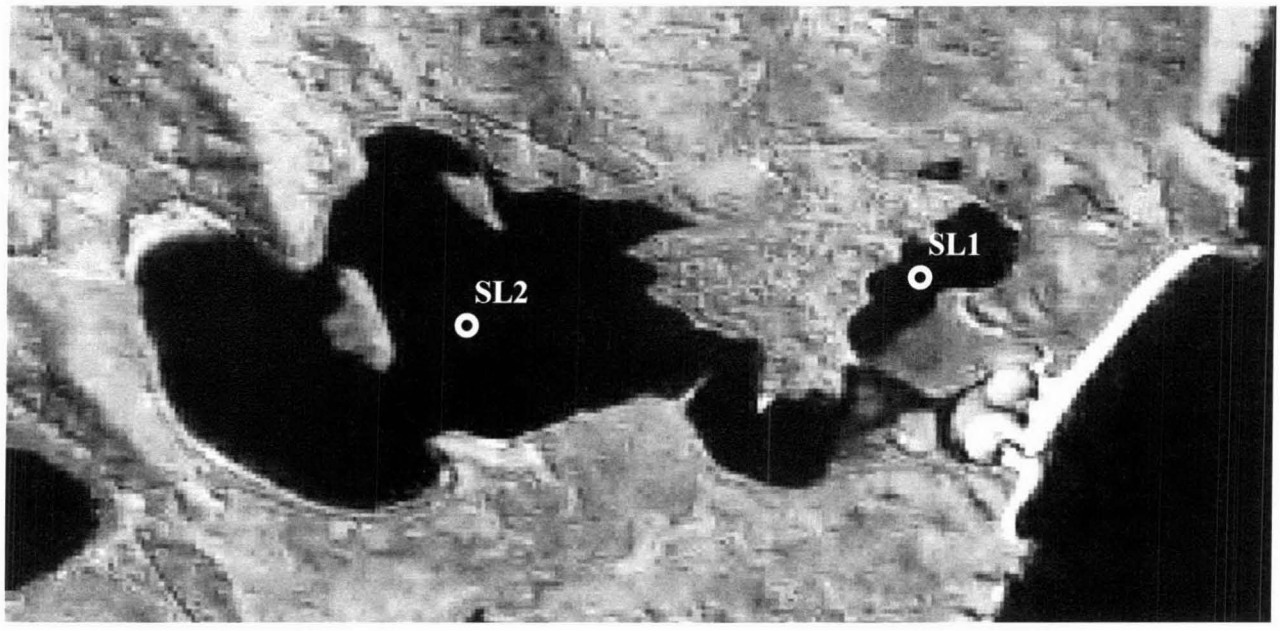

Figure 1 *Smiths Lake sample locations*

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.* (1998). 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 nutrient and TCO_2 fluxes were then calculated from the rate of change in concentration measured within the chambers. The O_2 flux was calculated on the rate of change over the linear part of the uptake curve (obtained from YSI data logger).

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. The spike was also used to model transport across the sediment-water interface and determine the influence of bioirrigation.

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 (0.066052 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 involves incrementally heating the sample from 300 °C to 650 °C in a stream of nitrogen gas, and detecting the evolved hydrocarbons and oxides of carbon that relate to organic compounds. The oxidation process involves gradually heating the sample to 800 °C in a stream of air and detecting the evolved oxides of carbon that relate to

organic 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

Dissolved oxygen, temperature and salinity conditions were recorded at each site at the time of chamber deployment. These water column profiles are presented in Table 2.

Table 2 *Water Column Profiles in Smiths Lake*

	Depth (m)	Temperature (°C)	Salinity	DO (%)
Site 1	0	24.09	27.12	101.5
	1.0	24.06	27.63	98.4
	2.0	24.25	27.30	97.9
	3.0	24.46	27.21	94.4
	4.0	24.47	27.56	94.4
	4.7	25.05	27.68	87.7
Site 2	0	24.33	28.27	106.4
	1.0	24.93	28.37	104.6
	2.0	25.01	27.95	104.9
	3.0	24.97	27.77	102.6
	4.0	26.08	28.43	92.3
	4.3	26.15	29.09	86.0

Salinities in Smiths Lake (27.12 - 29.09) were slightly lower than marine water due to the entrance being closed and the inflow of freshwater from the catchment. Density differences between fresh and marine water often lead to stratification during these periods. These changes in salinity (from marine to brackish) are typical of ICOLL's.

Both sites within Smiths Lake showed some degree of stratification. Dissolved oxygen is also lower at depth at each site. These lower concentrations are primarily a result of oxygen consumption by sediment biota and limited downward transport of oxygen.

Table 3 shows the average bottom water nutrient concentrations at the time of deployment for Smiths, Wallis and Myall Lakes. Apart from Site 2 at Wallis Lake (June 2003), Smiths Lake has the highest NH_4 concentrations and among the highest NO_X concentrations. This indicates that there were biologically available nutrients in the water column at the time of survey. Typically, a waterbody will cycle between periods of high concentrations of biologically available nutrients in the water column (often with low biomass) and periods of high biomass (with low water column nutrients). Nutrients will be depleted in the water column when taken up by organisms; when these organisms die, nutrients are released into the water column.

Table 3 *Average Bottom Water Nutrient Concentrations for Smiths, Wallis and Myall Lakes*

Site	NH_4 (µM)	PO_4 (µM)	NO_X (µM)	SiO_4 (µM)	Date
Smiths Lake 1	6.80	0.16	0.58	25.1	Feb 2003
Smiths Lake 2	5.51	0.11	0.61	20.3	Feb 2003
Wallis Lake 2	6.67	0.22	0.36	40.9	Feb 2003
Wallis Lake 3	0.34	0.35	0.06	6.3	Feb 2003
Wallis Lake 4	0.87	0.37	0.07	4.4	Feb 2003
Wallis Lake 10	2.12	0.34	0.31	10.0	Feb 2003
Wallis Lake 2	0.58	0.02	0.06	1.02	June 2000
Wallis Lake 3	0.53	0.04	0.08	0.8	June 2000
Wallis Lake 4	0.39	0.02	0.20	0.3	June 2000
Myall Lake 1	1.89	0.04	2.54	40.0	June 2000
Myall Lake 2	2.75	0.06	0.69	61.5	June 2000
Myall Lake 3	0.58	0.06	0.26	66.7	June 2000

3B. SEDIMENT CORES

Core descriptions for each site are presented in Table 4. Both sites showed similar core characteristics with a thin apparent oxic layer over mud or sandy-mud. Shell fragments were seen at both sites as was a H_2S odour in the lower part of the core. Site 1 (Eastern Basin) showed evidence of bioturbation in the upper 5 cm of the core and large bivalves (~ 3 cm diameter) were also identified.

Table 4 *Sediment Core Descriptions*

	Depth	Description
Site 1	Surface	Olive-black layer (1.5 cm thick)
	0 - 5 cm	Brown-black mud with shell fragments and evidence of bioturbation
	5 - 12 cm	Sandy-mud with larger shell fragments
	12 - 40 cm	Sandy-mud
	40 - 65 cm	Sandy-mud with slight H_2S odour, Shell bed at 45 cm
Site 2	Surface	Brownish olive-grey mud
	0 - 4 cm	Brown mud with no shells
	4 - 17 cm	Dark grey mud with large bivalves, Shell fragments decreasing with depth
	17 - 38 cm	Dark grey mud with small shell fragments
	38 - 60 cm	Dark grey mud with slight H_2S odour

3C. PORE WATERS

Down-core porewater profiles for Smiths Lake are shown in Figure 2 and Figure 3 below. Significant observations from the pore water profiles include:

- NO_X concentrations down-core at both sites indicated that nitrification occurred in the sediments. These NO_X concentrations are unusually high and may have resulted from bioirrigation moving oxygenated water down core.
- SiO_4 profiles for both sites showed that diatoms are an important form of organic matter in the sediments.
- PO_4 concentrations increase with depth at both sites. This indicated that P was being released from degrading organic matter.

