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Nitrogen and Phosphorus Budgets for the Central Great Barrier Reef Shelf

**Miles Furnas, Alan W. Mitchell
and Michele Skuza**



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Great Barrier Reef Marine Park Authority

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Tropical Oceanography Program
Australian Institute of Marine Science
Townsville

A REPORT TO THE GREAT BARRIER REEF MARINE PARK AUTHORITY

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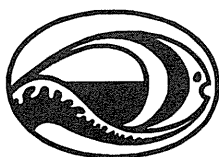
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TABLE OF CONTENTS

SUMMARY	1
1. INTRODUCTION	3
2. THE STUDY AREA	5
3. PHYSICAL OCEANOGRAPHY	17
4. CONCEPTUAL MODELS OF NUTRIENT POOLS AND FLUXES	18
5. METHODS	23
5.1 Water Sampling	23
5.2 Underwater and Diurnal Light Measurements	23
5.3 Zooplankton Sampling	23
5.4 Nutrient Subsampling	24
5.5 River Sampling	24
5.6 Rainwater Sampling	25
5.7 Analytical Procedures	25
5.8 Primary Production Measurements	26
5.9 Frequency and Magnitude of Intrusive Activity off Cairns	27
5.10 Sediment Trap Sampling	30
5.11 Moored Traps	34
5.12 Drifter Traps	36
5.13 Carbon and Nitrogen Analyses of Trapped Materials	36
5.14 Phosphorus Analyses of Trapped Materials	37
6. NUTRIENT STOCKS	40
7. TEMPORAL AND SPATIAL VARIABILITY OF NUTRIENT SPECIES IN THE CAIRNS AND TULLY BOXES	60
8. RIVER INPUTS OF NUTRIENTS	71
8.1 Longitudinal Variations of Nutrient Concentrations within Catchments	80
8.1.1 Herbert River	80
8.1.2 Tully River	86
8.2 Inter-River Comparisons	87
8.3 Estuarine Processes	87
8.4 Riverine Nitrogen and Phosphorus Exports to Coastal Waters	98
9. RAINFALL INPUTS OF NUTRIENTS	100
10. INTRUSIONS FROM THE CORAL SEA	107
11. NITROGEN FIXATION BY <i>TRICHODESMIUM</i>	114
12. ATMOSPHERIC NITROGEN FIXATION BY REEF COMMUNITIES	116
13. SEDIMENTATION OF PARTICULATE MATERIALS AND NUTRIENTS	118
13.1 Moored Traps	118

13.2 Lagrangian Drifting Traps.....	127
14. BENTHIC NUTRIENT FLUXES.....	142
15. PHYTOPLANKTON NUTRIENT DEMAND	146
16. WATER COLUMN NUTRIENT MINERALIZATION BY ZOOPLANKTON AND MICROBIAL POPULATIONS.....	149
16.1 Macro- and Microzooplankton	149
17. MICROBIAL MINERALIZATION.....	155
18. BUDGET SYNTHESIS AND DISCUSSION	158
19. THE BALANCE BETWEEN UPTAKE DEMAND AND SOURCES OF NITROGEN AND PHOSPHORUS	178
20. SUMMATION	179
ACKNOWLEDGEMENTS.....	182
REFERENCES.....	183

TABLES

1. Shelf areas and volumes of water between isobaths on the central Great Barrier Reef shelf	7
2. Areas of reefs in the study area and the estimated area of reef flat	10
3. Mean annual discharges and ranges for rivers flowing into the Cairns and Tully boxes.....	13
4. Acronyms and symbols for nutrient species used in this report.....	18
5. Summary statistics for dissolved and particulate water column nutrient concentrations in the Cairns box for the summer (October - April) season.....	41
6. Summary statistics for dissolved and particulate water column nutrient concentrations in the Cairns box for the winter (May - September) season	42
7. Summary statistics for dissolved and particulate water column nutrient concentrations in the Tully box for the summer (October - April) season	43
8. Summary statistics for dissolved and particulate water column nutrient concentrations in the Tully box for the winter (May - September) season	44
9. Distribution of shelf nutrient stocks within long-shelf depth bands in the Cairns box during summer (October - April).....	51
10. Distribution of shelf nutrient stocks within long-shelf depth bands in the Cairns box during winter (May - September)	52

11.	Distribution of shelf nutrient stocks within long-shelf depth bands in the Tully box during summer (October - April)	53
12.	Distribution of shelf nutrient stocks within long-shelf depth bands in the Tully box during winter (May - September)	54
13.	Calculated stocks of nutrients per metre of coastline within the Cairns box during summer.....	55
14.	Calculated stocks of nutrients per metre of coastline within the Cairns box during winter	55
15.	Calculated stocks of nutrients per metre of coastline within the Tully box during summer.....	56
16.	Calculated stocks of nutrients per metre of coastline within the Tully box during winter	56
17.	Locations of longshore transect stations between Cape Tribulation and Green Island	60
18.	Overall station means and standard errors for water column variables measured at transect stations between Cape Tribulation and Cape Grafton	68
19.	Summary of ANOVAs for significance of variability related to cruises and stations on the transect between Cape Tribulation and Green Island	69
20.	River sampling sites, sampling frequencies and analyses carried out	71
21.	Summary statistics for concentrations of dissolved nutrients and particulate matter measured contemporaneously at three sites in the Herbert River.....	86
22.	Summary statistics for four water quality constituents sampled contemporaneously in eight north Queensland rivers between 1989 and 1991	87
23.	Estimated nitrogen and phosphorus inputs from gauged rivers discharging into the Cairns and Tully boxes.....	99
24.	Dissolved nutrients in rainfall collected at sites throughout the GBR and western Coral Sea	106
25.	Empirical relationships derived for estimating volumes of Subtropical Lower Water and stocks of nitrate and phosphate intruded onto the shelf in the Cairns and Tully boxes from measured near-bottom shelfbreak water temperatures	109
26.	Estimates of gross and net nitrogen and phosphorus inputs to outer-shelf waters of the Cairns and Tully boxes from intrusions during the summers of 1989-90, 1990-91 and 1991-92	113
27.	Preliminary estimates of nitrogen fixation by <i>Trichodesmium</i> in the Cairns and Tully boxes.....	115

28.	Mean daily deposition rates of carbon, nitrogen and phosphorus on a cross-shelf transect seaward of the Family Islands	123
29.	Estimated annual organic nutrient sedimentation rates in the Cairns and Tully boxes.....	141
30.	Daily benthic nutrient excretion rates used to estimate benthic nutrient recycling.....	142
31.	Estimated annual shelf-scale benthic nutrient fluxes for the Cairns and Tully boxes.....	143
32.	Water column primary production rates off Cairns during November-December 1990.....	148
33.	Summary statistics for depth-averaged zooplankton biomass in the Cairns and Tully boxes	150
34.	Summary statistics for areal zooplankton standing crop in the Cairns and Tully boxes.....	151
35.	Estimates of water column nitrogen and phosphorus mineralization by macro- and microzooplankton in the Cairns box	153
36.	Estimates of water column nitrogen and phosphorus mineralization by macro- and microzooplankton in the Tully box	154
37.	Estimates of water column nitrogen mineralization by heterotrophic microbes in the Cairns and Tully boxes.....	155
38.	Estimates of mean seasonal replacement times (days) for water column stocks of ammonium, DIN, DON and PON in the Cairns and Tully boxes based on <i>in situ</i> mineralization rates of Hopkinson et al. (1987)	157
39.	Calculated water column stocks of biogeochemically active nitrogen and phosphorus in the Cairns and Tully boxes and estimated annual fluxes of nitrogen and phosphorus through major sources and sinks and within major water column recycling pools.....	161

FIGURES

1.	The central Great Barrier Reef and the shelf boxes covered for budgeting purposes	6
2.	Top: Reef area < 2 m deep estimated from satellite imagery in relation to total reef area for 209 reefs throughout the GBR. Middle: Area of reefs classified as hard substrate < 2 m deep in relation to total classified reef area. Bottom: Area of reefs classified as sand < 5 m deep in relation to total classified reef area.....	8
3.	Top: The proportion of reef area classified as hard substrate < 2 m deep in relation to total classified reef area. Bottom: The proportion of reef area classified as sand < 5 m deep in relation to total classified reef area.....	9

4.	Locations of hydrographic stations used to develop the nutrient budget.....	11
5.	Locations of transect stations in the Cairns box resampled ten times between February 1989 and July 1991	12
6.	Major rivers discharging into or adjacent to the Cairns and Tully boxes	14
7.	Top: Zones (shaded boxes) where free-drifting sediment traps were deployed in the Cairns box between May 1990 and July 1991. Bottom: Transect sites off the Family Islands where moored sediment traps were deployed between September 1988 and August 1989.....	15
8.	Location of stations where water column primary production measurements were made between January 1983 and December 1990	16
9.	Schematic depiction of the water column nitrogen budget.....	19
10.	Schematic depiction of the water column phosphorus budget.....	20
11.	Carbon and nitrogen as a percentage of dry weight for zooplankton samples net collected in the Great Barrier Reef between 1983 and 1992	22
12.	Bottom: Cross-shelf section through a cold-water intrusion into Palm Passage during January 1983. Top: The same intrusion event masked with the bathymetry down the central axis of Grafton Passage	28
13.	Temperature-salinity plots for water masses in Palm Passage on three occasions during the summer of 1983	29
14.	Representative seasonal temperature-salinity relationships from a station in the East Australian Current, immediately seaward of Palm Passage	31
15.	Mean cross-shelf bathymetric profiles for the Cairns and Tully boxes in comparison to the cross-shelf bathymetry down the central axis of Palm Passage.....	32
16.	Temperature-inorganic nutrient relationships from stations in the East Australian Current during 1983.....	33
17.	Moored sediment trap array used to collect sedimenting carbon, nitrogen and phosphorus in the Cairns and Tully boxes	35
18.	Free-drifting sediment trap array used to collect sedimenting carbon, nitrogen and phosphorus in the Cairns box	38
19.	Comparisons between calculated sedimentation fluxes of particulate carbon, nitrogen and phosphorus using drifting and moored sediment traps in simultaneous deployments at the same site.....	39
20.	Cross-shelf gradients and seasonal changes in depth-weighted mean water column concentrations of ammonium, nitrite and nitrate in the Cairns and Tully boxes	45
21.	Cross-shelf gradients and seasonal changes in depth-weighted mean water column concentrations of DON, PN and silicate in the Cairns and Tully Boxes	46

22.	Cross-shelf gradients and seasonal changes in depth-weighted mean water column concentrations of phosphate, DOP and PP in the Cairns and Tully Boxes	47
23.	Cross-shelf gradients and seasonal changes in depth-weighted mean water column concentrations of chlorophyll <i>a</i> , phaeophytin and suspended solids in the Cairns and Tully boxes	48
24.	Relationships between depth-weighted mean water column stocks of PN and PP and stocks of chlorophyll <i>a</i> in waters of the Cairns and Tully boxes.....	57
25.	Relationships between depth-weighted mean water column stocks of PN and PP and stocks of suspended solids in waters of the Cairns and Tully boxes	58
26.	Relationships between depth-weighted mean water column stocks of PN and PP in the Cairns and Tully boxes.....	59
27.	Depth-weighted mean water column concentrations of ammonium and nitrite along a transect between Cape Tribulation and Green Island, sampled ten times between February 1989 and July 1991	62
28.	Depth-weighted mean water column concentrations of nitrate and dissolved organic nitrogen along a transect between Cape Tribulation and Green Island, sampled ten times between February 1989 and July 1991.....	63
29.	Depth-weighted mean water column concentrations of phosphate and dissolved organic phosphorus along a transect between Cape Tribulation and Green Island, sampled ten times between February 1989 and July 1991.....	64
30.	Depth-weighted mean water column concentrations of particulate nitrogen and particulate phosphorus along a transect between Cape Tribulation and Green Island, sampled ten times between February 1989 and July 1991	65
31.	Depth-weighted mean water column concentrations of silicate and suspended solids along a transect between Cape Tribulation and Green Island, sampled ten times between February 1989 and July 1991	66
32.	Depth-weighted mean water column concentrations of chlorophyll and phaeophytin along a transect between Cape Tribulation and Green Island, sampled ten times between February 1989 and July 1991	67
33.	Cruise means for depth-weighted mean water column concentration of nitrogen species, phosphorus species and silicate and pigments on the 11 station Cairns box transect	70
34.	Temporal changes in concentrations of dissolved inorganic nitrogen, dissolved organic nitrogen and particulate nitrogen in the lower South Johnstone River during 1990 and 1991 in relation to the temporal pattern of discharge at South Johnstone.....	73
35.	Temporal changes in concentrations of dissolved inorganic phosphorus, dissolved organic phosphorus and particulate phosphorus in the lower South Johnstone River during 1990 and 1991 and their relation to discharge measured at South Johnstone.....	74

36.	Scatter plots showing relationships between measured water column concentrations of individual nutrient species and the contemporaneous discharge rate of the South Johnstone River as measured at South Johnstone	75
37.	Temporal changes in concentrations of dissolved silicate in the lower South Johnstone River during 1990 and 1991 and their relation to discharge measured at South Johnstone.....	76
38.	Top: Relative contributions of dissolved and particulate nitrogen species to total water-borne nitrogen concentrations and fluxes in the South Johnstone River. Middle: Cumulative export of dissolved and particulate nitrogen from the South Johnstone River. Bottom: Cumulative export of total nitrogen from the South Johnstone River in relation to discharge measured at South Johnstone	78
39.	Top: Relative contributions of dissolved and particulate phosphorus species to total water-borne phosphorus concentrations and fluxes in the South Johnstone River. Middle: Cumulative export of dissolved and particulate phosphorus from the South Johnstone River. Bottom: Cumulative export of total phosphorus from the South Johnstone River in relation to discharge measured at South Johnstone.....	79
40.	Temporal and longitudinal changes in concentrations of water-borne dissolved and particulate nitrogen in the Herbert River (1990-1992).....	81
41.	Temporal and longitudinal changes in concentrations of water-borne dissolved and particulate phosphorus in the Herbert River (1990-1992).....	82
42.	Temporal and longitudinal changes in concentrations of water-borne chlorophyll, dissolved silicate and suspended solids in the Herbert River (1990-1992)	83
43.	Functional relationships between particulate nitrogen, particulate phosphorus and suspended solids concentrations at three sites in the Herbert River	85
44.	Temporal and longitudinal changes in concentrations of water-borne nitrogen in relation to daily flow in the Tully River (1988-1992) at sites near the Koombooloomba Dam and the Bruce Highway bridge.....	89
45.	Temporal and longitudinal changes in concentrations of water-borne phosphorus in relation to daily flow in the Tully River (1988-1992) at sites near the Koombooloomba Dam and the Bruce Highway bridge.....	90
46.	Concentrations of particulate phosphorus measured contemporaneously at lower catchment sites under low-flow conditions in eight north Queensland rivers between 1989 and 1992	91
47.	Concentrations of phosphate measured contemporaneously at lower catchment sites under low-flow conditions in eight north Queensland rivers between 1989 and 1992	92
48.	Concentrations of nitrate measured contemporaneously at lower catchment sites under low-flow conditions in eight north Queensland rivers between 1989 and 1992.....	93

49.	Concentrations of suspended solids measured contemporaneously at lower catchment sites under low-flow conditions in eight north Queensland rivers between 1989 and 1992	94
50.	Longitudinal, cross-axial and vertical variability in total dissolved nitrogen and total dissolved phosphorus concentrations in the estuarine section of the Murray River	95
51.	Longitudinal, cross-axial and vertical variability in nitrate and phosphate concentrations in the estuarine section of the Murray River.....	96
52.	Longitudinal, cross-axial and vertical variability in ammonium and silicate concentrations in the estuarine section of the Murray River.....	97
53.	Mean monthly rainfall measured at Green Island (1949-1990) and Fitzroy Island (1962-1990).....	101
54.	Frequency distributions of measured ammonium and silicate concentrations in rainwater collected at AIMS and in the western Coral Sea (GBR included)	102
55.	Frequency distributions of measured nitrate and nitrite concentrations in rainwater collected at AIMS and in the western Coral Sea (GBR included).....	103
56.	Frequency distributions of dissolved inorganic nitrogen and phosphate concentrations in rainwater collected at AIMS and in the western Coral Sea (GBR included).....	104
57.	Frequency distribution of DIN/DIP ratios in rainwater collected at AIMS and in the western Coral Sea (GBR included).....	105
58.	Calculated volumes of undiluted Subtropical Lower Water per linear metre of shelf in the Cairns and Tully boxes in relation to (Top) calculated bottom water temperature at 58 m near Euston Reef and (Bottom) the calculated near-surface to bottom temperature difference at the shelfbreak near Euston Reef.	108
59.	Calculated volumes percentages of undiluted Subtropical Lower Water per linear metre of shelf in the Cairns and Tully boxes in relation to (Top) calculated bottom water temperature at 58 m near Euston Reef and (Bottom) the calculated near-surface to bottom temperature difference at the shelfbreak near Euston Reef.	109
60.	Calculated net charges in nitrogen (Top) and phosphorus (Bottom) stocks per linear metre of shelf in the Cairns and Tully boxes in relation to calculated shelfbreak bottom water temperatures near Euston Reef.....	111
61.	Near-bottom shelfbreak water temperatures recorded near Euston Reef (58 m depth) near the seaward end of Grafton Passage	112
62.	Near-bottom shelfbreak water temperatures recorded near Norman Reef (58 m depth) near the seaward end of Trinity Opening	112
63.	Seasonal and day-to-day variability in gross sedimentation measured with moored sediment traps on a cross-shelf transect seaward of the Family Islands.....	119

64.	Seasonal and day-to-day variability in gross organic carbon sedimentation measured with moored sediment traps on a cross-shelf transect seaward of the Family Islands.....	120
65.	Seasonal and day-to-day variability in gross organic nitrogen sedimentation measured with moored sediment traps on a cross-shelf transect seaward of the Family Islands.....	121
66.	Seasonal and day-to-day variability in gross particulate phosphorus sedimentation measured with moored sediment traps on a cross-shelf transect seaward of the Family Islands.....	122
67.	Seasonal and day-to-day variability in the percentage of the integrated water column stock of particulate nitrogen collected by moored sediment traps deployed on a cross-shelf transect seaward of the Family Islands	125
68.	Seasonal and day-to-day variability in the percentage of the integrated water column stock of particulate phosphorus collected by moored sediment traps deployed on a cross-shelf transect seaward of the Family Islands	126
69.	N/P ratios (atoms) of particulate material collected by moored sediment traps on a cross-shelf transect seaward of the Family Islands	128
70.	C/P ratios (atoms) of particulate material collected by moored sediment traps on a cross-shelf transect seaward of the Family Islands	129
71.	Scatter plots showing relationships between carbon, nitrogen and phosphorus in material collected by moored sediment traps off the Family Islands	130
72.	Top: Gross sedimentation fluxes measured in nearshore waters of the Cairns box with free drifting sediment traps. Bottom: Calculated percentages of the water column stock of suspended particulates sedimenting daily	131
73.	Top: Gross sedimentation fluxes of particulate organic carbon in nearshore waters of the Cairns box with free drifting sediment traps. Bottom: Gross sedimentation fluxes of particulate organic carbon in mid- and outer-shelf waters of the Cairns box	132
74.	Top: Particulate nitrogen sedimentation fluxes measured in nearshore waters of the Cairns box with free drifting sediment traps. Bottom: Calculated percentages of the water column stock of particulate nitrogen sedimenting daily.....	133
75.	Top: Particulate phosphorus sedimentation fluxes measured in nearshore waters of the Cairns box with free drifting sediment traps. Bottom: Calculated percentages of the water column stock of particulate phosphorus sedimenting daily	134
76.	Day-to-day and between-cruise variability in atomic ratios between carbon, nitrogen and phosphorus in material collected by free-drifting sediment traps in nearshore waters of the Cairns box.....	135
77.	Top: Gross sedimentation fluxes measured in mid- and outer-shelf waters of the Cairns box with free-drifting sediment traps. Bottom: Calculated percentages	

	of the water column stock of suspended particulates sedimenting daily	137
78.	Top: Particulate nitrogen sedimentation fluxes measured in mid- and outer-shelf waters of the Cairns box with free-drifting sediment traps. Bottom: Calculated percentages of the water column stock of particulate nitrogen sedimenting daily	138
79.	Top: Particulate phosphorus sedimentation fluxes measured in mid- and outer-shelf waters of the Cairns box with free-drifting sediment traps. Bottom: Calculated percentages of the water column stock of particulate phosphorus sedimenting daily	139
80.	Day-to-day and between-cruise variability in atomic ratios between carbon, nitrogen and phosphorus in material collected by free-drifting sediment traps in mid- and outer-shelf waters of the Cairns box	140
81.	Calculated annual inputs of nitrogen and phosphorus to the Cairns box.....	159
82.	Calculated annual inputs of nitrogen and phosphorus to the Tully box	160
83.	Calculated stocks of nitrogen and phosphorus in the Cairns box in relation to system-scale input, export and recycling fluxes where they could be measured or estimated	162
84.	Calculated stocks of nitrogen and phosphorus in the Tully box in relation to system-scale input, export and recycling fluxes where they could be measured or estimated	163

SUMMARY

Shelf-scale budgets were developed for the nutrient elements nitrogen (N) and phosphorus (P) in the central Great Barrier Reef between Cape Tribulation (16°S) and Dunk Island (ca. 18°S). The intent was to quantify:

- 1) stocks of nutrients (nitrogen (N), phosphorus (P) and silicon (Si)) naturally occurring in central Great Barrier Reef waters;
- 2) natural gradients and variability in water column nutrient concentrations;
- 3) natural fluxes of nutrients into and out of shelf waters for comparison with anthropogenic or anthropogenically affected nutrient sources.

Based upon features of shelf geometry and differing patterns of development on the adjoining coastal plain, the shelf was divided into two boxes, a northern box between Cape Tribulation and Cape Grafton (the **Cairns box**: area = 5940 km², volume = 197 km³) and a southern box between Cape Grafton and Farquharson Reef (the **Tully box**: area = 7830 km², volume = 312 km³).

Stocks of dissolved and particulate nutrients in the two boxes were estimated from the results of extensive hydrographic sampling within and immediately adjacent to the boxes. The concentration data was partitioned by season (Summer: October-April, Winter: May - September) and cross-shelf (depth) location. Mean concentrations of a number of individual nutrient species varied significantly between seasons. Regardless of season, however, the highest concentrations of individual nutrient species generally occur near the coast (depth < 20 m), but these shallow waters contribute relatively little to total shelf nutrient stocks because of their relatively small volume (< 5 percent of shelf volume). Most water column nutrients reside on the outer shelf (> 30 m depth) because of the greater volume of water.

Dissolved organic nitrogen (DON = 50,100 metric tonnes) is, by far, the largest water column nitrogen pool (ca. 80 percent of total water column nitrogen), followed by particulate nitrogen (PN = 10,300 m.t.) and ammonium (NH₄ = 1,400 m.t.). Nitrate (NO₃) and nitrite (NO₂) stocks are very small (< 300 m.t.) in comparison. Phosphorus stocks are more evenly divided between phosphate (PO₄ = 2,200 m.t.), dissolved organic phosphorus (DOP = 5,000 m.t.) and particulate phosphorus (PP = 1,600 m.t.).

System-level inputs of nitrogen and phosphorus from rivers (7,000 and 700 metric tonnes. p.a., respectively), rainfall (2,700 and 160 m.t. p.a.) and shelfbreak upwelling (1,200-4,000 and 400-1,000 m.t. p.a.) were quantified from the results of field sampling programs. Sedimentation (= resuspension) fluxes of nitrogen and phosphorus (657,000 and 62,000 m.t. p.a.) were measured with sediment traps. Nitrogen and phosphorus inputs from sewage (400 and 110 m.t. p.a.), benthic mineralization (39,000 and 12,000 m.t. p.a.), atmospheric nitrogen fixation by coral reef cyanobacteria (1,400 m.t. p.a.) and *Trichodesmium* (4,600-213,000 m.t. p.a.), microzooplankton nitrogen and phosphorus excretion (21,000 and 2,700 m.t. p.a.) and mineralization of organic nitrogen by microbial communities (173,000 m.t. p.a.) were estimated using literature sources, locally collected data and appropriate regional studies. Phytoplankton nitrogen and phosphorus demand (277,000 and 38,000 m.t. p.a.) were estimated from regional measurements of primary production. Only indirect estimates could be made for removal of nitrogen and phosphorus through burial in sediments and sediment denitrification. No estimate could be made for cross-shelf mixing rates of water-borne nutrients. For a variety of reasons, there are very considerable uncertainties in estimates of the magnitude of atmospheric nitrogen fixation by *Trichodesmium* and shelf sediments.

Total external inputs of both nitrogen (17,000+ m.t. p.a.) and phosphorus (1400+ m.t. p.a.) are small relative to natural nitrogen and phosphorus recycling fluxes (>200,000 and >>15,000 m.t. p.a.) on the shelf. In particular, large vertical exchanges of detrital and/or inorganic carbon, nitrogen and phosphorus take place between the water column and benthos through resuspension and (re-)deposition of particulate materials. Microbially mediated recycling (water column and benthic) supplies 80-90 percent of phytoplankton demand for nitrogen, and likely a similar percentage of phosphorus, though at present no appropriate information is available for estimating local microbial phosphorus mineralization. Overall, external inputs of nitrogen likely contribute < 10 percent of natural phytoplankton nitrogen demand. For phosphorus, external inputs contribute on the order of 2 percent of estimated demand.

Direct human inputs of nitrogen and phosphorus through sewage discharge (< 30 and < 5 m.t. p.a., respectively) are currently very small relative to natural nutrient inputs. River inputs of nitrogen and phosphorus comprise a large proportion of external inputs, but are still small relative to internal recycling fluxes. Data on riverine inputs of nitrogen and phosphorus are currently inadequate to reliably partition river nutrient inputs into natural and anthropogenic (e.g. fertilizer and land-use related) components. A very large percentage of annual nutrient inputs from rivers are delivered by flood events within relatively short intervals (days - 2 weeks). Sediment and nutrient delivery during these events are still poorly sampled in most north Queensland rivers.

Variability in measured water-column nutrient, phytoplankton biomass and suspended solids concentrations are large relative to mean ambient concentrations. The detection of spatial and temporal trends will require a long-term commitment to the collection of data sets covering regional spatial scales.

Although nutrient levels are currently low in central Great Barrier Reef waters and external inputs are small relative to natural fluxes and stocks, our understanding of ecosystem behaviour is still not developed to the extent that the assimilative capacity of the central Great Barrier Reef for enhanced nutrient inputs can be predicted with any certainty. Caution is therefore advised in the management of nutrient inputs to Great Barrier Reef waters to ensure the conservation of the reef in perpetuity.

1. INTRODUCTION

This report summarizes an attempt by the Australian Institute of Marine Science (AIMS) Biological Oceanography Group to quantify the major natural pools and fluxes of the nutrient elements nitrogen (N) and phosphorus (P) in shelf waters of the central Great Barrier Reef Marine Park between Cape Tribulation (16°S) and Dunk Island (18°S). This latitudinal section of the Marine Park lies adjacent to coastal and hinterland regions with long established, but still expanding, agricultural land use and a rapidly developing coastal/rural/urban infrastructure focused upon lifestyle and reef-based tourism. An unquantified perception (Baldwin, 1990) exists that incremental increases in nutrient and sediment runoff from coastal watersheds to the adjacent marine park are having, or will have, a detrimental effect on water quality within the Marine Park. This change in water quality would, in turn, adversely affect the reef and coastal ecosystems of the Marine Park. In order to rigorously assess the impact of any anthropogenic changes to the inputs of sediments, nutrient and pollutant materials to Marine Park waters, it is first essential to understand the natural sources, pools and fluxes of these materials within the Great Barrier Reef (**hereafter GBR**) ecosystem and the natural levels of variability at both the local and regional scales that would affect local observations of trends in water quality.

What is the relationship between nutrients, water quality and ecosystem status in the Great Barrier Reef ecosystem? Nutrients are the material currency of ecosystem structure and function. The total amount (standing stock) of nutrients biogeochemically active within a system set a limit to ecosystem biomass through the natural stoichiometric ratios between the elements (C, N, P, S, Si, Fe, Cu etc.) from which all living things are made (e.g. Redfield et al., 1963). The growth rate, physiological state and reproductive potential of most marine organisms, particularly micro-organisms, are in turn closely coupled to their biochemical composition (e.g. Droop, 1974; Goldman, 1980; O'Connor, 1992). Trophic relationships within ecosystems are essentially about the acquisition and processing of nutrients and the energy associated with them. After carbon (C) which is present in abundance in seawater, nitrogen (N) and phosphorus (P) are the two most important structural elements required by all pelagic and reef associated plants and through them, the animals. By mass, nitrogen and phosphorus are the major nutrient elements exported to the GBR from human sources. The budgeting activity described herein will therefore focus upon nitrogen and phosphorus, including other elements (e.g. silicon) as relevant.

The concentrations and availability of nitrogen and phosphorus directly and indirectly affect plankton biomass and the perceived "quality" of GBR shelf waters, and through both direct and indirect modes of action, the amenity and ecological status of the coral reefs immersed within them. At the most direct level, Kinsey and Davies (1979) have shown that elevated phosphorus inputs to coral reef systems simultaneously stimulate organic production and reduce net system calcification rates. Dissolved nutrient materials are directly taken up by planktonic algae and other micro-organisms which convert them to particulate organic matter, which in turn reduces the water clarity generally associated with coral reef systems and their perceived amenity value. High nutrient concentrations further stimulate the growth of benthic algae which both competes with hard corals for space (Smith et al., 1981) or may provide additional substrate for grazers which physically destroy the reef surface (Steneck, 1989) and substratum (e.g. Hein and Risk, 1975).

It has been suggested (Bell and Gabric, 1990, 1991) that nutrient-related changes in water quality have already taken place within the GBR ecosystem. These suggestions are based upon a sparse data set (Walker, 1991) that is difficult to integrate and evaluate objectively. The difficulties in resolving the ambiguities have led to controversy (Bell and Gabric, 1990, 1991; Kinsey, 1991a; Hopley et al., 1991; Walker, 1991).

From a management perspective, two straightforward questions can be distilled from the complex issues related to nutrients, nutrient loading and the status of the GBR ecosystem:

Are human-related or terrestrial inputs of nutrients and other materials which influence water quality large or small relative to natural inputs and fluxes of those materials within the system of interest?

Can local or regional trends in water quality status tied to nutrient inputs be identified within the scope of natural system variability?

It is important to remember that “water quality” is a political or management concept. Ecosystems will change quite naturally over a range of time scales in response to both acute and chronic changes in nutrient loading rates and sedimentation regimes. Such changes are and have been part of the normal evolutionary process of marine ecosystems. It is the human definition of a desired or perceived ecosystem state that requires a definition of water quality believed to be associated with the maintenance of that state. Several workers (Tomasik and Sanders, 1985; Bell et al., 1989) have attempted to define nutrient-related standards of water quality relevant to the health of corals or coral reefs. These suggested standards are yet to be rigorously tested for natural reef communities in the GBR ecosystem and such a judgement is beyond the scope of this study. While objective criteria may be set to define a state of water quality, the setting of these criteria is ultimately subjective and must be linked to a particular management objective.