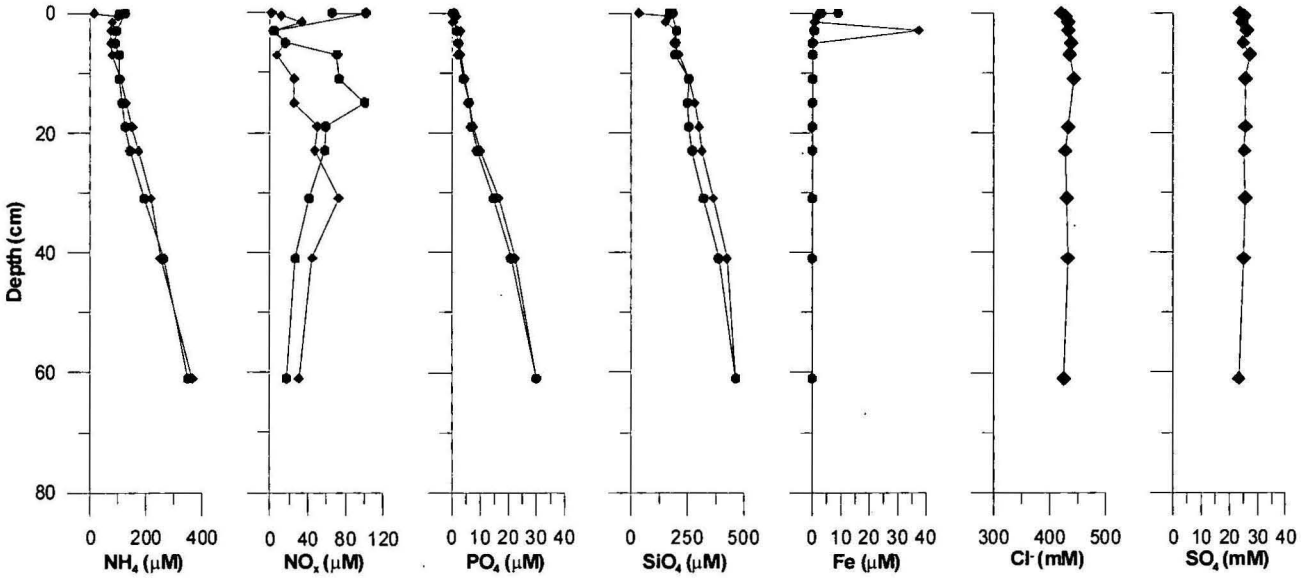

Figure 2 *Pore Water Profiles for Site 1 (Eastern Basin)*

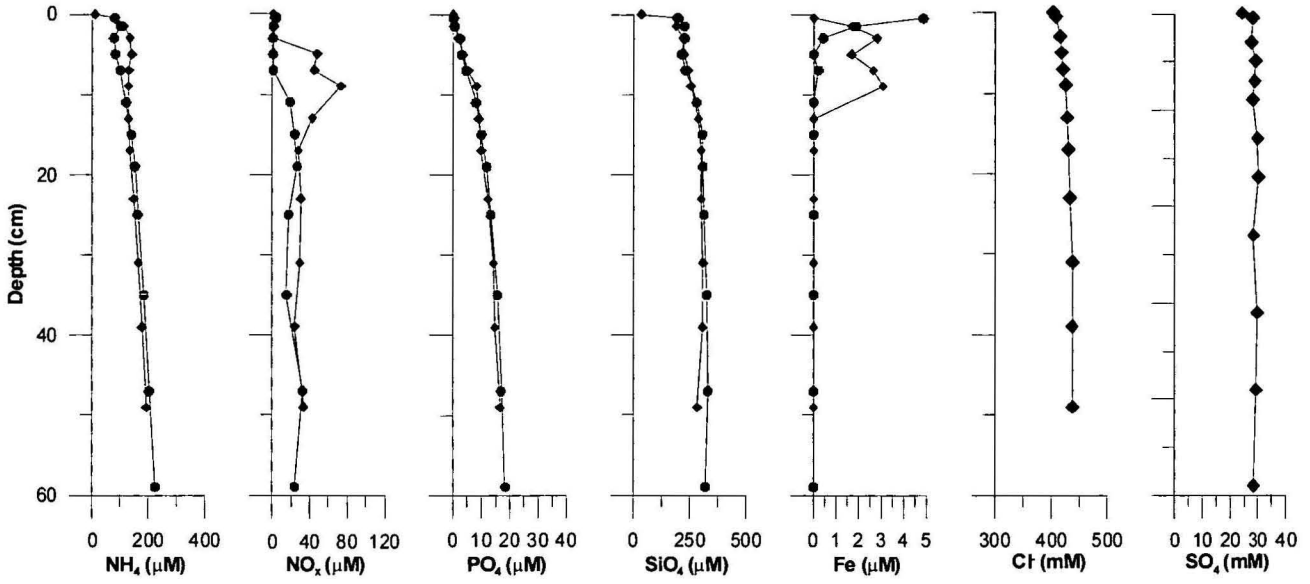

Figure 3 *Pore Water Profiles for Site 2 (Western Basin)*

3D. BENTHIC CHAMBERS AND BENTHIC NUTRIENT FLUXES

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

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

Based on these criteria, we are confident that 7 of the 8 benthic chamber deployments within Smiths Lake were successful. However, 1 chamber placed at Site 1 (1A_3) showed dissolved oxygen "draw-down" before the chamber door was closed, indicating that there was insufficient mixing of chamber and ambient water prior to the start of the incubation. The results for this chamber have been included in this report but not used for the site interpretation.

The calculated benthic fluxes are summarized in Table 5 and the data for all chamber deployments is presented in Appendix 1.

Table 5 *Summary of Fluxes from Smiths 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
1A_1	Light	23.55	4.69	-10.45	7.21	3.74	2.03	0.31	-0.03	0.02	2.00	0.31	2.66	6.74	0.38	0.02	0.07
1A-2	Dark	8.17	3.79	-10.19	-0.92	2.60	0.16	0.17	-0.01	0.01	0.16	0.17	0.37	0.44	0.13	-0.06	0.09
~~1A_3~~	~~Dark~~	~~16.64~~	~~12.24~~	~~-9.03~~	~~-3.95~~	~~13.13~~	~~2.99~~	~~0.11~~	~~-0.03~~	~~0.05~~	~~2.95~~	~~0.12~~	~~2.21~~	~~8.14~~	~~0.24~~	~~0.10~~	~~0.06~~
1A_4	Dark	10.18	1.32	-11.32	-1.63	0.63	0.69	0.10	0.01	0.01	0.70	0.10	3.79	2.01	0.50	0.02	0.04
2A_5	Light	24.54	4.90	-27.53	1.21	4.72	2.34	0.26	0.08	0.01	2.41	0.26	0.97	7.99	0.33	-0.04	0.01
2A_6	Dark	13.85	3.07	-27.22	-9.01	2.57	1.95	0.17	0.15	0.02	2.10	0.17	1.58	6.07	0.15	-0.01	0.02
2A_7	Dark	35.31	4.55	-45.54	3.44	6.35	3.62	0.02	0.10	0.02	3.72	0.03	1.44	7.13	0.17	0.09	0.05
2A_8	Dark	43.23	0.37	-28.33	18.89	0.95	3.07	0.24	0.06	0.03	3.13	0.25	2.38	9.90	0.60	0.01	0.13

4. DISCUSSION

4A. OXYGEN AND CARBON FLUXES

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 4. 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.

Data falling within the envelope marked indicate that aerobic oxidation dominates the degradation of organic matter. Data lying to the right of the envelope (SL1A_1, SL1A_3 and SL2A_8) probably indicate some sulphate reduction occurring in the near surface sediments at the time of survey. Site 2A_6 lies to the left of the envelope indicating that there is an excess of oxygen consumed for the amount of carbon released; oxidation of some sulphides in sediments may explain this result.

A comparison of oxygen consumption and TCO_2 respiration rates for a selection of Australian estuaries is shown in Table 6. While oxygen and TCO_2 flux rates correspond well in Smiths Lake, these rates are lower than those for most Australian estuaries. Site 1 is considered oligotrophic (< 23 mmol m^{-2} day^{-1}) while Site 2 is oligotrophic to mesotrophic (< 68 mmol m^{-2} day^{-1}) using the trophic status classification system proposed by Nixon (1995).

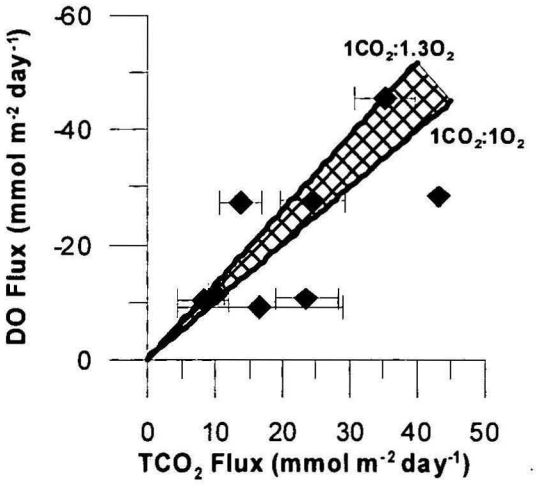

Figure 4 *Dissolved Oxygen Flux versus TCO_2 Flux in Smiths Lake*

Table 6 *Summary of O_2 and TCO_2 Fluxes from Selected Australian Waterways (1. this study, 2. Smith, et al., 2000, 3. Palmer, et al., 2000a, 4. Berelson, et al., 1998, 5. AGSO, 1998, 6. Palmer, et al., 2000b, 7. Fredericks, D.J. and 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
Smiths Lake[1]	-9.0 to -45.54 mean = -21.2	8.17 to 43.23 mean = 21.9	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)
Myall Lakes[3]	-11.5 to –40.9 mean = -26.3	3.2 to 47.1 mean = 18.4	Winter 2000 (June)
Port Philip Bay[4]	-21.0 to –86.2 mean = -42.1	18.2 to 119.8 mean = 48.4	Summer 1995 (Jan)
Moreton Bay[5]	-14 to –87 mean = -40	26 to 204 mean = 75	Summer 1998 (Feb)
Durras Lake[6]	-17 to –77 mean = -40	39 to 106 mean = 67	Summer 1999 (Dec)
Wilson Inlet[7]	-4.7 to –135.1 mean = -55.4	15 to 275 mean = 73.8	Spring 1998 (May)

4B. N BIOGEOCHEMISTRY AND DENITRIFICATION

Nitrogen is delivered to coastal lakes in dissolved and particulate forms. This nitrogen is either taken-up by primary producers, including diatomaceous and other phytoplankton, various macrophytes, 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 waterbody. Denitrification is a process by which the estuary can naturally cleanse itself of this nitrogen. This process converts nitrates (NO_3^-) and nitrites (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 5 shows the flux of dissolved inorganic nitrogen (DIN) plotted against the carbon flux. The expected nitrogen flux based on the carbon flux rate, assuming a C:N of 106:16, is also shown. In

most cases, the measured DIN flux is less than that predicted from degradation of Redfield-like organic matter. This result is indicative of denitrification in the sediments of Smiths Lake.

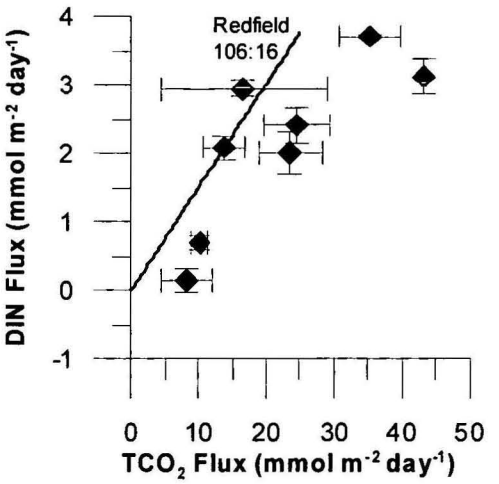

Figure 5 *TCO_2 Flux versus Dissolved Inorganic Nitrogen (DIN) Flux in Smiths Lake*

Denitrification efficiency (expressed as a percentage) is the proportion of total nitrogen released within the sediments as N_2 gas. It is calculated as:

$$DenitrificationEfficiency = \frac{N_2 Flux}{TIN} * 100$$

where N_2 Flux is the direct measurement of N_2 and TIN is the sum of NH_4, NO_X and N_2.

Using data shown in Table 5 it was found that Site 1 had up to twice the denitrification efficiency as Site 2 (means of 71 % ± 14 % and 36 % ± 8 % respectively). The lower denitrification efficiency at Site 2 results in the majority of nitrogen recycled from organic matter being returned to the water column as ammonia (refer to Table 3 and Table 5).

Figure 6 shows the denitrification efficiency plotted against TCO_2 flux for both sites within Smiths Lake. It can be seen that the lower denitrification efficiencies occur in Site 2 where there is also a higher TCO_2 flux. This was also found in Port Philip Bay (Berelson *et al.* 1998) where it was suggested that increased carbon loading to the sediment short-circuits the denitrification pathway. We have used the combined results of carbon loading and denitrification efficiency to rank the 2 sites with respect to 'risk' of deteriorating water quality and report a low risk at Site 1 and a low-to-moderate risk at Site 2.

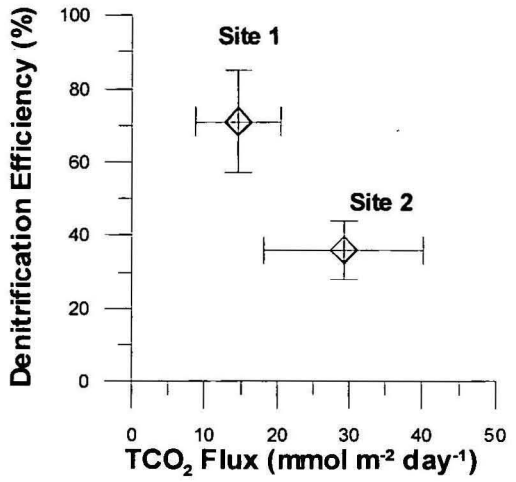

Figure 6 *TCO_2 Flux versus Denitrification Efficiency in Smiths Lake*

4C. PHOSPHORUS DYNAMICS

Benthic chamber incubations have shown that PO_4 fluxes were generally low or negative in Smiths Lake (Figure 7). The maximum flux rate recorded was 0.10 mmol m^{-2} day^{-1} with the average being 0.02 mmol m^{-2} day^{-1}. These rates were less than would be predicted from the degradation of a phytoplankton source of organic matter (Redfield C:P = 106:1), indicating 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).