There is good evidence at both local and system scales (e.g. Kinsey and Domm, 1974; Wood and Johannes, 1975; Smith et al., 1981; Hatcher et al., 1989) that enhanced, unnatural inputs of sediments and/or nutrients to coral reef ecosystems will result in changes to individual classes of reef organisms and to the degradation of the biological condition of reefs in general. These effects can be direct, through inhibition of calcification (Kinsey and Domm, 1974) and/or smothering of hard corals (Smith et al., 1981), or indirect, through alteration of reef trophic structure to the detriment of the previously dominant hard corals (Smith et al., 1981). Nutrient materials, particularly those coming from terrestrial sources, are rarely added to the ecosystem in pure form, in ratios optimal for reef communities (Atkinson, 1989; Atkinson and Smith, 1983) or without extraneous materials detrimental to reef communities. In most cases, inorganic nutrient inputs from terrestrial sources are accompanied by inputs of fresh water, suspended sediments and organic matter which can adversely affect reef communities at the same time.

The nutrient budgets presented herein will not be complete or closed. Time did not permit the direct measurement of a number of important processes (e.g. microbial mineralization of nitrogen and phosphorus in the water column, denitrification in sediments) or a complete resolution of spatial and temporal variability for a number of key processes (e.g. organic sedimentation). If anything, this study has illustrated the tremendous gaps in our knowledge of nutrient inputs, cycling and outputs in tropical shelf systems, the difficulty in accurately quantifying nutrient processes at the system scale and the magnitude of variability at all system levels which confounds interpretation of environmental data sets.

2. THE STUDY AREA

The approach taken in this study is to quantify or estimate nutrient pools within and fluxes into or out of two arbitrarily defined boxes encompassing a contiguous section of the central GBR shelf: a northern box (hereafter the **Cairns box**; 16° 5' - 16° 52.5'S) between Cape Tribulation and Cape Grafton, and a southern box (hereafter the **Tully box**; 16° 52.5' - 17° 55'S) between Cape Grafton and Dunk Island (Figure 1). The Cairns box covers a north-south distance of approximately 88 km while the Tully box is 116 km in north-south length. Each box is taken to extend from the coastline to the shelfbreak (100 m isobath). For specific calculations, estimations of nutrient stocks and fluxes will also be made for thin (ca. 1 m wide) sections normal to the coast or smaller areas (e.g. per m²) appropriate to the scale of sampling and measurement. Wherever possible, calculations will be extrapolated to the full areas of the two boxes. Time periods of interest for rates are either per day or per year.

There are several reasons for dealing with nutrient processes within sections of the shelf (boxes). First, terrestrial inputs are derived from both point and diffuse sources along an extended length of the coast. These inputs can be most reasonably averaged over a larger area. Nutrient processes associated with reefs are also most conveniently area-averaged over larger areas, rather than a m² or a narrow latitudinal basis. While adjacent to each other, the two boxes front coastlines with different levels of riverine freshwater input, agricultural land use and development. There is a well agriculturalized coastal plain adjoining the Tully box, while the coastal plain adjacent to much of the Cairns box is relatively narrow or absent. The Cairns box is the site of extensive urban, suburban and semi-rural development. The Cairns coastal region now supports a permanent population on the order of 98,000 people and continues to grow. In contrast, agricultural development still overwhelmingly predominates in the watersheds adjacent to and feeding into the Tully box.

Computed area and volume statistics for the two boxes are given in Table 1. Areas between defined isobaths were estimated from navigational charts by trapezoidal integration of polygons within narrow latitude bands (5'). Shelf water volumes were estimated by ruling a series of parallel lines normal to the shelfbreak between Cape Tribulation and Farquharson Reef, NE of Dunk Island. The distances of defined isobaths (5, 10, 20, 30, 40, 50, 60 m) from the coast along each cross-shelf line were then measured. Areas of the individual cross shelf sections were determined by trapezoidal integration. Volumes between adjacent sections were calculated from the mean areas of the two adjacent sections and the mean horizontal distance between the sections. An estimation of the volume displaced by reefs was made by subtracting the area of reefs as given in the Great Barrier Reef Marine Park Authority (GBRMPA) Reef Gazetteer within each box, multiplied by the approximate mean depth of the outer shelf (ca. 40 m).

The width of the continental shelf varies considerably within the two sections. The shelf is narrowest (42 km) off Cape Tribulation, increasing to 57 km in width off Cairns and then to 81 km seaward of Dunk Island at the southern end of the Tully box. South of Dunk Island the shelf widens quickly. The increasing width of the shelf south of Dunk Island and poor depth charting on the wide outer shelf made volume and area estimates for the Dunk Island-Farquharson Reef line difficult to quantify or connect with terrestrial processes. To avoid the added complexity of shelf bathymetry near Hinchinbrook Island, the southern boundary of the Tully box was defined at Farquharson Reef to give the Tully box a tractable size and shape.

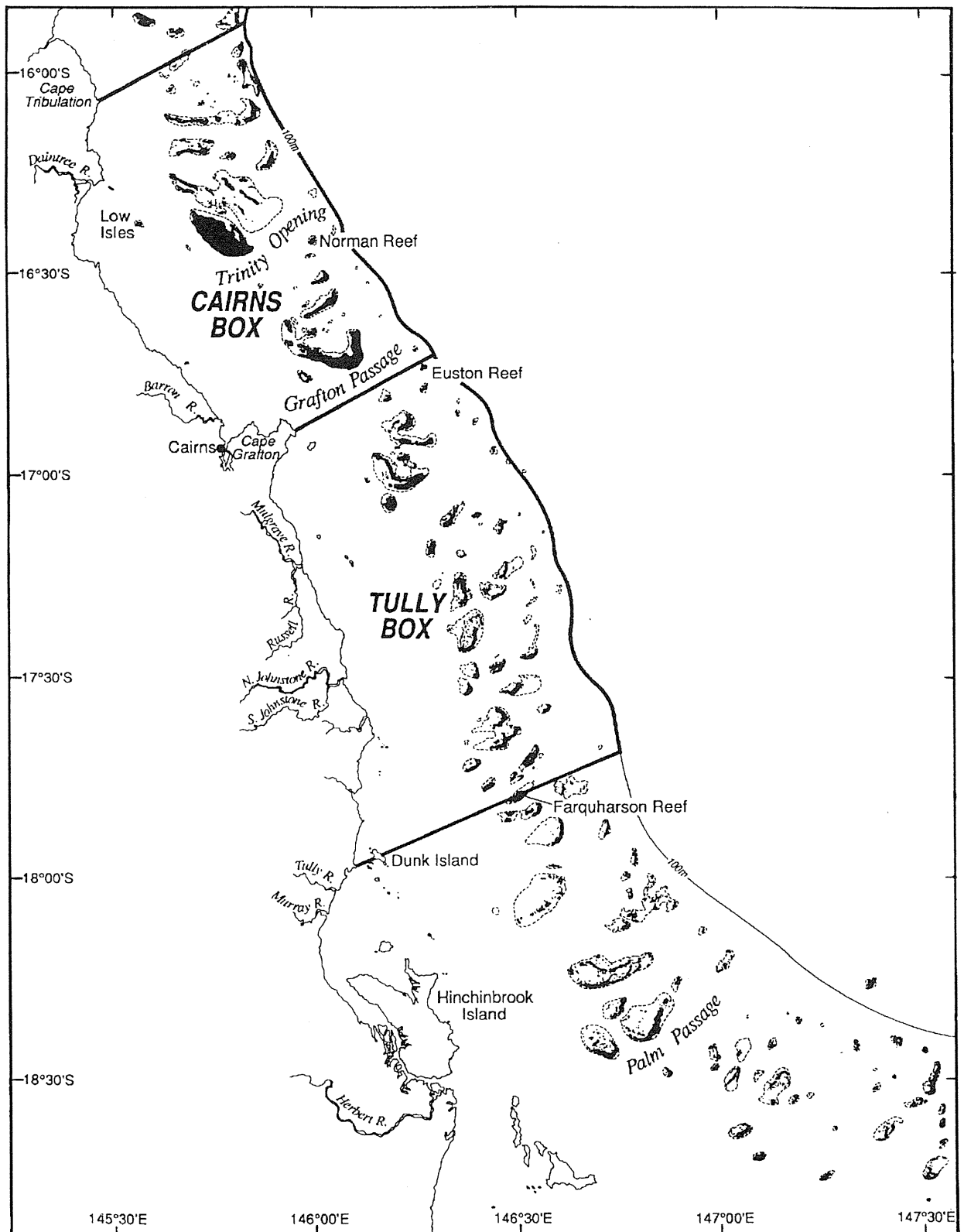


Figure 1. The central Great Barrier Reef and the shelf boxes covered for budgeting purposes. Near-bottom temperature recorders were deployed near Euston Reef and Norman Reef to collect long-term records of shelfbreak water temperatures.

Table 1. Shelf areas and volumes of water between isobaths on the central GBR shelf. Volumes estimates include a correction for the displaced volumes of reefs. Volumes in italics are percentages of the total areas or volumes given for the sections.

	0-10 m	10-20 m	20-30 m	30-100 m	Total
Area (km ²)					
Cape Tribulation to Cape Grafton	377	636	856	4068	5937
	<i>6.4</i>	<i>10.7</i>	<i>14.4</i>	<i>68.5</i>	
Cape Grafton to Farquharson Reef	310	535	1306	5675	7826
	<i>4.0</i>	<i>6.8</i>	<i>16.7</i>	<i>72.5</i>	
Volume (km ³)					
Cape Tribulation to Cape Grafton	1.9	10.9	20	164	197
	<i>1.0</i>	<i>5.5</i>	<i>10.3</i>	<i>83.2</i>	
Cape Grafton to Farquharson Reef	1.5	8.5	31	271	312
	<i>0.5</i>	<i>2.7</i>	<i>10.0</i>	<i>86.8</i>	

Most of the coral reefs in both boxes are free-standing platform reefs on the outer half of the continental shelf in water depths exceeding 30 m. A small number of coastal fringing reefs occur in both boxes. The areas of the outer-shelf platform reefs in the Cairns and Tully boxes are estimated to be 724 and 731 km², respectively (GBRMPA Reef Gazetteer; Table 2). No explicit estimate was made of the area of coastal fringing reefs in either box, though on a shelf-scale, their contribution to total reef areas is relatively small. Analysis of LANDSAT MSS imagery of a subsample of reefs situated throughout the entire GBR (209 reefs - imagery processing provided by AUSLIG) indicates that reef area < 2 m in depth makes up approximately 18 percent of the total classified area of the sample reefs (Figure 2 Top). Areas classified as hard substrate in the imagery, presumably corals, coral rubble and calcareous algae, comprised 12 percent of total classified reef area (Figure 2 Middle), though the percentage of total area is quite variable for reefs of similar size (Figure 3 Top). The area covered by sand at depths < 5 m averaged 33 percent of total classified reef area (Figure 2 Bottom), again with highly variable percentages for individual reefs (Figure 3 Bottom). Classification of sand cover at depths > 5 m was uncertain, but it is highly likely that the total sand area and percentage of total area are higher. These classifications have not as yet been rigorously ground-truthed using a subsample of the classified reefs. Visual comparisons with aerial photographs and maps indicate the broad categories of depth and shallow cover classification are reasonable as a first approximation.

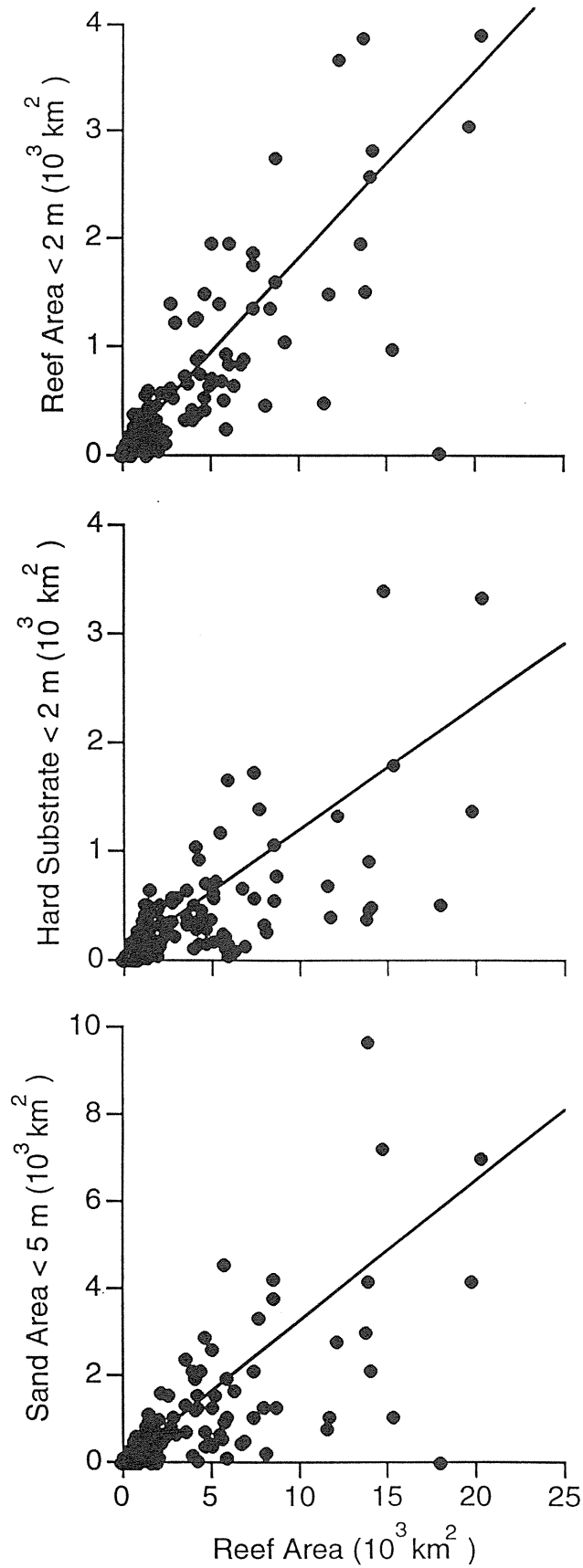


Figure 2. Top: Reef area < 2 m deep estimated from satellite imagery in relation to total reef area for 209 reefs throughout the GBR. Middle: Area of reefs classified as hard substrate < 2 m deep in relation to total classified reef area. Bottom: Area of reefs classified as sand < 5 m deep in relation to total classified reef area. The lines shown are the GM functional regressions (Ricker, 1973).