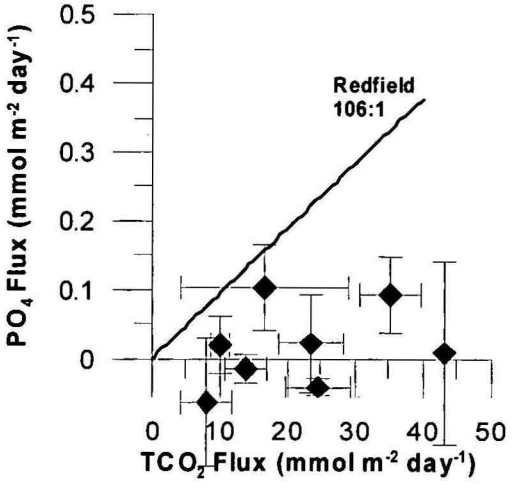

Figure 7 *PO_4 Flux versus TCO_2 Flux in Smiths Lake*

4D. SILICATE DYNAMICS

The silicate fluxes in Smiths Lake (Figure 8) show that there are generally more silicate than can be attributed to diatomaceous organic matter alone. Excess silicate could be the result of the dissolution of some silicate-rich clays (probably smectite) in the warm waters of Smiths Lake.

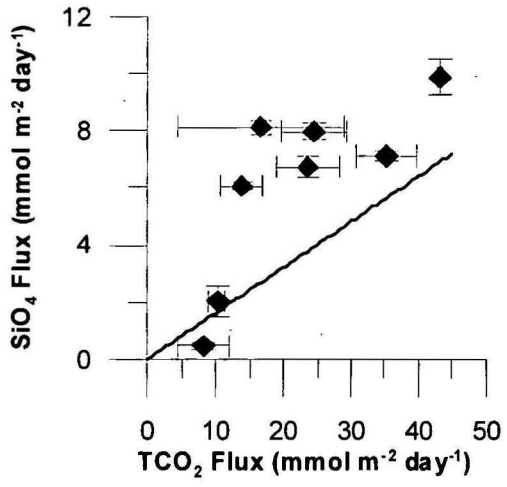

Figure 8 *TCO_2 Flux versus SiO_4 Flux in Smiths Lake*

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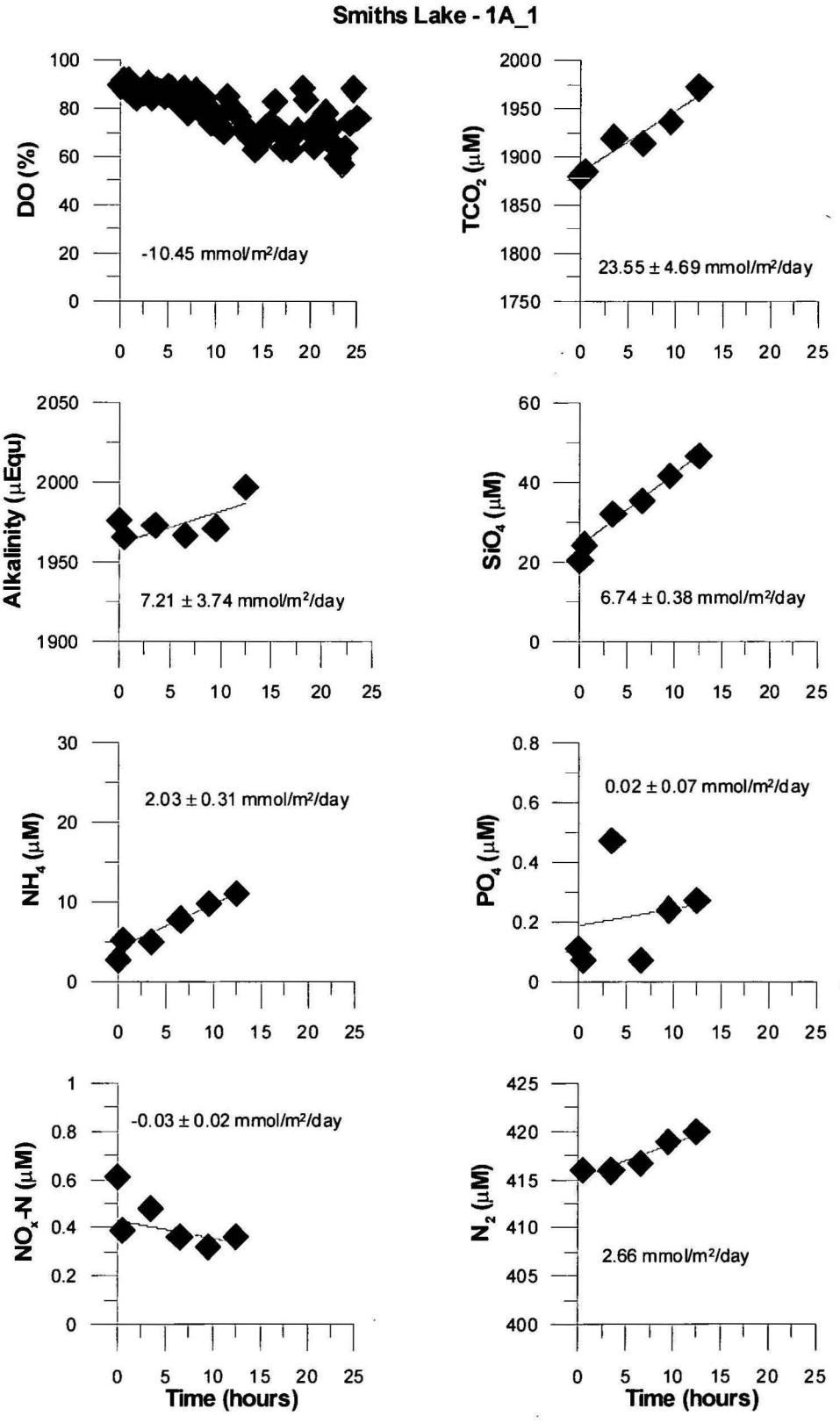
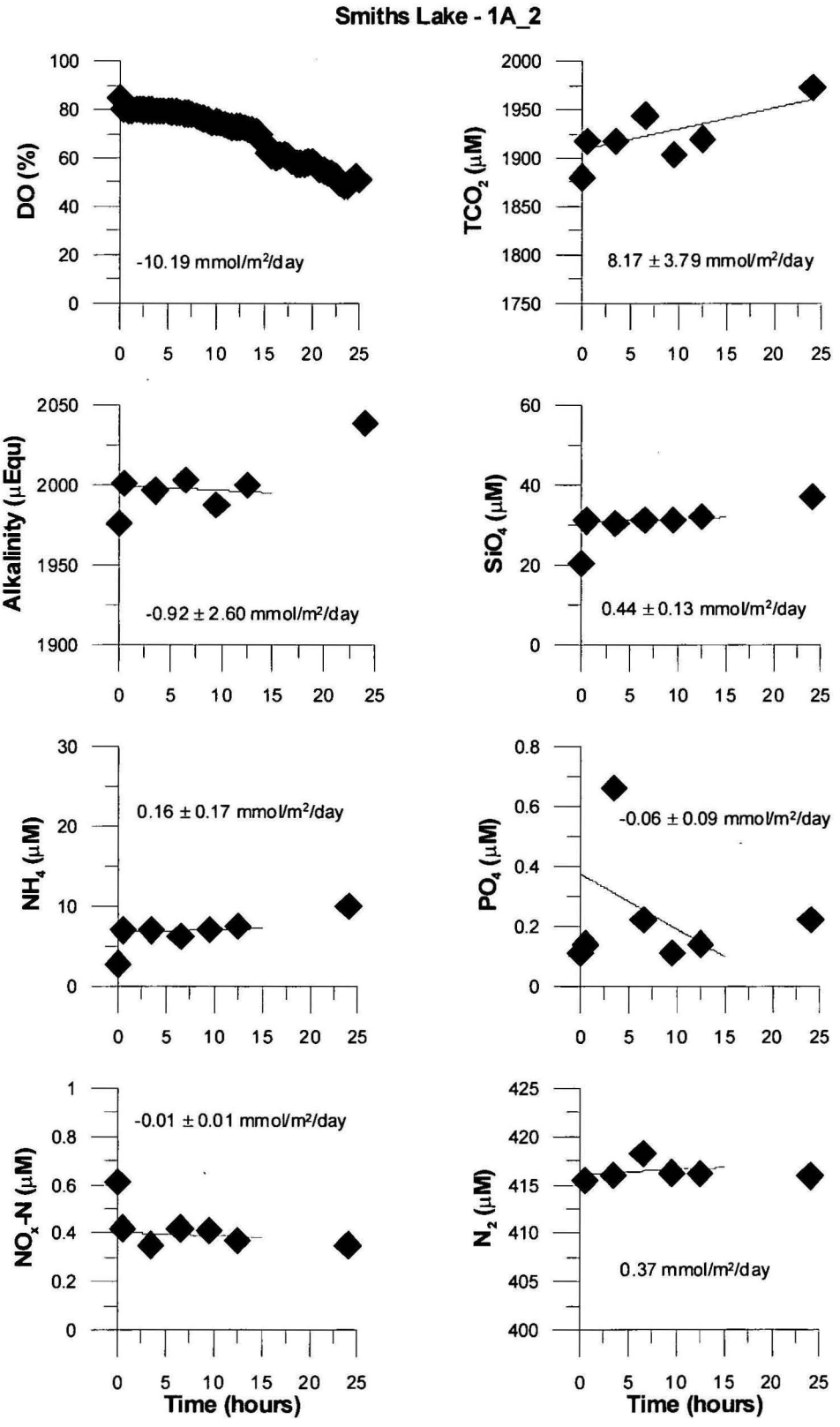
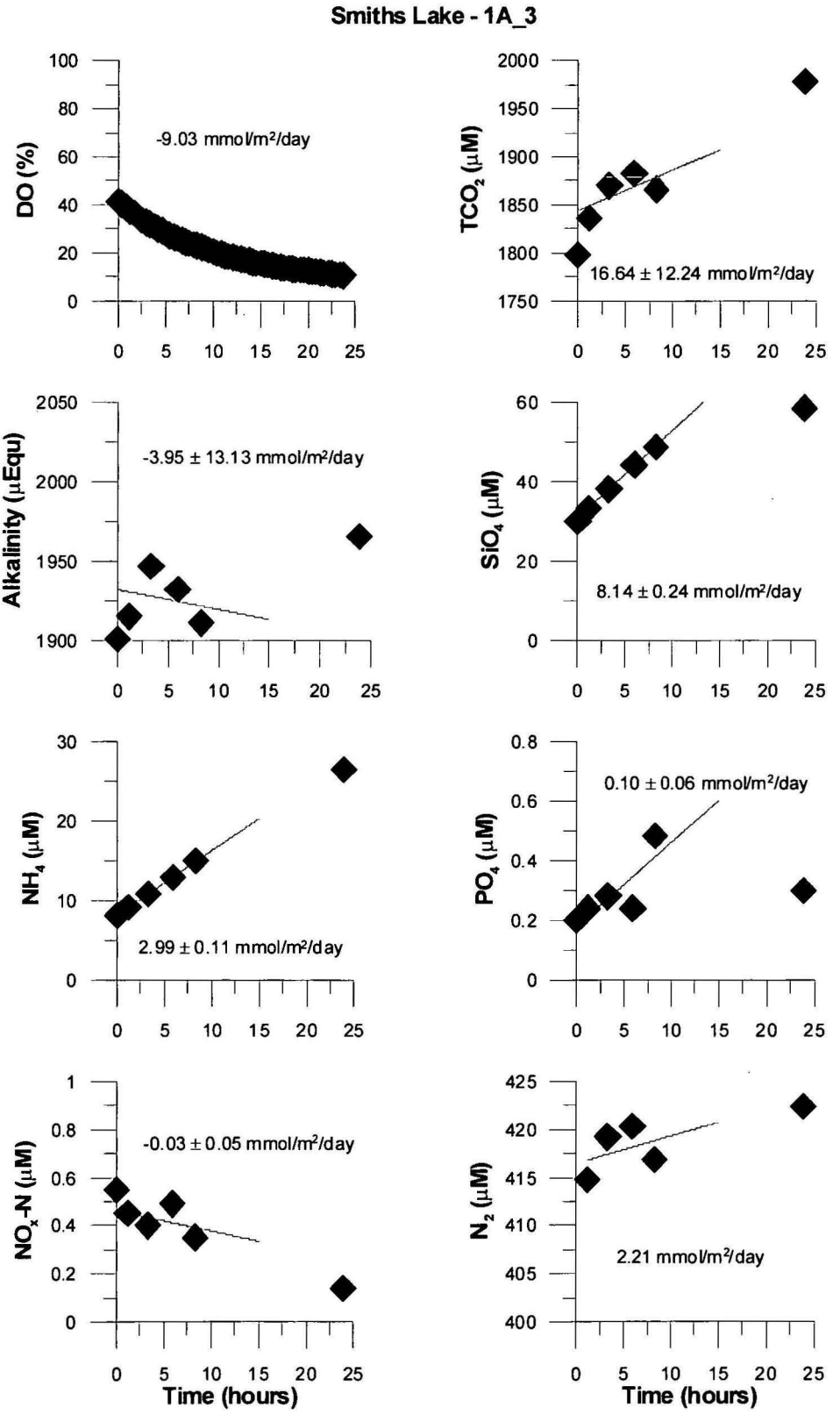
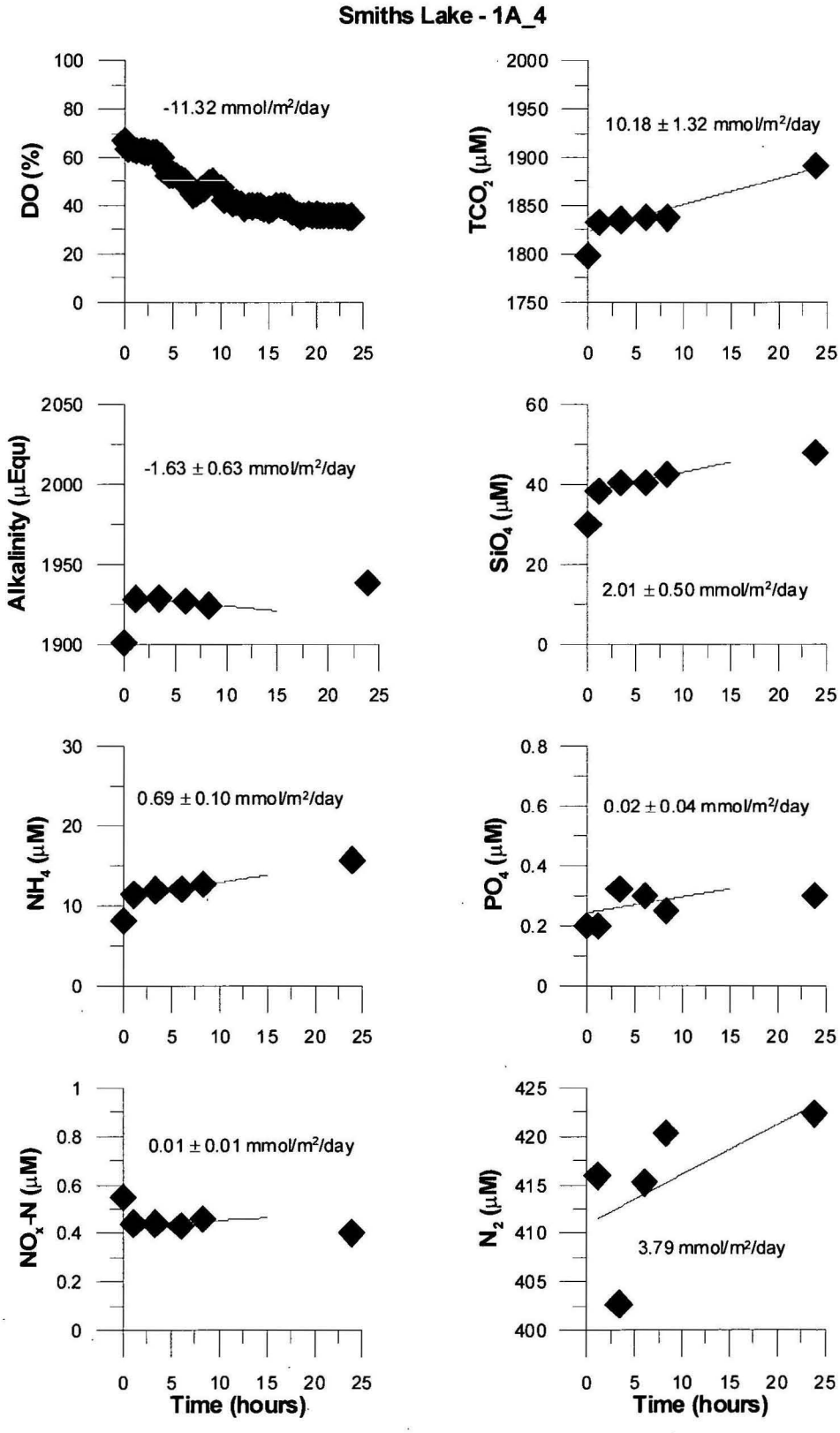
APPENDIX