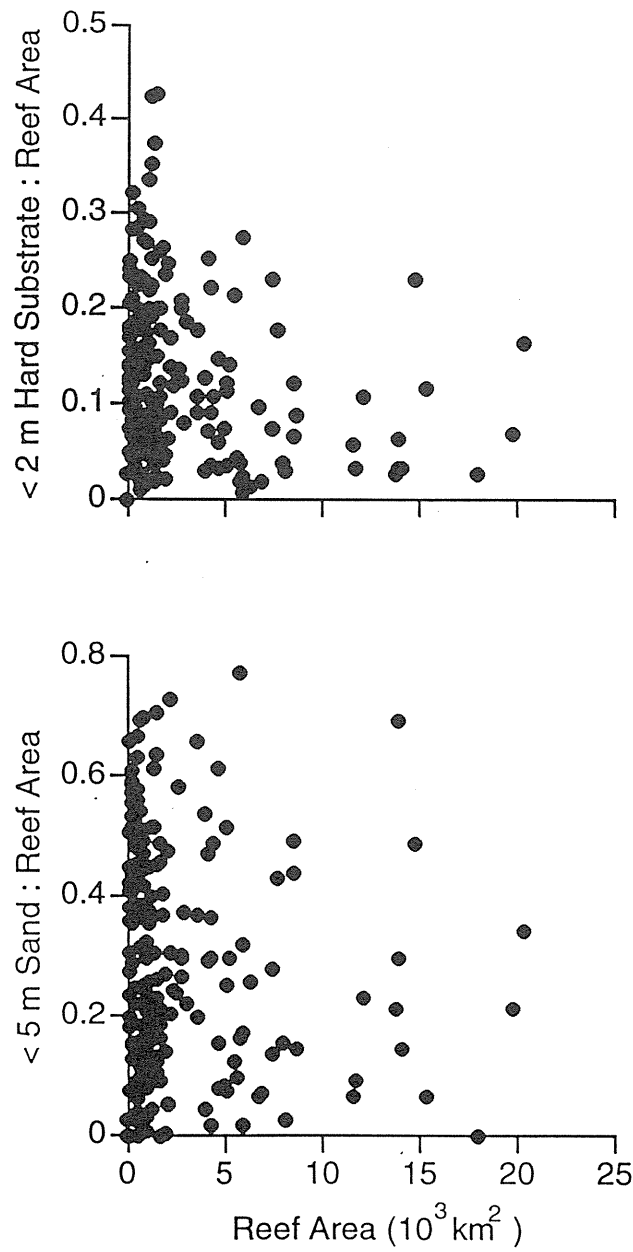


Figure 3. Top: The proportion of reef area classified as hard substrate < 2 m deep in relation to total classified reef area. Bottom: The proportion of reef area classified as sand < 5 m deep in relation to total classified reef area.

Table 2. Areas of reefs in the study area (km²) and the estimated area of reef flat. Area values are summed from the GBRMPA Reef Gazetteer. Reef flat and shallow (< 5 m) sand areas are taken as 18 and 33 percent of total reef area based upon analysis of LANDSAT MSS imagery.

	Total Area	Reef Flat	Shallow Sand
Cape Tribulation to Cape Grafton	724	130	239
Cape Grafton to Farquharson Reef	731	132	241

Approximately 70 percent of shelf area within the two boxes and > 80 percent of estimated water volume (reef corrected) occurs seaward of the 30 m isobath. The obvious implication is that sampling to estimate total shelf stocks of nutrients and the impact of area-specific processes needs to be weighted toward this depth band to resolve both spatial variability and define any subtle spatial gradients present. In contrast, the 10 m isobath encompasses only 4-6 percent of total shelf area, depending on the box considered and no more than 1 percent of total shelf water volume within a particular box. Even though small in area and volume, the shallow coastal depth band directly receives the inputs of nutrient materials from river runoff and urban sewage, and because of its shallow depth, is prone to a greater degree of sediment resuspension from wave action. The residence time of water within the < 10 m depth band is therefore a key consideration in future nutrient budgeting activities.

Figure 4 identifies the location of all hydrographic stations occupied in support of nutrient budgeting for the Cairns and Tully boxes. At several sites, stations were occupied on more than one occasion. In particular, a transect of eleven stations lying along the coast between Cape Tribulation and Cairns, then extending seaward to Green Island, was occupied 11 times during the study period (Figure 5). Over the course of this study (1988-1992), 300+ hydrographic stations were occupied within the Cairns box. For consistency, all hydrographic stations within the Cairns box are designated with the prefix CNS. The situation for the Tully box is somewhat different. Fewer hydrographic stations were occupied within the defined area of the box; however, a considerable number (108) were occupied immediately to the south of the box. Oceanographic conditions on the shelf to the south of the box, particularly along its southern boundary are analogous to those inside the box. The results should therefore be readily transferable to conditions within the Tully box, avoiding complications associated with the wider continental shelf south of Dunk Island and complicated circulation and mangroves around Hinchinbrook Island.

Eighty (80) hydrographic stations were occupied at five sites on a cross-shelf line parallel to, but just south of, the southern boundary of the Tully box (prefix FAM) during 1988 and 1989. The FAM stations are complemented by an earlier series of stations occupied in the same region during 1987-88 (prefixed - COT, n = 28 stations). Wherever appropriate, the FAM and COT stations are considered collectively.

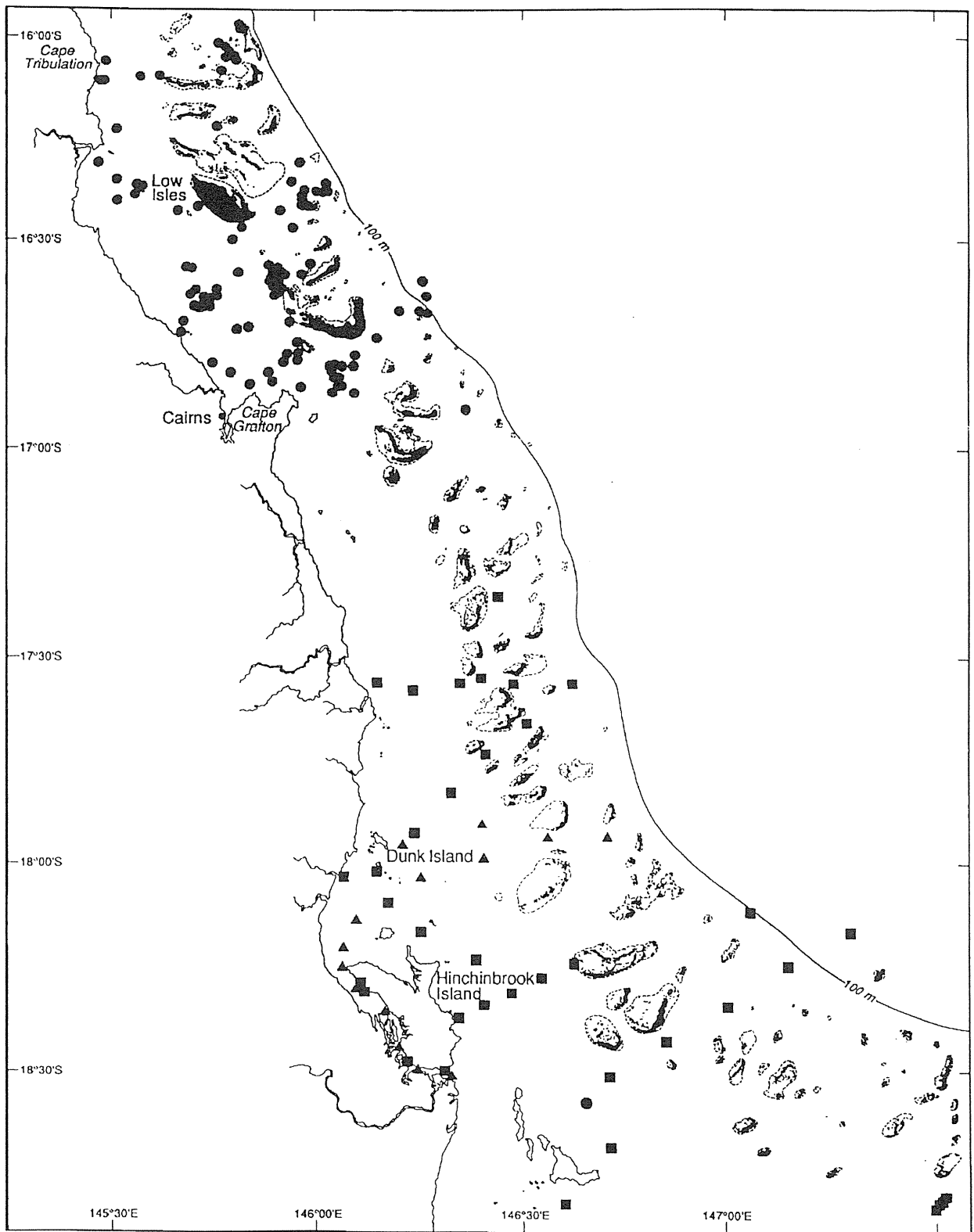


Figure 4. Locations of hydrographic stations used to develop the nutrient budget (● - CNS, ▲ - FAM, ■ - COT).

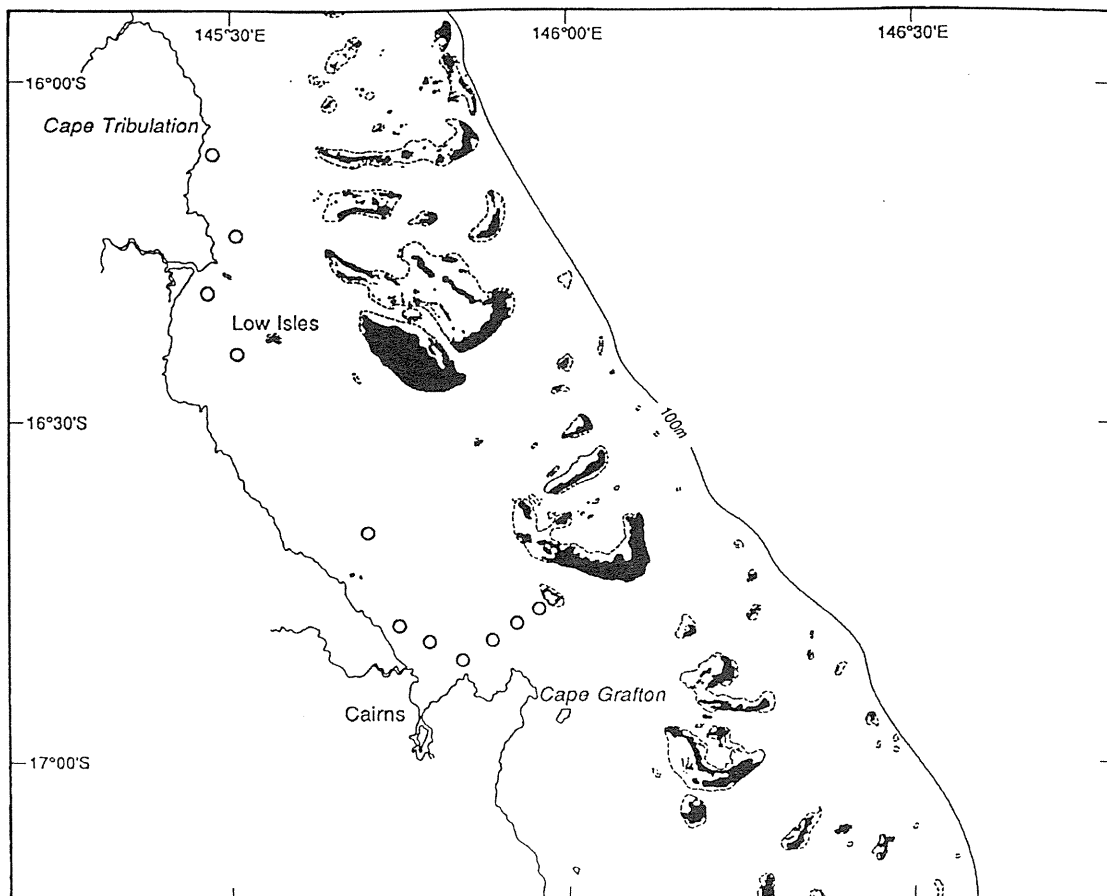


Figure 5. Locations of transect stations in the Cairns box (O) resampled ten times between February 1989 and July 1991.

Four gauged rivers (South Johnstone, North Johnstone, Russell, Mulgrave) discharge directly into the Tully box (Figure 6). Three other regionally significant rivers (Herbert, Murray, Tully) discharge onto the shelf immediately south of the southern boundary of the box. Because of geostrophic forces associated with the buoyancy in the freshwater plumes from these rivers, their waters tend to run northward along the coast and into the Tully box as well. The combined mean discharge of these seven rivers is 11.4 km³ of water per year. In contrast, only two significant gauged rivers (Barron, Daintree) with an average combined discharge of 4.4 km³ per year discharge directly into the Cairns box. Discharge statistics for the rivers in question are summarized in Table 3. The length of gauged periods for individual rivers varies. On a year-to-year basis, total discharge from individual rivers or groups of rivers can vary significantly, particularly in response to variability in heavy rainfall during and after cyclones or incursions of monsoonal low pressure systems (Lough, 1993). During periods of heavy flooding, identifiable plumes of low salinity water from the Burdekin River have also been tracked northward into the Tully box (Wolanski and van Senden, 1983).

Table 3. Mean annual discharges (x 10⁶m³) and ranges for rivers flowing into the Cairns and Tully boxes. Streamflows are obtained from Queensland Water Resources Commission.

River	Watershed km ²	No. Years	Mean	Maximum	Minimum
Cairns box					
Daintree	2125		3560		
Barron	2175	70	839	2611	203
Tully box					
Mulgrave	555	15	766	1537	324
Russell	1475	39	1036	2121	455
No. Johnstone	1940	22	1880	3852	1059
So. Johnstone	555	72	811	1574	200
Tully	1685	14	3119	4973	1632
Murray	1140	17	170	420	52
Herbert	10131	72	3582	11559	468

Sedimentation fluxes of particulate materials and particulate phase nutrients were measured with moored sediment traps over an annual cycle at four sites on a cross-shelf transect parallel to the southern end of the Tully box between September, 1988 and August, 1989 (Figure 7 Bottom). Particulate nutrient sedimentation fluxes in the Cairns box were measured between May, 1990 and July, 1991 with both moored and free-drifting sediment traps. Because of the actions of currents, the drifting sediment traps moved within general areas (Figure 7 Top).

Water column primary production rates used to indirectly estimate phytoplankton nitrogen and phosphorus demand were measured at three sites in Palm Passage during 1983-85 (n= 41 expts.) and at seven (7) sites within the Cairns box during November-December, 1990 (Figure 8).

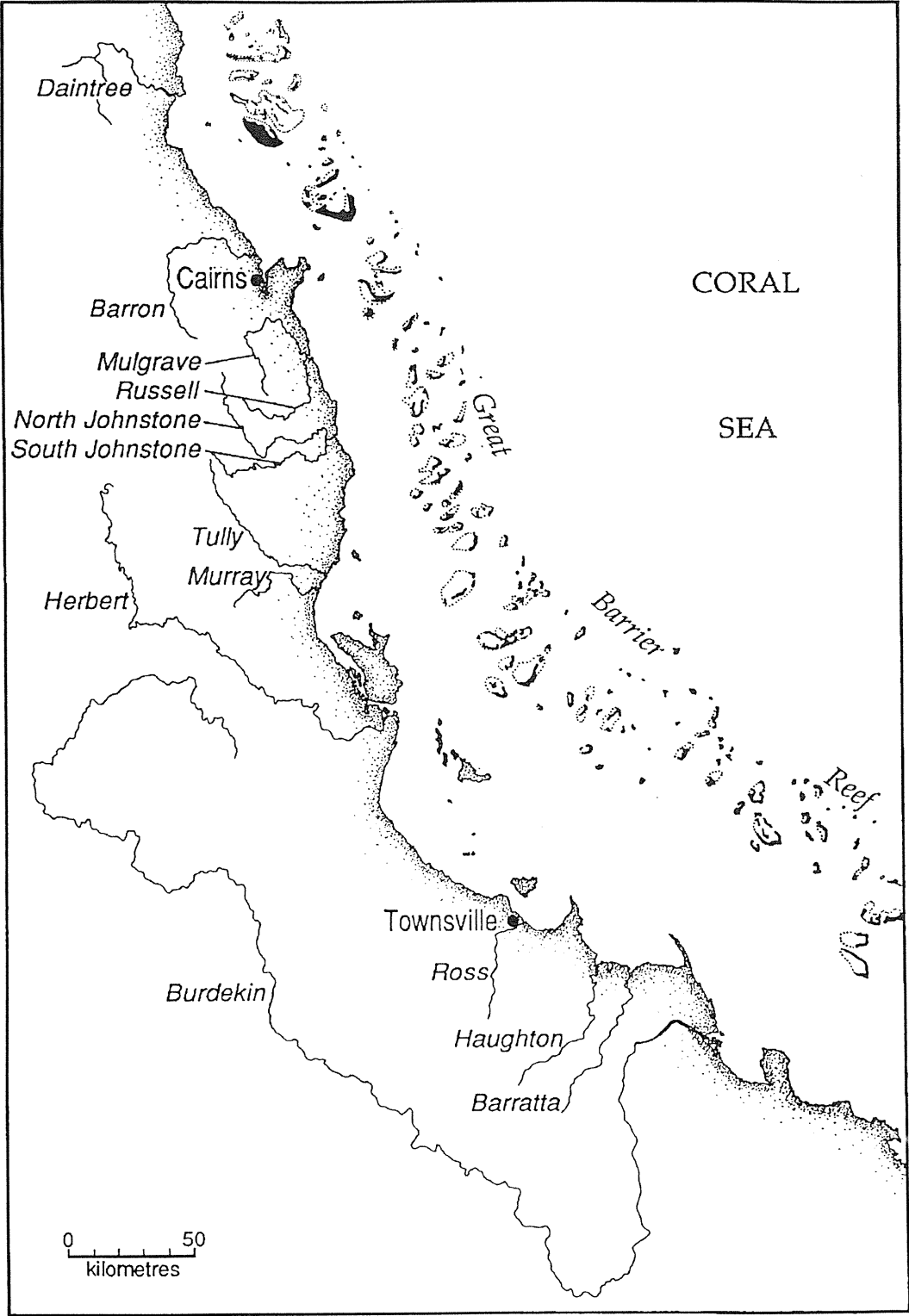


Figure 6. Major rivers discharging into or adjacent to the Cairns and Tully boxes.

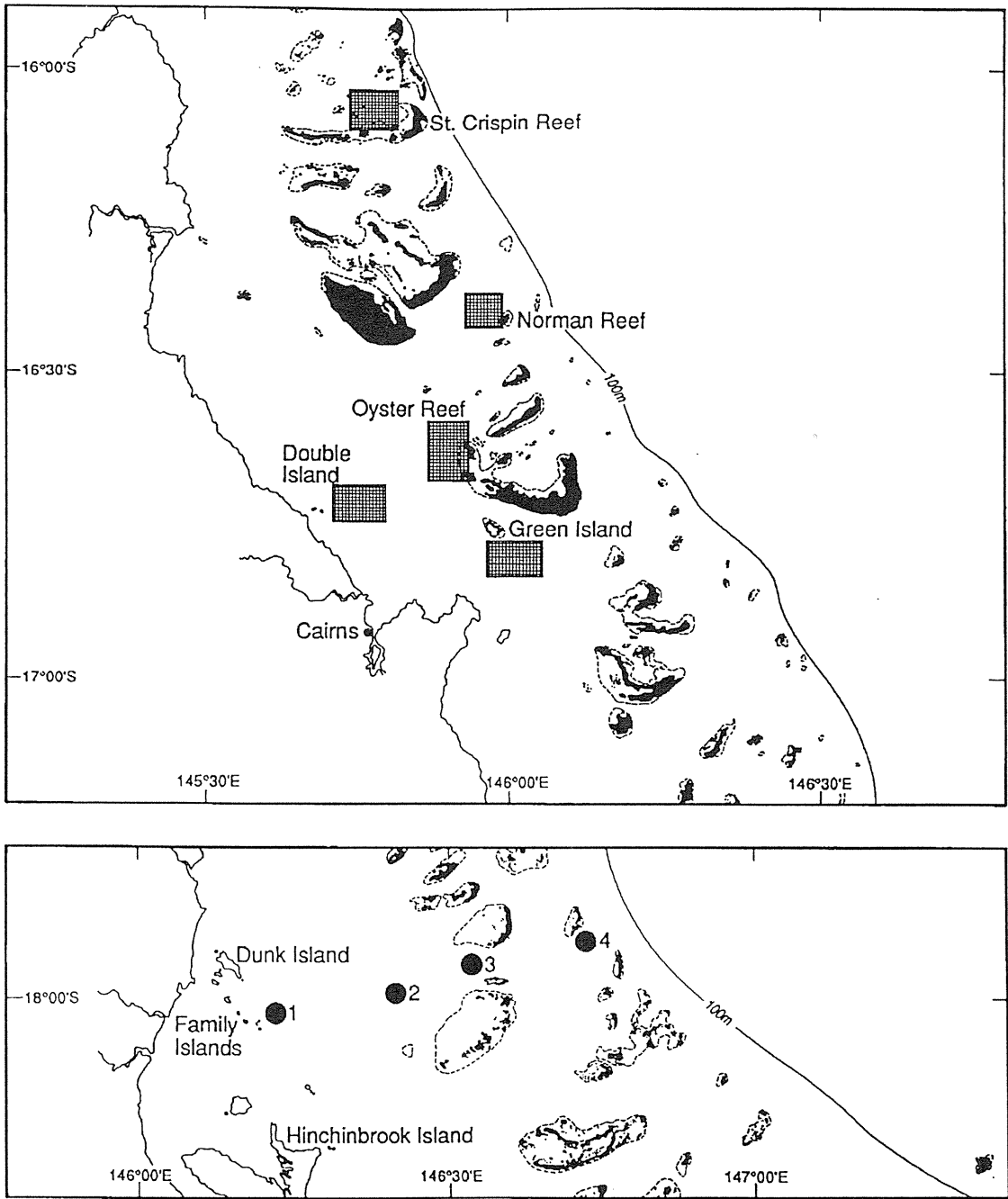


Figure 7. Top: Zones (shaded boxes) where free-drifting sediment traps were deployed in the Cairns box between May 1990 and July 1991. Moored sediment traps were deployed several times in the zones near Green Island and St. Crispin Reef. Bottom: Transect sites off the Family Islands where moored sediment traps were deployed between September 1988 and August 1989.

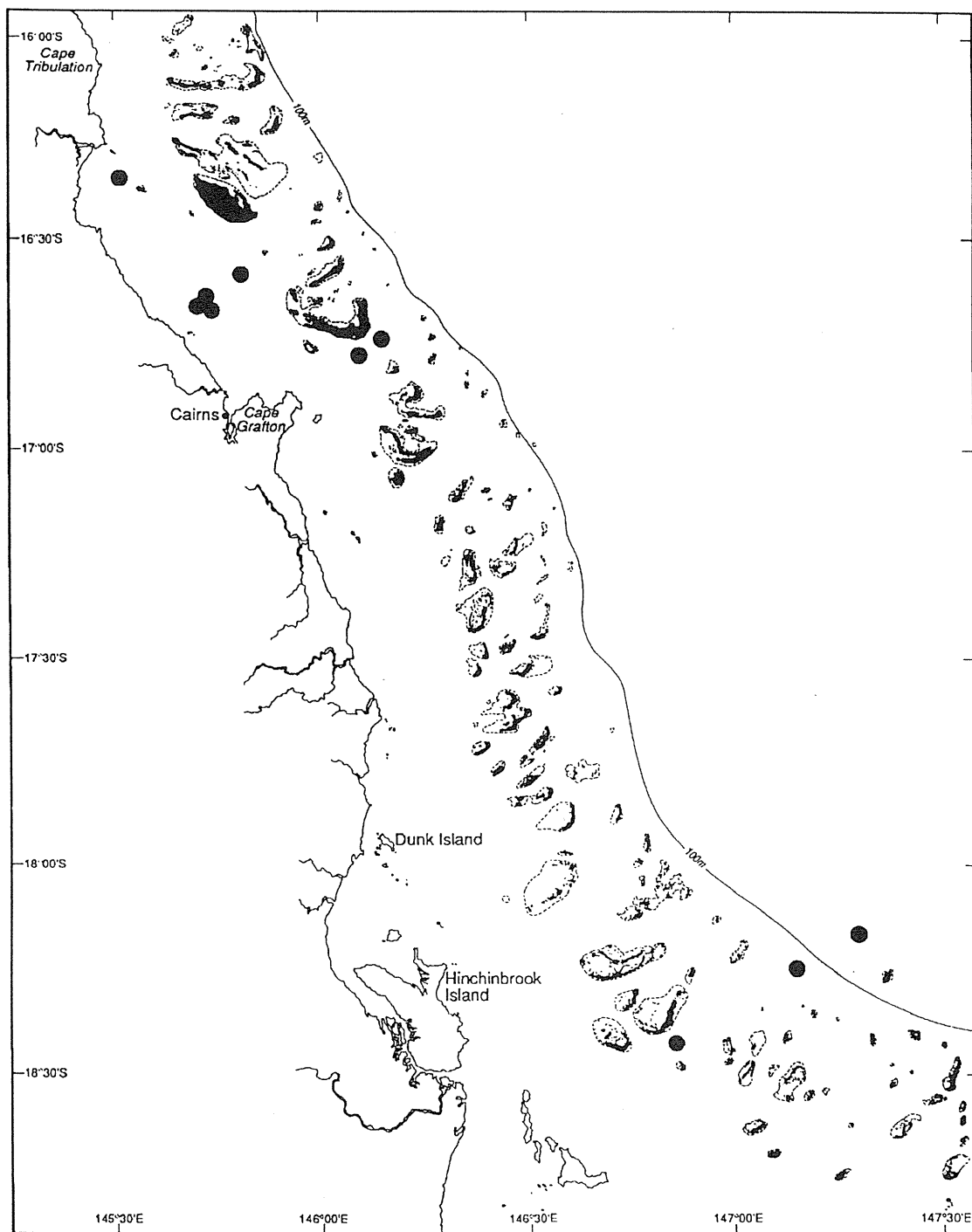


Figure 8. Locations of stations (●) where water column primary production measurements were made between January, 1983 and December, 1990.

3. PHYSICAL OCEANOGRAPHY

While there have been several reviews of physical oceanographic processes in the GBR (Pickard et al., 1977; Andrews and Pickard, 1990; Wolanski, 1991) relatively little is known regarding the detailed behaviour of water currents within the two study boxes (Cresswell and Greig, 1978; Andrews, 1983; Wolanski and Pickard, 1985; Andrews and Furnas, 1986). Few measurements of currents have been made within either the Cairns and Tully boxes. The overwhelming bulk of oceanographic current measurements made to date in the central GBR have been made south of Palm Passage where the shelf is wider and reefs are dispersed. Local flows within the reef matrix are strongly affected by topographic steering around individual reefs, groups of reefs and coastal features (Hamner and Hauri, 1977, 1981; Hamner and Wolanski, 1988; King and Wolanski, 1991; Wolanski, 1983, 1986, 1991). This complexity of flow leads to subtle spatial variability in the distribution of biological and chemical variables (e.g. Wolanski et al., 1989; Liston et al., 1992). However, the magnitude of variability in surface temperature and chlorophyll signals is such that acceptable descriptions of regional distributions can be made from discrete samples (Liston et al., 1992). Cross-shelf tidal currents are generally slower than 20 cm sec^{-1} , (Andrews and Bode, 1988; Wolanski, 1983), with local accelerations as waters are deflected around reefs.

In the absence of winds, geostrophic pressure gradients associated with the East Australian Current (hereafter EAC) drive a southward (poleward) flowing longshore current through the reef matrix. Wolanski and Pickard (1985) showed that current speeds at Green Island were well correlated with regional wind stress. Mean southward residual current velocities on the continental slope average 30 cm sec^{-1} (Burrage et al., 1991). Currents on the shelf may briefly reach 60 cm sec^{-1} , but in most cases are $< 50 \text{ cm sec}^{-1}$ (Wolanski and Pickard, 1985). At this maximal velocity, parcels of water would require 41 and 54 hours, respectively, to pass unimpeded through the Cairns and Tully boxes. Because of the hydrographic impedance of the numerous reefs within each box and the presence of Cape Grafton, it is unlikely that north-south transit times or residence times of water parcels would be this brief. A cross-shelf line of reefs at the northern end of the Cairns box (Undine Reef, St. Crispin Reef) would appear to block significant southerly flow on the outer shelf, though detailed current measurements are needed to confirm this. The presence of terrestrial muds along the northern side of Cape Grafton suggests the presence of a persistent eddy feature in the southern end of the Cairns box.

In shallow waters near the coast, buoyancy effects associated with riverine freshwater inputs and wind stress episodically overcome the southward pressure gradient and drive northward flowing boundary currents along the coast (Wolanski and Pickard, 1985; King and Wolanski, 1991). Tongues of fine terrestrial sediments extend northward from all of the major rivers along the coastal strip. This northerly flow along the coast brings freshwater and nutrients derived from the Herbert, Tully and Murray Rivers into the southern end of the Tully box.

Near-surface exchanges of water between water masses on the outer shelf and EAC, driven by wind stress, tidal currents, internal waves and topographically generated shear (Andrews and Gentian, 1982; Andrews and Furnas, 1986; Wolanski and Pickard, 1983), are at present not adequately quantified on the regional scale and are likely to be highly variable in time and space (Andrews and Furnas, 1986; Wolanski et al., 1988).

4. CONCEPTUAL MODELS OF NUTRIENT POOLS AND FLUXES

Table 4 defines the individual nutrient species which were directly measured and the acronyms for operationally defined nutrient categories used throughout this report.

Table 4. Acronyms and symbols for nutrient species used in this report.

Species		Units
NH ₄	- Ammonium	μM, μmol/litre
NO ₂	- Nitrite	μM, μmol/litre
NO ₃	- Nitrate	μM, μmol/litre
DIN	- Dissolved Inorganic Nitrogen = NH ₄ +NO ₂ +NO ₃	μmol/litre
DON	- Dissolved Organic Nitrogen	μmol/litre
TDN	- Total Dissolved Nitrogen = DIN + DON	μmol/litre
PN	- Particulate Nitrogen	μmol/litre
PON	Particulate Organic Nitrogen	μmol/litre
PO ₄	- Phosphate, ortho-phosphate	μM, μmol/litre
DIP	- Dissolved Inorganic Phosphorus = PO ₄	μM, μmol/litre
DOP	- Dissolved Organic Phosphorus	μmol/litre
TDP	- Total Dissolved Phosphorus = DIP + DOP	μmol/litre
PP	- Particulate Phosphorus	μmol/litre
POP	Particulate Organic Phosphorus	μmol/litre
Si(OH) ₄	- Silicate, silicic acid	μM, μmol/litre
SiO	Silicate, silicic acid	μM, μmol/litre
Chl	- Chlorophyll	μg/litre
Phaeo	- Phaeophytin	μg/litre
S.S.	- Suspended Solids	mg/litre

1 megamole (Mmol) = 1,000 kilomoles (kmol) = 1,000,000 moles
1 kmol N = 14.01 kg N = 0.01401 metric tonnes N
1 kmol P = 30.98 kg P = 0.03098 metric tonnes P

The budgets being developed herein are based on the simplifying assumptions of spatial averaging over regional scales, that is, within the full area of the Cairns and Tully boxes and temporal averaging over seasonal or annual time periods. Within a year, two seasons are defined, a summer period (October-April, inclusive; 212 days) encompassing the normal ‘wet season’ and a winter season (May-September, 153 days) when SE trade winds predominate. Schematic depictions of the conceptual models for nitrogen (N) and phosphorus (P) pools and fluxes are shown in Figure 9 and Figure 10, respectively. These schematic models depict the major pools of soluble and particulate nitrogen and phosphorus, most of which are accessible to either direct measurement or indirect estimation by various approaches. Fluxes are identified by the arrows connecting pools, external sources and sinks. Again, most of these fluxes can either be measured directly or can be estimated by other means. Where possible, calculated annual fluxes have been weighted with reference to seasonal differences in the parameters measured and cross-shelf gradients in either concentrations or rates.