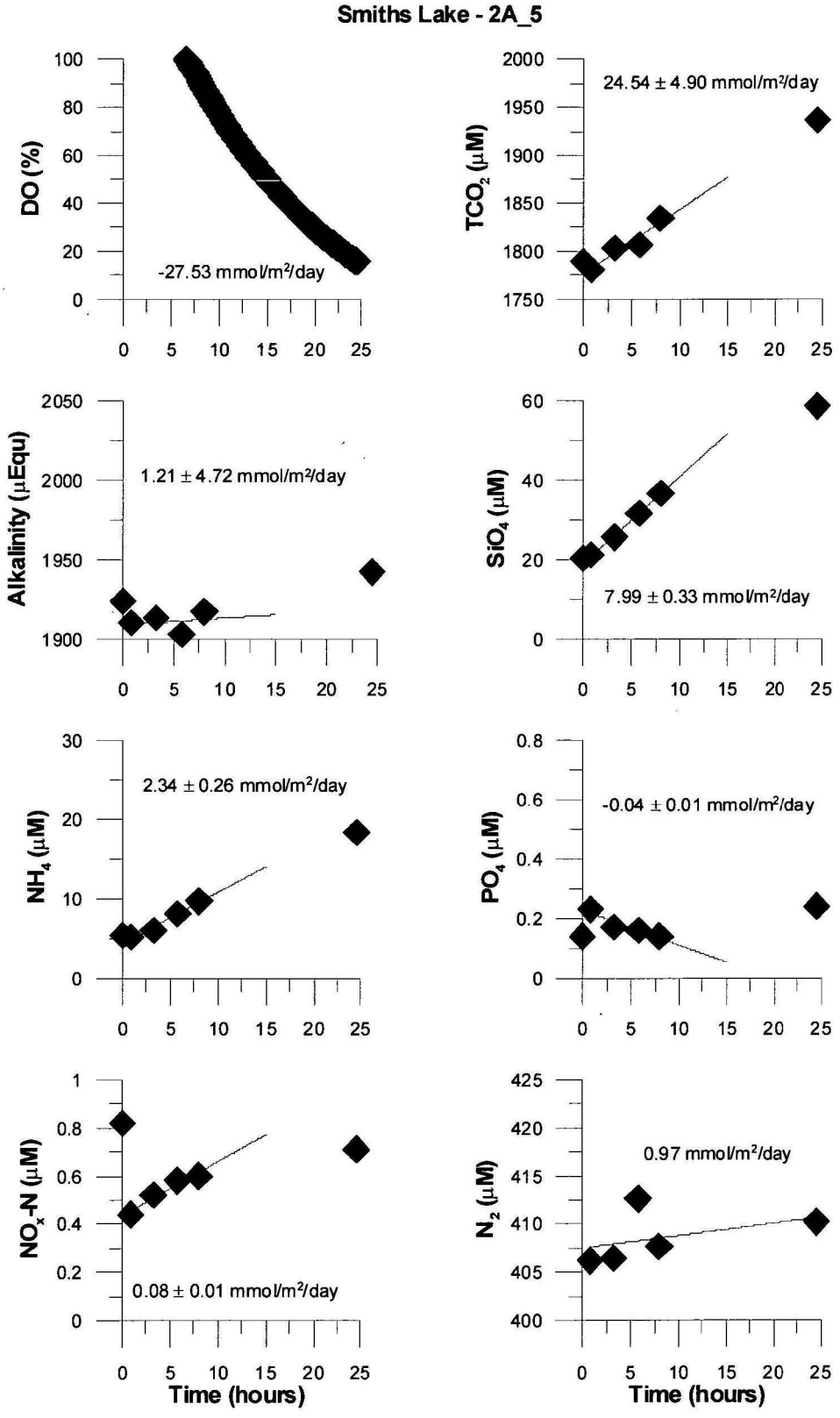
1. CHAMBER METABOLITE CONCENTRATIONS

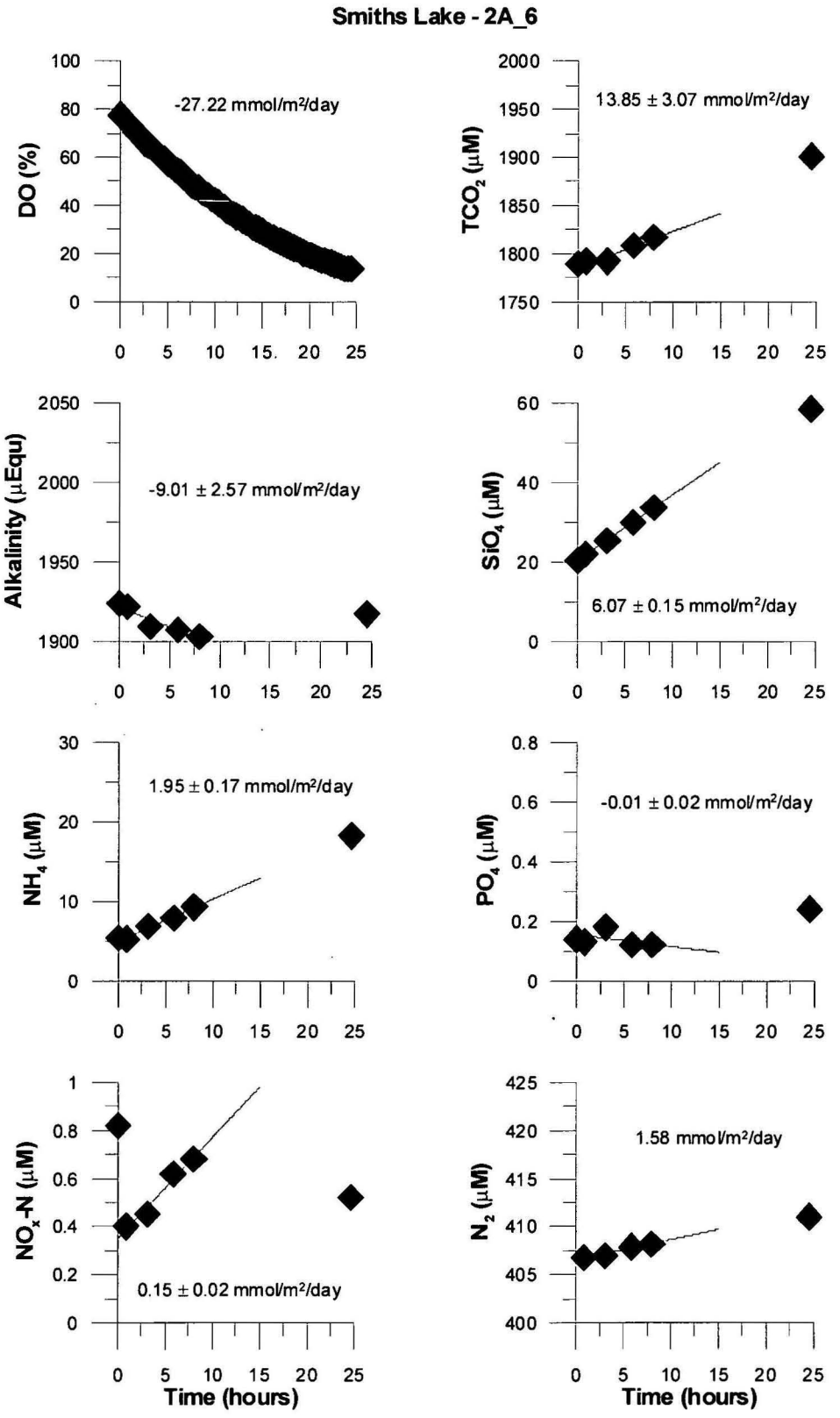

Smiths Lake - 1A_1
DO (%)
-10.45 mmol/m²/day
TCO2 (µM)
23.55 ± 4.69 mmol/m²/day
Alkalinity (µEqu)
7.21 ± 3.74 mmol/m²/day
SiO4 (µM)
6.74 ± 0.38 mmol/m²/day
NH4 (µM)
2.03 ± 0.31 mmol/m²/day
PO4 (µM)
0.02 ± 0.07 mmol/m²/day
NOx-N (µM)
-0.03 ± 0.02 mmol/m²/day
N2 (µM)