Figure 9. Schematic depiction of the water column nitrogen budget

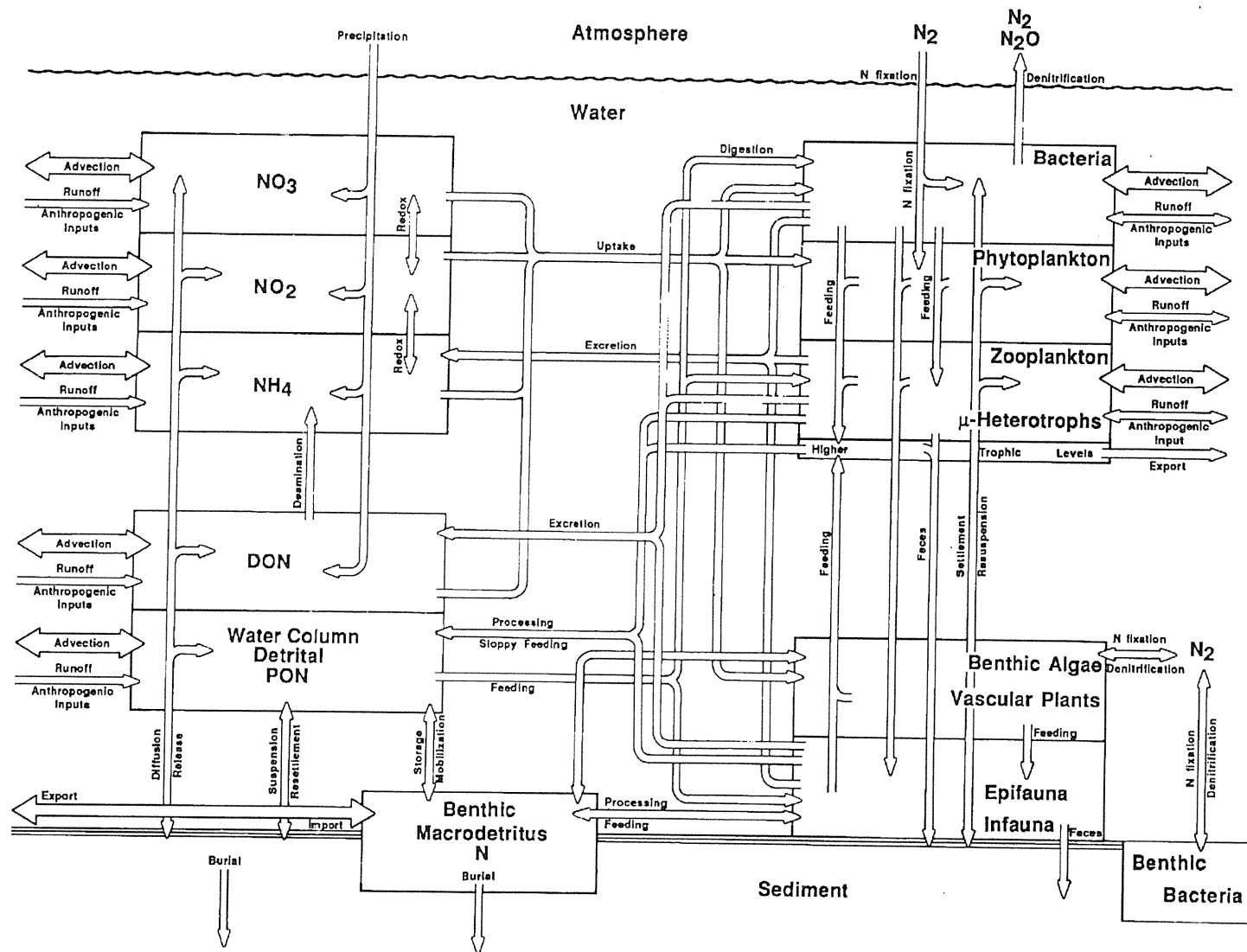
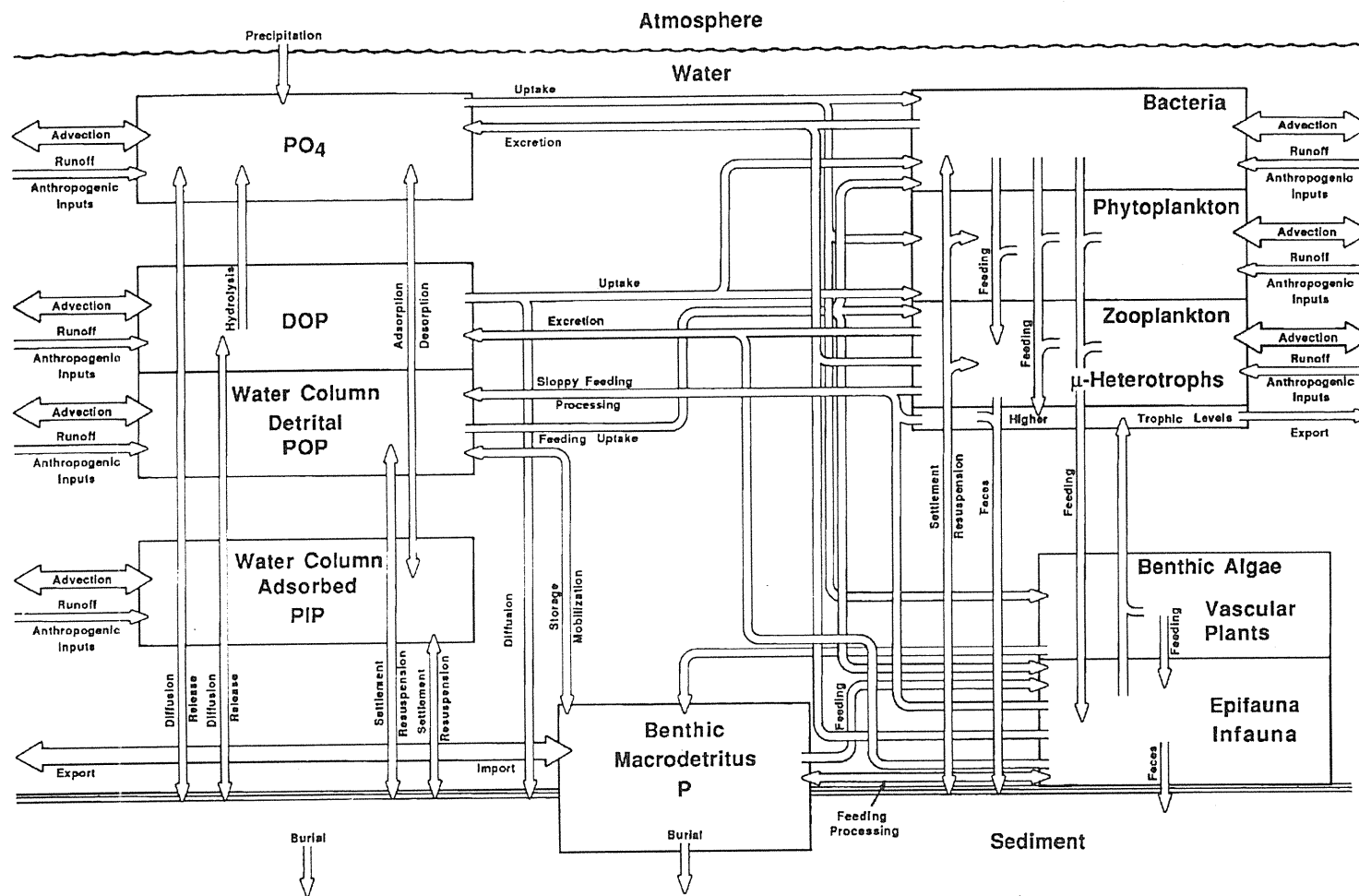


Figure 10. Schematic depiction of the water column phosphorus budget.



Nitrogen: Direct measurements were made of water column concentrations of inorganic nitrogen species (NH_4 , NO_2 and NO_3), dissolved organic nitrogen (DON) and total particulate nitrogen (PN). Indirect estimates of the phytoplankton-nitrogen component of PN can be made from concurrent measurements of chlorophyll the N/chl *a* ratios of natural phytoplankton populations (e.g. Goldman, 1980). Zooplankton nitrogen stocks are calculated from direct measurements of zooplankton dry weight ($> 73 \mu\text{m}$ size fraction) and the median nitrogen content of dry zooplankton weight (Figure 11). Zooplankton samples collected with a $73 \mu\text{m}$ net contained varying amounts of amorphous organic matter and large phytoplankton. This material dilutes the nitrogen content of the dried zooplankton. Its impact was reduced by basing calculations of zooplankton nitrogen on the median nitrogen content. In general, the nitrogen content of dried oceanic zooplankton ranges between 5 and 10 percent by weight (Parsons et al., 1977). It was not possible to calculate the amount of nitrogen present as either bacterial or microheterotroph (e.g. protozoan) biomass with any degree of confidence due to the lack of quantitative abundance data. Ikeda et al. (1982b) estimated that microzooplankton biomass (not including heterotrophic microflagellates) ranged between 7 and 15 percent of macrozooplankton biomass. The amount of nitrogen incorporated into water column detritus (dead organic matter) can be calculated in the first instance as the difference between total PN, as determined by direct chemical analysis and estimable stocks of phytoplankton and zooplankton nitrogen.

In the budgets presented herein, estimates can be made for nitrogen inputs from rivers (both dissolved and particulate forms), fixation of gaseous nitrogen by *Trichodesmium* and coral reef benthic communities, rainfall and shelfbreak upwelling, water column microbial remineralization and macro/microzooplankton excretion. Measured or estimable sinks include denitrification and net burial in sediments, particle sedimentation from the water column, and phytoplankton demand. No direct estimates could be made at this time for the magnitude of nitrogen fluxes associated with lateral mixing at the shelfbreak and longshore advection. Assuming the shelf system is at long-term steady state, net fluxes associated with longshore flows should be zero. Phytoplankton nutrient demand was estimated indirectly from measurements of primary production made in and adjacent to the study area. Benthic mineralization and water column mineralization fluxes are estimated from literature sources.

Phosphorus: Direct measurements were made of water column concentrations of dissolved inorganic and organic phosphorus (PO_4 , DOP) and particulate phosphorus (PP). As with nitrogen, estimates of phytoplankton and zooplankton components of the particulate phase can be made from appropriate composition ratios. For oceanic and temperate estuarine zooplankton assemblages dominated by copepods, the phosphorus content usually falls between 0.5 and 1 percent of dry weight (Parsons et al., 1977). The limitations applying to estimates of bacterial and microheterotroph nitrogen stocks also apply to phosphorus. Non-living particulate phosphorus (detrital organic and acid persulfate extractable inorganic particle-associated phosphorus) can be estimated as the difference between total and biomass associated pools of particulate phosphorus. With the exception of fixation from an atmospheric source, the major system-level inputs or sinks of phosphorus can be measured or estimated in parallel with those of nitrogen.

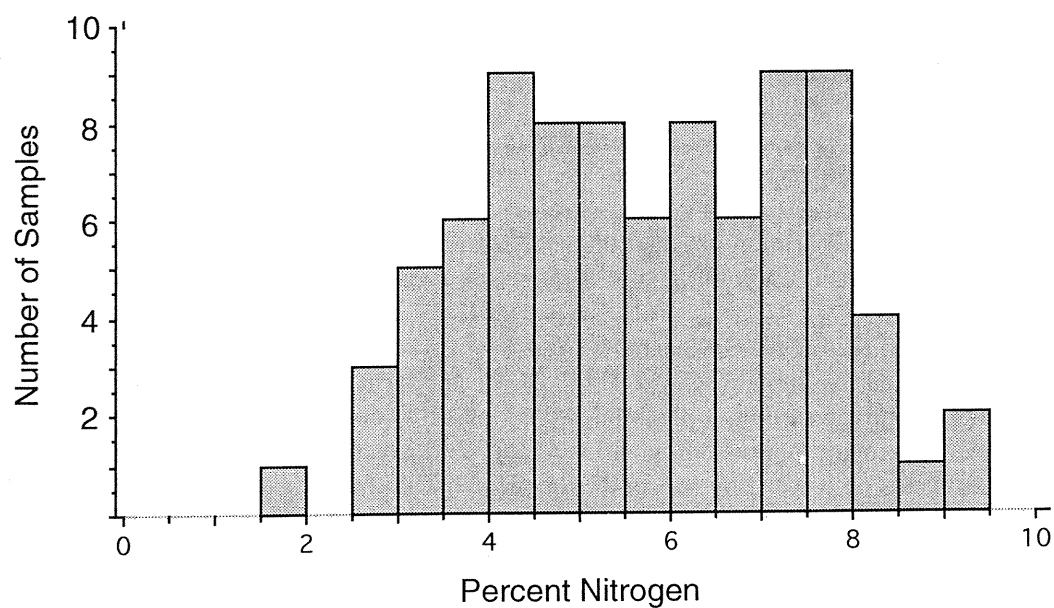
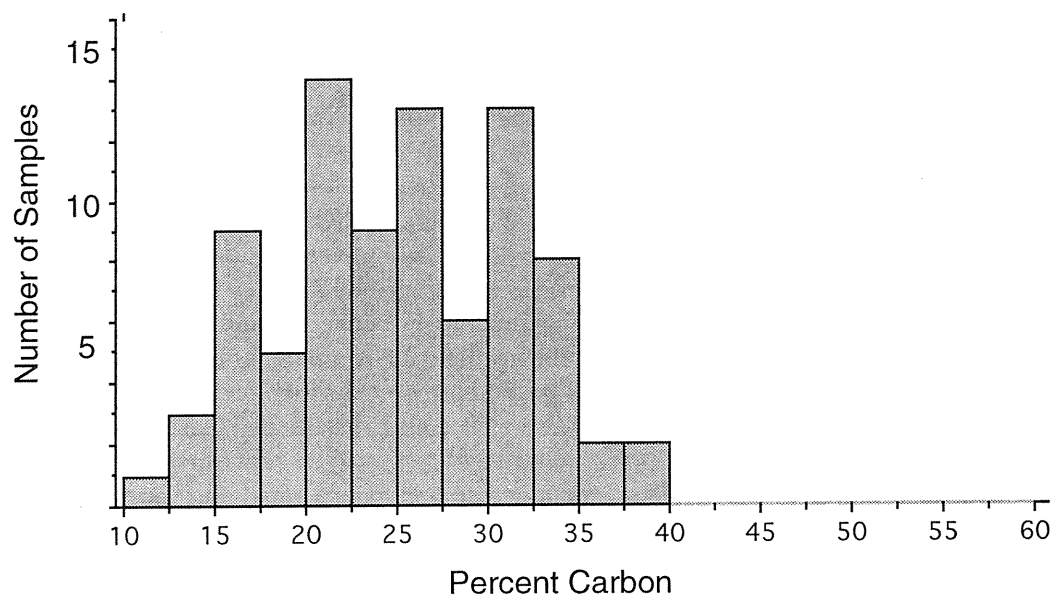


Figure 11. Carbon and nitrogen as a percentage of dry weight for zooplankton samples (73 μm) net collected in the Great Barrier Reef between 1983 and 1992.