2.66 mmol/m²/day
Time (hours)
Time (hours)

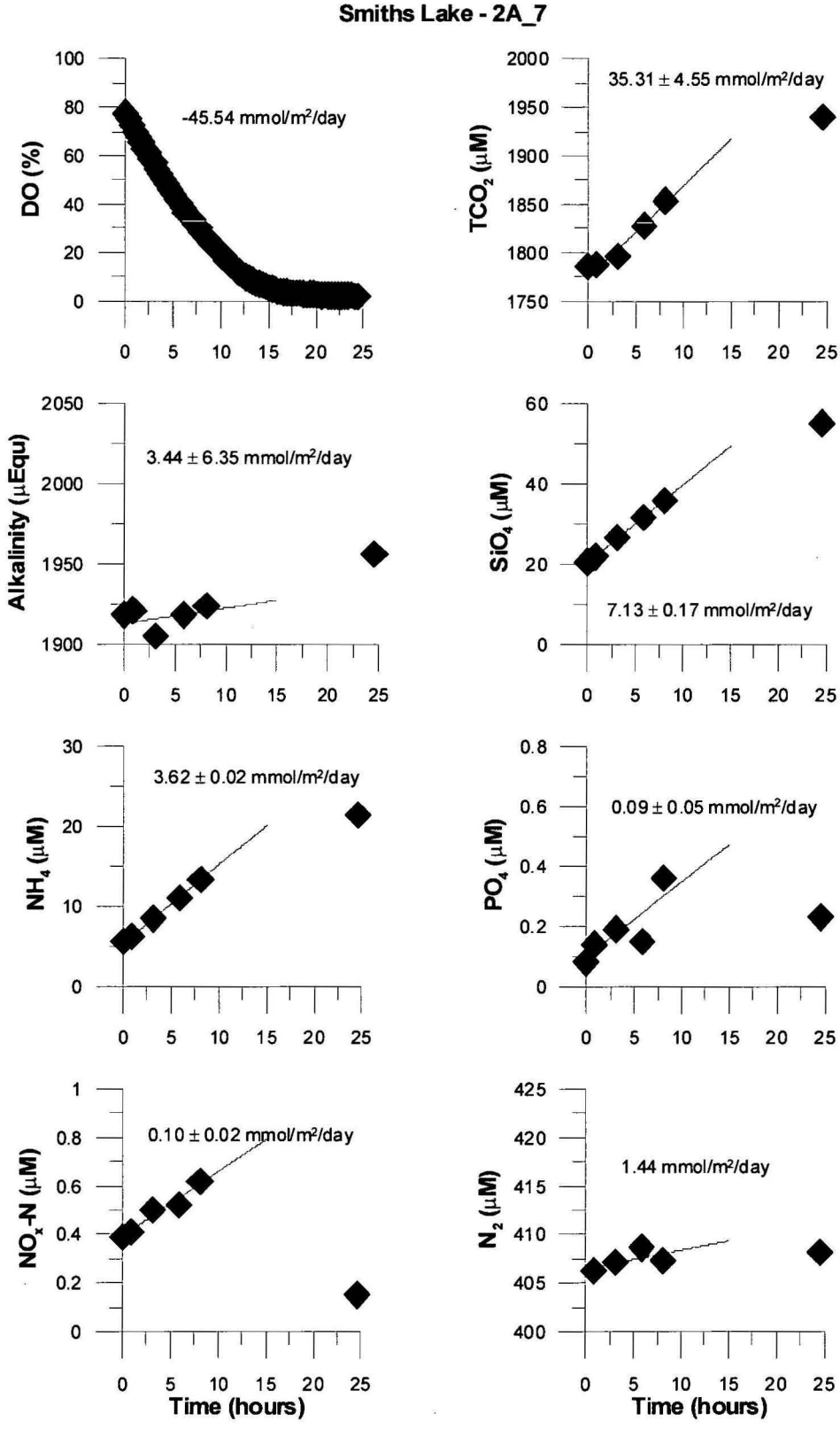

Smiths Lake - 1A_2
DO (%)
-10.19 mmol/m²/day
TCO2 (µM)
8.17 ± 3.79 mmol/m²/day
Alkalinity (µEqu)
-0.92 ± 2.60 mmol/m²/day
SiO4 (µM)
0.44 ± 0.13 mmol/m²/day
NH4 (µM)
0.16 ± 0.17 mmol/m²/day
PO4 (µM)
-0.06 ± 0.09 mmol/m²/day
NOx-N (µM)
-0.01 ± 0.01 mmol/m²/day
N2 (µM)
0.37 mmol/m²/day
Time (hours)
Time (hours)