5. METHODS

5.1 Water Sampling

Water samples were collected with Niskin bottles through the full depth of the water column or upper 300 m at deep stations seaward of the shelfbreak (2-10 sampling depths per hydrocast). Sampling depths were spaced evenly throughout the water column or mixed layer. The Niskin bottles were acid-soaked (ca. 1% AR grade HCl) prior to each cruise and stored with unused sample water between hydrocasts. At most stations, vertical profiles of salinity and temperature were recorded with a conductivity/temperature/depth (CTD) instrument (either the AIMS constructed CTD or an EG&G SCTD). The CTDs were calibrated each cruise against discrete *in situ* temperature measurements made with reversing thermometers and salinity samples collected on the same CTD cast or a hydrocast immediately following the CTD cast. In the event of a CTD malfunction, water temperatures were measured with reversing thermometers (two protected and one unprotected per Niskin bottle) and discrete water samples were collected for salinity measurements. Discrete salinity measurements were made ashore with a Plessey 6230N salinometer calibrated against IAPSO standard seawater.

5.2 Underwater and Diurnal Light Measurements

Subsurface irradiance profiles were measured at a number of stations with a Biospherical QSP-200 underwater scalar (4π) irradiance sensor. Surface irradiance was measured concurrently with a QSR-240 reference sensor. The underwater sensor was lowered in 1 to 5 m steps with surface and subsurface irradiance and wire angle being recorded at each depth stop. To the extent possible, light readings were not taken when clouds or haze obscured the sun. Underwater light values are presented as the percent of surface irradiance.

Diurnal time series of surface irradiance were measured on days when phytoplankton productivity measurements were made. Between 1983 and 1985, light readings were taken at half-hourly intervals by a remote weather station located at Rib Reef (18° 24'S 146° 53'E), somewhat to the south of the Tully box. The weather station was fitted with a LICOR LS-90 (2π) quantum sensor. Daily fluxes were calculated by trapezoidal integration. For the 1990 Cairns box productivity measurements, the analog output from the ship-based surface reference sensor (Biospherical QSR-240) were digitized at one second intervals from 0400 to 2000 local time by a JED data logger (JED Microprocessors P/L, Boronia, Vic.). Individual readings were averaged over one minute intervals and stored in the logger until downloaded to a microcomputer each day. The 4π light collecting sphere of the Biospherical QSR-240 quantum sensor is relatively insensitive to ship motion. The sensor was empirically calibrated at various natural sun angles on a clear day against a vertically pointing LICOR LS-190 quantum sensor (2π geometry).

5.3 Zooplankton Sampling

Water column zooplankton stocks were sampled at most hydrographic stations with duplicate near-bottom to surface vertical net hauls. The net (0.5 m diameter, 73 μ m mesh net) was equipped with a Rigosha flow meter to estimate the volume of water filtered. Zooplankton samples collected on individual net tows were split once with a Folsom splitter. One half of the sample was then filtered onto a pre-weighed disk of 73 μ m mesh netting. The other split was preserved in formalin for archiving and later microscopic examination if warranted. The filtered disk of zooplankton was frozen until further processing could take place.

Filtered zooplankton biomass samples were dried for several days at 60°C. The zooplankton and netting disk were weighed together and the zooplankton dry weight calculated by

difference. The carbon and nitrogen composition (as % of dry weight) was determined for a number of samples collected over several years (Figure 11) with a LECO CHN analyzer standardized against AR grade EDTA.

5.4 Nutrient Subsampling

Water samples were collected using single (unreplicated) casts at individual sites. Shortly after collection of the water samples, subsamples of seawater were dispensed from each Niskin bottle into a new or acid-soaked 60-ml plastic syringe for dissolved nutrient analyses. The water was then filtered through a Sartorius Minisart-N[®] cellulose acetate filter cartridge (0.45 µm pore diameter) directly into replicate (2X for inorganic nutrients plus 2X for dissolved organic nutrients, if collected) acid-washed plastic test tubes or plastic scintillation vials with screw cap closures. In most cases, one filter cartridge could be used for all samples at a single station without significant clogging. Approximately 10 ml of seawater was flushed through the filter before subsamples were dispensed into the sample tubes. The tubes/vials were frozen immediately in a clean laboratory freezer. Care was taken not to over-fill sample tubes/vials or to tip them while they were being frozen.

Duplicate 250 ml subsamples of water from each sampling depth were filtered onto precombusted (> 400°C overnight) Whatman GF/F filters (25 mm diameter, for particulate nitrogen (PN) and phosphorus (PP) analyses. The filters for each analysis were folded and stored frozen in envelopes of pre-combusted aluminium foil. The stated pore size for GF/F filters is 0.7 µm (Grasshoff, 1983), but in practice, they behave in a manner similar to membrane filters with 0.45 µm pores (Furnas, unpubl. data).

Duplicate 100 ml subsamples of water from each sampling depth were filtered onto Whatman GF/F glass fiber filters for chlorophyll analyses (Parsons et al., 1984). At a smaller number of stations additional 100 ml aliquots were filtered onto polycarbonate membrane filters (25 mm diameter, 10 and 2 µm pore diameter - Nuclepore) to assess the contribution of pico (< 2 µm size fraction) and nanoplankton (2-10 µm size fraction) to total community chlorophyll. Small amounts (a few drops) of MgCO₃ suspension were added to the water samples during filtration and the filters were stored frozen in aluminium foil packets until analysed.

From November 1989 onward, duplicate 1-litre subsamples of water were filtered onto pre-weighed Nuclepore filters (47 mm diameter, 0.4 µm pore diameter) for gravimetric suspended solids determinations. The filters were sucked dry, but not rinsed with deionized water, and stored in pre-combusted scintillation vials until processed further. The mass of salt (mean = 0.23 mg l⁻¹ equivalent) associated with the small amount of seawater remaining on the filters was estimated by covering clean filters with small volumes (2-3 ml) of filtered seawater, then sucking them dry and processing them in parallel with sample filters.

5.5 River Sampling

Dissolved and particulate nutrient samples were collected periodically from most of the major rivers (Herbert, Murray, Tully, So. Johnstone, No. Johnstone, Russell, Mulgrave, Barron) along the north Queensland coast which discharge directly into or immediately downstream of the two study boxes. No water samples were collected from the Daintree River. All rivers were sampled at least four (4) times per year from 1988 onward, and some, particularly the Herbert, Tully and So. Johnstone, at frequencies up to several times per day during flood events by individuals (A. Mitchell, H. Sturmey) or through cooperative arrangements with government agencies (Queensland Department of Primary Industries, Bureau of Sugar Experiment Stations (BSES), Cairns City Council). Water samples were generally collected at mid-channel from road bridges that crossed the river above the level of saltwater intrusion. Samples were taken

near the surface with 1-2 litre weighted glass or plastic bottles that filled slowly as the sampler sank. Water samples were processed immediately in the field, where possible, or at nearby laboratory facilities soon after collection. Storage and processing temperatures were not greatly different from *in situ* temperatures. Dissolved nutrient samples were processed in a manner similar to the seawater nutrient samples. Because of the increased particle loads in the rivers, smaller volumes (25-100 ml) were filtered for PN, PP and suspended solids determinations. Only a small number of chlorophyll samples were collected. Processed river nutrient samples were stored in local laboratory freezers or in chests of dry ice until returned to AIMS for analysis. All water subsamples were taken in duplicate. Replicate samples were collected on a number of occasions to assess the level of variability associated with sampling and sample processing. Samples were also collected on north- and southward legs of sampling trips (1-2 days separation) to assess day-to-day variation in nutrient concentrations.

On four occasions during 1987-88, more detailed longitudinal sampling was carried out in the estuary of the Murray River. The intent was to establish: 1) lateral variability in nutrient concentration and speciation across sections of the lower river, 2) vertical variability within the water column and 3) changes in chemical speciation occurring within the estuarine sections of north Queensland rivers. On these occasions, water samples were collected with an acid-washed Niskin bottle from an inflatable boat.

5.6 Rainwater Sampling

Fifty-one (51) rainwater samples were collected over a four year period (1987-91). Most were collected at AIMS (Cape Cleveland), but samples were also taken at sea in the central GBR and northern Coral Sea. Rainwater samples were collected in either an acid-washed PVC cylinder fitted with a drain spout or a polyethylene collector made from a 2.5 litre reagent bottle (previously containing AR grade HCl). The samplers were mounted on either the ship's superstructure or an unobstructed corner of the AIMS building. The samplers were acid-soaked prior to cruises or periods of use and were kept covered with a tight fitting lid or plastic bag when no rain was falling. Regardless of the sampler used, replicate subsamples were taken whenever possible. The samples were stored frozen until analysed in acid-washed plastic test tubes or scintillation vials. No record was kept of the amount of rainfall associated with particular rain collections or the total volume collected. Rainfall over the GBR sections considered herein was estimated from historical records of the Bureau of Meteorology for Low Isles, Green Island and Fitzroy Island (J. Lough, pers. comm.).

5.7 Analytical Procedures

Inorganic nutrient (NH_4 , NO_2 , NO_3 , PO_4 , Si(OH)_4) concentrations were determined by standard wet chemical procedures (Treguer and Le Corre, 1975) implemented on a Skalar 20/40 segmented flow analyzer (adapted from Ryle et al., 1981). Frozen samples were thawed to room temperature immediately prior to analysis. Baselines were run against an artificial seawater (for marine samples) or deionized water (for river and rain water samples). Beginning in 1991, river water samples were run first for nitrogen and phosphorus species, then allowed to stand for several days at room temperature to allow the silicate polymers produced by freezing to re-equilibrate to monomeric or dimeric species measurable by normal colorimetric methods. In most recent samples separate subsamples were collected for silicate analyses and stored at room temperature. Dissolved organic nitrogen (DON) and phosphorus (DOP) concentrations were calculated by difference after oxidation of the samples with high intensity UV light (Armstrong et al., 1966; Walsh, 1989). Seawater samples were oxidized for ca. 7-8 hours while river water samples were oxidized overnight (ca. 14 hours). Irradiated water samples were re-frozen until the re-analysis of DIN and DOP was carried out. Nowicki (1986) has shown that

this results in negligible losses of DIN and DIP. Total nitrogen in the irradiated samples was calculated as the sum of $\text{NO}_2 + \text{NO}_3 + \text{NH}_4$ (Walsh, 1989).

Particulate nitrogen concentrations were determined by high temperature combustion of the organic matter collected on glass fibre filters using an ANTEK Model 707 Nitrogen Analyzer. The filters were freeze dried before analysis. The sample was inserted into the primary combustion oven of the analyzer and ramp heated ($150^\circ\text{C min}^{-1}$) to 650°C in an oxygen-argon atmosphere. The combustion gases were swept into an oxygenated secondary oven (1050°C) with a ceramic catalytic surface. The nitrogen oxides produced (NO_x) were dried and quantified by chemiluminescence after mixing with ozone in the detector. Initially, sample filters were combusted in pre-ashed sample boats pressed from heavy gauge aluminium foil. From mid-1990 onward, pre-combusted brass punchings used to make .22 calibre rimfire cartridge cases (Winchester Australia) were used as sample boats. A semi-automated sample loader that could be pre-purged with argon and hold up to 30 samples in cartridges was fabricated by the AIMS workshops. The nitrogen analyzer was initially standardized with crystals of AR grade EDTA weighed out on a micro-balance. After the introduction of the brass cartridges as sample boats, standards were made up by blotting small volumes (ca. 10-100 μl) of an EDTA standard solution onto a glass fibre filter pre-combusted in a cartridge casing. The standard samples were oven dried and run in a manner similar to field samples. At the detector attenuation setting normally used, neither the brass cartridge cases or pre-fired filters produced measurable N blanks. A correction for adsorption of dissolved nitrogen (organic and inorganic) to the sample filters and from water retained by the filters was made by blotting small volumes (ca. 1 ml) of filtered surface seawater onto 25 ml GF/F filters at sea, sucking them dry and processing them in parallel with sample filters. Measurable nitrogen in these wet filter blanks (WFB) was on the order of 0.25-0.3 μg nitrogen per filter.

Particulate phosphorus retained on glass fibre filters was determined colorimetrically (Parsons et al., 1984) after acid-persulfate digestion (e.g. Menzel and Corwin, 1965) of the organic matter on the filters (taking suggestions from Smith et al., 1981). Filters were placed in acid-washed glass scintillation vials with 5 ml of 5% w/v potassium persulfate. The persulfate was refluxed to dryness using an aluminium block heater holding 100 vials. Acid-washed cat's eye glass marbles were used as stoppers for the vials. Following the digestion, 5 ml of deionized water were added to each vial and the filter and salt residue resuspended and pulverized to dissolve all soluble material. The residue in the vials was cleared by centrifugation and the inorganic phosphorus determined colorimetrically in aliquots of supernatant. Organic and inorganic phosphorus standards were run with each batch of samples. In the case of sediments, weighed subsamples of agate ground sediment were placed in acid-washed scintillation vials, acidified with 25% v/v AR grade HCl and refluxed to dryness to remove all carbonates and extraneous acid. The residue was then redissolved in 5% persulfate and treated as above.

Chlorophyll on filters was determined fluorometrically after grinding in 90% (v/v) acetone (Parsons et al., 1984). The fluorometer (Turner Designs-005R) was standardized spectrophotometrically (Jeffrey and Humphrey, 1975) against extracts of pigments from exponentially growing cultures of the diatom *Chaetoceros simplex* (chlorophylls *a* and *c*).

Suspended solids concentrations were determined gravimetrically from the difference between loaded and unloaded filter weights after the filters were dried overnight at 80°C . Wet filter salt blanks were subtracted from the resulting weight.

5.8 Primary Production Measurements

Water column primary production and coupled nutrient demand in the Cairns and Tully boxes were estimated from the uptake of ^{14}C bicarbonate by phytoplankton (Furnas and Mitchell,

1987, 1989, unpubl. data). Subsurface water samples were collected with General Oceanics Niskin or Go Flo bottles. Surface samples were occasionally collected with acid-cleaned plastic buckets or with an acid and seawater pre-soaked Niskin bottle. Depending upon depth, up to six water samples were collected at depths with nominal mid-day *in situ* irradiance levels on the order of 100, 50, 30, 20, 8 and 4 percent of surface irradiance. Three to nine 250 ml polycarbonate bottles (pre-soaked with 0.2% Baker Instra-analysed HCl and deionized water) were filled with water from each sampling depth and spiked with 5 μCi (185 kBq) of radioactive bicarbonate. A third of the bottles from each depth were wrapped in aluminium foil as dark bottles. The bottles were incubated at simulated *in situ* irradiance levels (as above) corresponding to the depth of collection in seawater cooled deck incubators screened with neutral density shade cloth. At the end of the incubation, the samples were filtered onto either Whatman GF/F (0.4 μm pore diameter) or Nuclepore filters (2 and 10 μm pore size). After counting, the filters were placed in scintillation vials and the remaining inorganic carbon removed by addition of 0.1 ml of 1N HCl (Hitchcock, 1986). Radioactivity remaining on the filters was determined by liquid scintillation counting. Hourly primary production rates were calculated according to Parsons et al. (1984). Daily production was estimated by dividing the production measured during the experiment by the proportion of daily irradiance impinging during the ca. 4 hour incubation period. Nutrient demand was estimated by dividing the daily production estimated by the appropriate C:N (6.6:1) and C:P (106:1) ratios (Redfield et al., 1963) after converting the primary production estimate to a molar rate.

5.9 Frequency and Magnitude of Intrusive Activity off Cairns

Sea Data Temperature-Depth Recorders (TDR) were moored approximately 1 m off the bottom at shelfbreak sites adjacent to the entrances to Grafton Passage (seaward of Euston Reef: 56-58 m depth) and Trinity Opening (north of Norman Reef: 52 m depth). The instruments were deployed for periods of 5-7 months and were set to sample at intervals of 15-20 minutes. Two years of data were collected at each site. The instruments were calibrated in the laboratory to derive relationships between instrument digital counts and *in situ* temperature. The calibrations were checked in the field against CTD casts or discrete *in situ* temperature measurements using reversing thermometers.