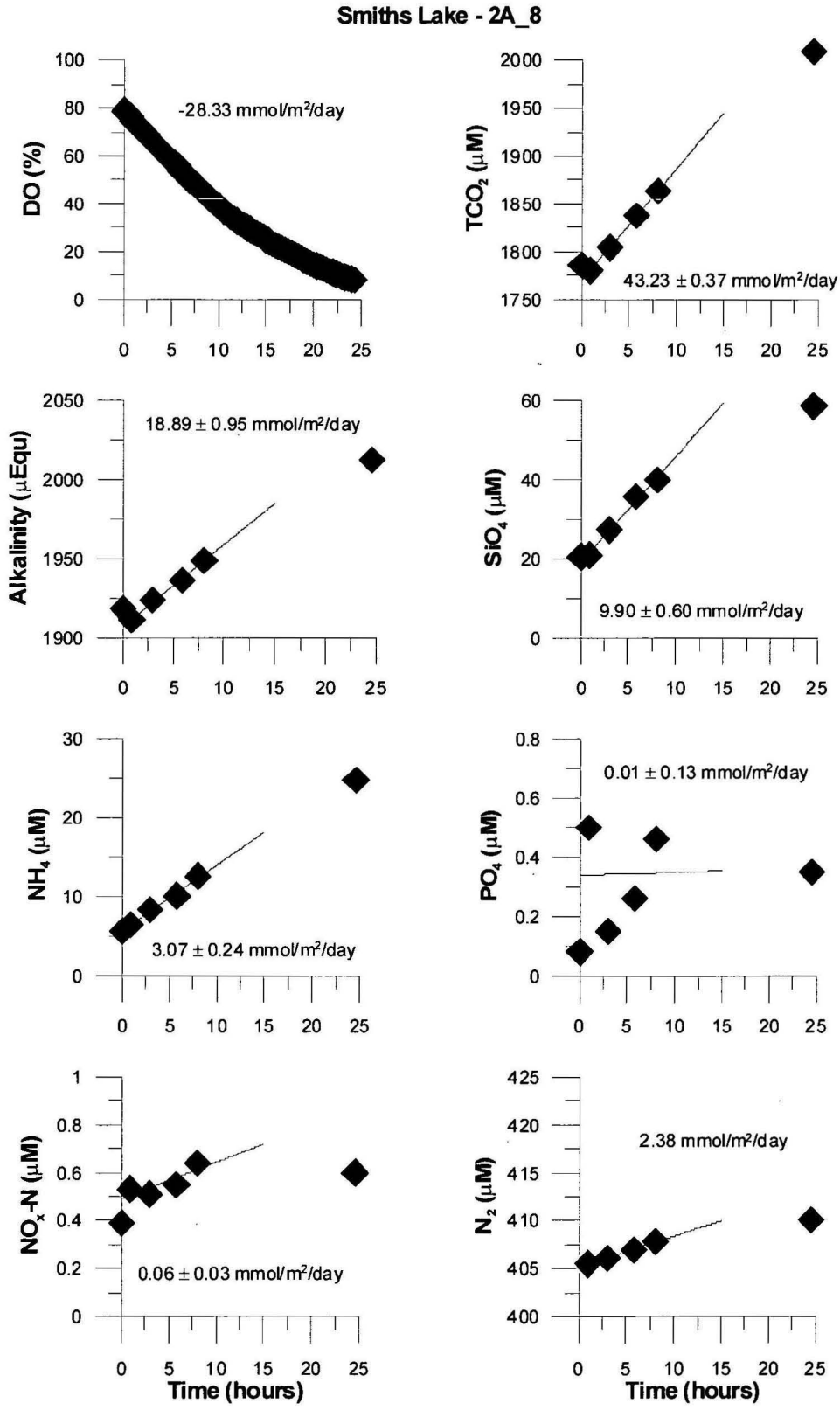

Smiths Lake - 1A_3
DO (%)
-9.03 mmol/m²/day
TCO2 (µM)
16.64 ± 12.24 mmol/m²/day
Alkalinity (µEqu)
-3.95 ± 13.13 mmol/m²/day
SiO4 (µM)
8.14 ± 0.24 mmol/m²/day
NH4 (µM)
2.99 ± 0.11 mmol/m²/day
PO4 (µM)
0.10 ± 0.06 mmol/m²/day
NOx-N (µM)
-0.03 ± 0.05 mmol/m²/day
N2 (µM)
2.21 mmol/m²/day
Time (hours)
Time (hours)


Smiths Lake - 1A_4
DO (%)
-11.32 mmol/m²/day
TCO2 (µM)
10.18 ± 1.32 mmol/m²/day
Alkalinity (µEqu)
-1.63 ± 0.63 mmol/m²/day
SiO4 (µM)
2.01 ± 0.50 mmol/m²/day
NH4 (µM)
0.69 ± 0.10 mmol/m²/day
PO4 (µM)
0.02 ± 0.04 mmol/m²/day
NOx-N (µM)
0.01 ± 0.01 mmol/m²/day
N2 (µM)
3.79 mmol/m²/day
Time (hours)
Time (hours)


Smiths Lake - 2A_5
DO (%)
-27.53 mmol/m²/day
TCO2 (µM)
24.54 ± 4.90 mmol/m²/day
Alkalinity (µEqu)
1.21 ± 4.72 mmol/m²/day
SiO4 (µM)
7.99 ± 0.33 mmol/m²/day
NH4 (µM)
2.34 ± 0.26 mmol/m²/day
PO4 (µM)
-0.04 ± 0.01 mmol/m²/day
NOx-N (µM)
0.08 ± 0.01 mmol/m²/day
N2 (µM)
0.97 mmol/m²/day
Time (hours)
Time (hours)


Smiths Lake - 2A_6
DO (%)
-27.22 mmol/m²/day
TCO2 (µM)
13.85 ± 3.07 mmol/m²/day
Alkalinity (µEqu)
-9.01 ± 2.57 mmol/m²/day
SiO4 (µM)
6.07 ± 0.15 mmol/m²/day
NH4 (µM)
1.95 ± 0.17 mmol/m²/day
PO4 (µM)
-0.01 ± 0.02 mmol/m²/day
NOx-N (µM)
0.15 ± 0.02 mmol/m²/day
N2 (µM)
1.58 mmol/m²/day
Time (hours)
Time (hours)


Smiths Lake - 2A_7
DO (%)
-45.54 mmol/m²/day
TCO₂ (µM)
35.31 ± 4.55 mmol/m²/day
Alkalinity (µEqu)
3.44 ± 6.35 mmol/m²/day
SiO₄ (µM)
7.13 ± 0.17 mmol/m²/day
NH₄ (µM)
3.62 ± 0.02 mmol/m²/day
PO₄ (µM)
0.09 ± 0.05 mmol/m²/day
NOx-N (µM)
0.10 ± 0.02 mmol/m²/day
N₂ (µM)
1.44 mmol/m²/day
Time (hours)
Time (hours)


Smiths Lake - 2A_8
DO (%)
-28.33 mmol/m²/day
TCO₂ (µM)
43.23 ± 0.37 mmol/m²/day
Alkalinity (µEqu)
18.89 ± 0.95 mmol/m²/day
SiO₄ (µM)
9.90 ± 0.60 mmol/m²/day
NH₄ (µM)
3.07 ± 0.24 mmol/m²/day
PO₄ (µM)
0.01 ± 0.13 mmol/m²/day
NOx-N (µM)
0.06 ± 0.03 mmol/m²/day
N₂ (µM)
2.38 mmol/m²/day
Time (hours)
Time (hours)