As no extensive hydrographic sampling has been carried out during an intrusion event in the Cairns region, data from twenty-three (23) hydrographic sections sampled in Palm Passage between January, 1983 and October, 1987 (e.g. Figure 12) were used to derive empirical relationships between near-bottom temperature at the shelfbreak in Palm Passage and the calculated volume of intruded Subtropical Lower Water (SLW) on the shelf in Palm Passage. The volume of intruded SLW was estimated by a two-stage process which is summarized as follows. Water masses within the outer shelf of the GBR can be considered a mixture between three water types (Pickard et al., 1977): Lagoonal Water (LW), Coral Sea Surface Water (CSSW) and SLW (Figure 13). In the case of LW and CSSW water types, the temperature-salinity (T/S) characteristics on individual transects were taken as the means of temperatures and salinities between the depths of 10 and 25 m to minimize distortion due to near-surface diurnal heating effects or dilution by rainwater. Within the 10-25 metre depth stratum, temperatures and salinities are usually fairly constant. Over the course of the sampling program, a variety of T/S relationships were observed.

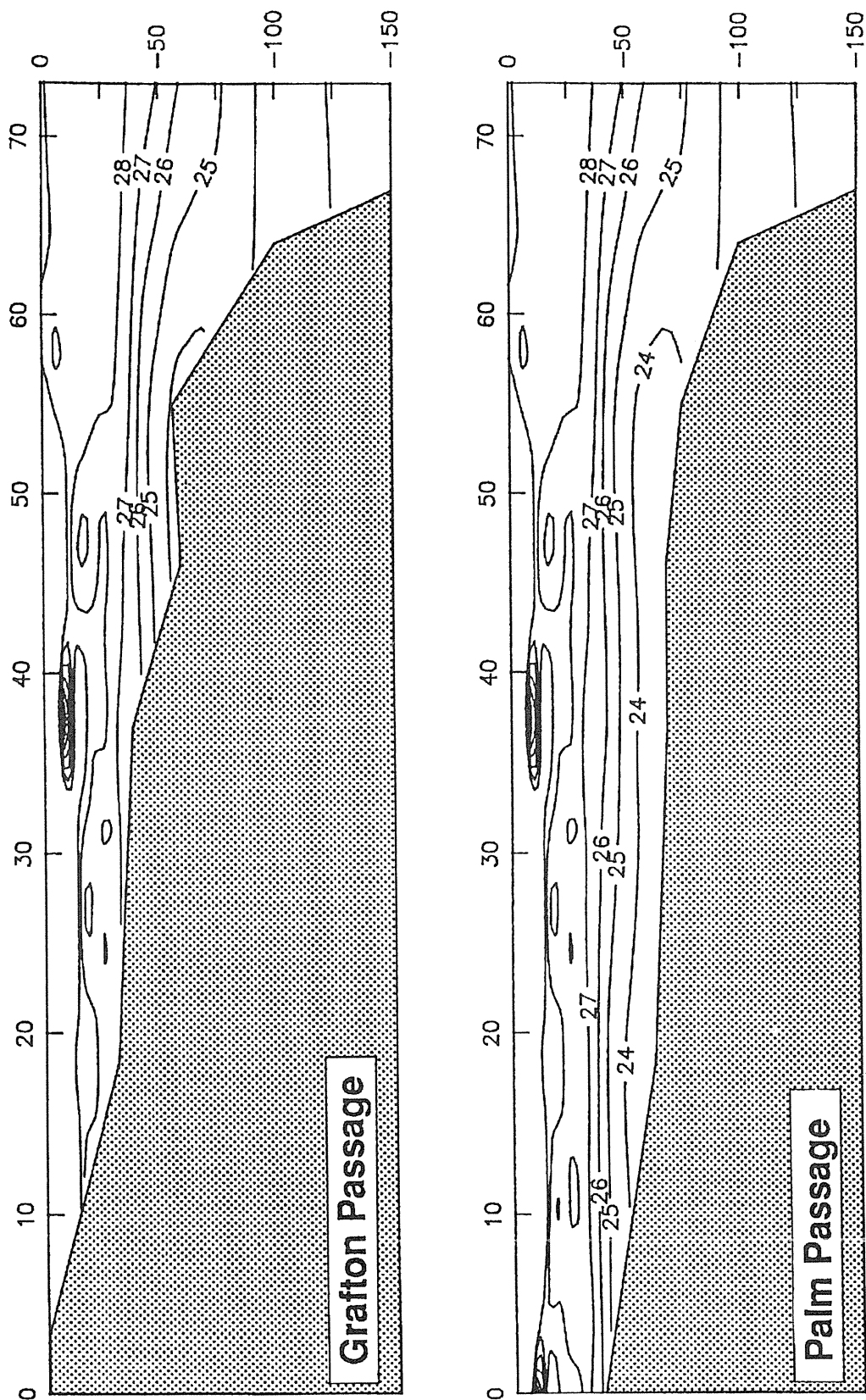


Figure 12. Bottom: Cross-shelf section through a cold-water intrusion into Palm Passage (19°S) during January 1983. Top: The same intrusion event masked with the bathymetry down the central axis of Grafton Passage.

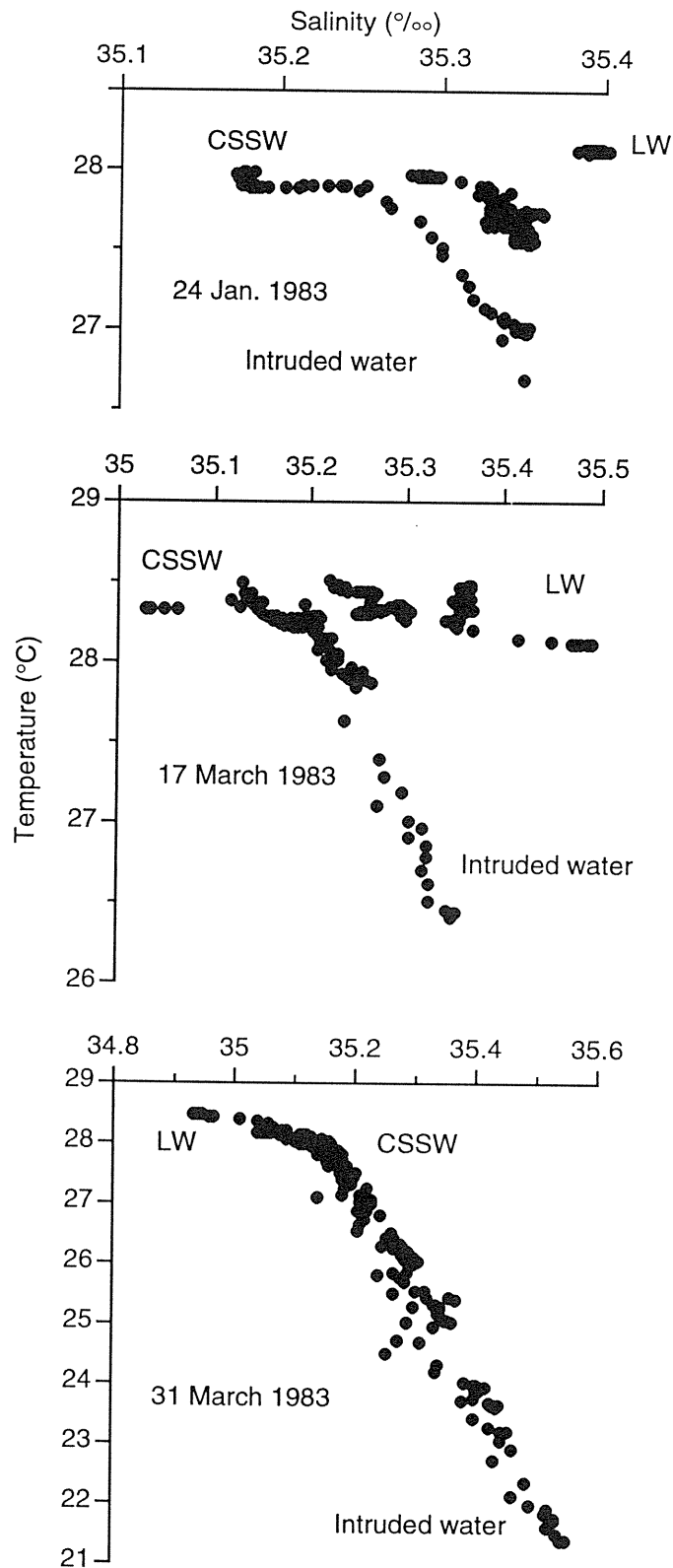


Figure 13. Temperature-salinity plots for water masses in Palm Passage on three occasions during the summer of 1983. Each T/S plot combines data from four stations spaced between the GBR Lagoon and the shelfbreak.

To estimate the volume of SLW in individual Palm Passage sections, the local salinity and temperature characteristics of surface water at a particular station were assumed to be derived from a conservative (linear) mixing relationship between CSSW and LW. The volume percent of intruded water at each 1 metre depth step at each station was then calculated from the T/S data assuming a conservative mixing relationship between the calculated “local” surface water T/S characteristics and the defined T/S character of SLW. Figure 14 shows two representative T/S plots from stations in the EAC seaward of the transect through Palm Passage. The seasonal changes in the temperature characteristics of CSSW are clearly evident, but the linear mixing relationships between CSSW and SLW in the profiles still apply. The calculated profiles of volume percent SLW were averaged between adjacent 1-metre depth increments and then horizontally between stations and finally multiplied by the distance between stations to calculate the volume of undiluted SLW at metre depth intervals between adjacent stations. Where the bottom intervened between stations, appropriate trapezoids were calculated for the depth increment. The total volume percent SLW for each transect was then numerically integrated.

To convert shelfbreak water temperature time series to estimates of SLW intrusion volumes in the Cairns and Tully boxes, a calculated “mean” bathymetry of the outer shelf for each box (Figure 15) was masked over each of the Palm Passage intrusions. The mean bathymetric shape of the outer shelf in the two boxes was derived from the cross-shelf transects used to calculate water volumes within each box. Figure 12 Top illustrates masking of a Palm Passage intrusion sampled in January, 1983 with a bathymetric section from the central axis of Grafton Passage. Because of the narrow width of the shelf in the Cairns box, the Palm Passage transect extended across the full width of the shelf. In the Tully box, the transect extended shoreward to the 10 m isobath. After the mean bathymetric transects were masked over each of the Palm Passage sections, the volumes of SLW remaining were integrated and plotted against the nominal shelfbreak water temperatures.

Temperature - nutrient relationships (Figure 16) determined at hydrographic stations located seaward of the shelfbreak in the EAC were used to calculate the mean nitrate (NO_3 - $4.77 \mu\text{M}$) and phosphate (PO_4 - $0.64 \mu\text{M}$) concentrations expected at the core of the SLW water layer. A similar inverse relationship also applied for silicate. Ammonia concentrations were near the limits of detection at all depths and showed no functional relationship to *in situ* temperature. A more limited data set (not shown) indicates that PP, PN, DOP and DON concentrations at the SLW core (and in Coral Sea waters in general) were similar to, or less than, concentrations in shelf waters. As a result, inputs of nitrogen and phosphorus from intrusions are almost exclusively due to NO_3 and PO_4 fluxes.

5.10 Sediment Trap Sampling

Sedimentation fluxes of particulate carbon, nitrogen and phosphorus were measured over an annual cycle (September 1988 - August 1989) using moored traps at four sites along a cross-shelf transect extending seaward from the Family Islands, just south of the Tully box (Figure 7 Bottom). Nutrient and particulate sedimentation rates in the Cairns box (Figure 7 Top) were measured with both moored traps (as above) and Lagrangian drifter traps (Knauer et al., 1979) between May, 1990 and July, 1991. For the Cairns box, only results from the drifting traps will be considered in detail. Inter-calibration runs between the two trap types were carried out in six series of paired deployments off Cairns in August, 1990.

In the case of carbon and phosphorus, the drifter traps collected approximately twice as much material per unit area as the moored traps (Figure 19). The situation for nitrogen was less clear, but on average, the area-normalized fluxes of PN into the drifting traps were 1.6 times the concurrent fluxes calculated for the moored traps. For consistency between series of

experiments, the fluxes measured with the moored traps have been multiplied by a factor of 2 to be equivalent to the rates measured with the drifting traps.

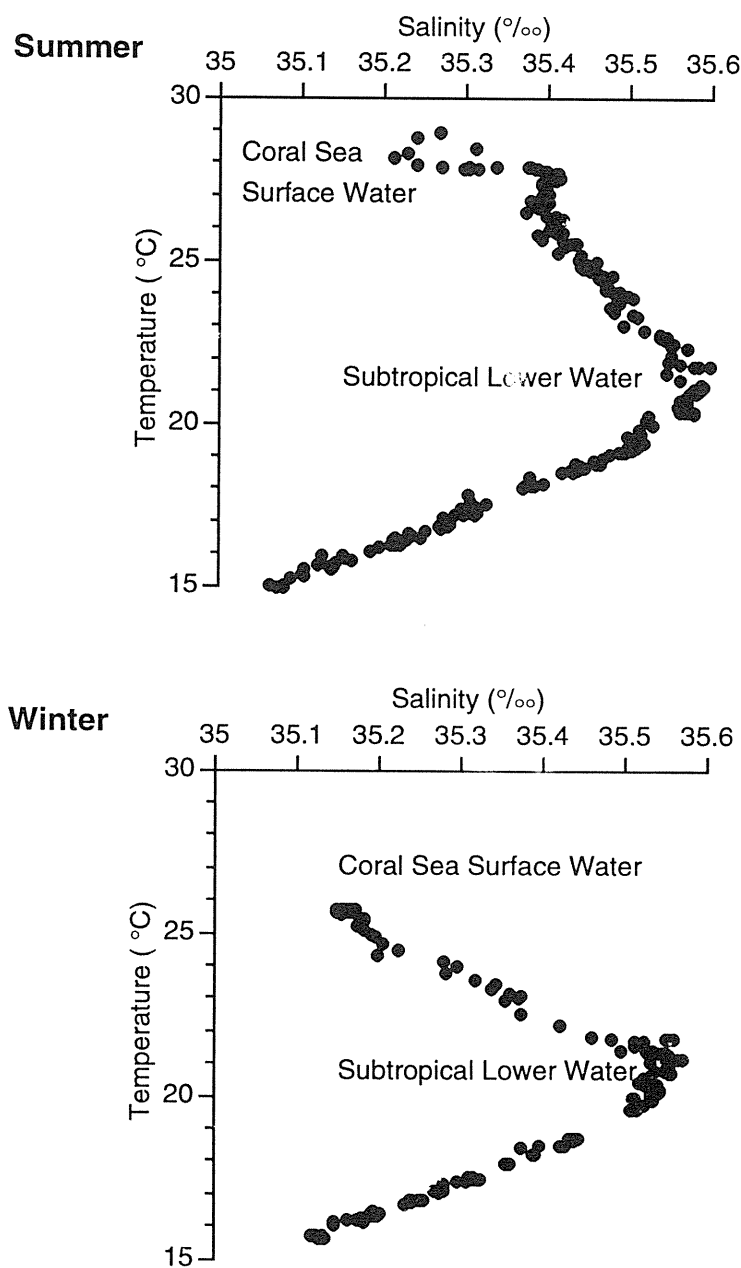


Figure 14. Representative seasonal temperature-salinity relationships from a station in the East Australian Current, immediately seaward of Palm Passage.

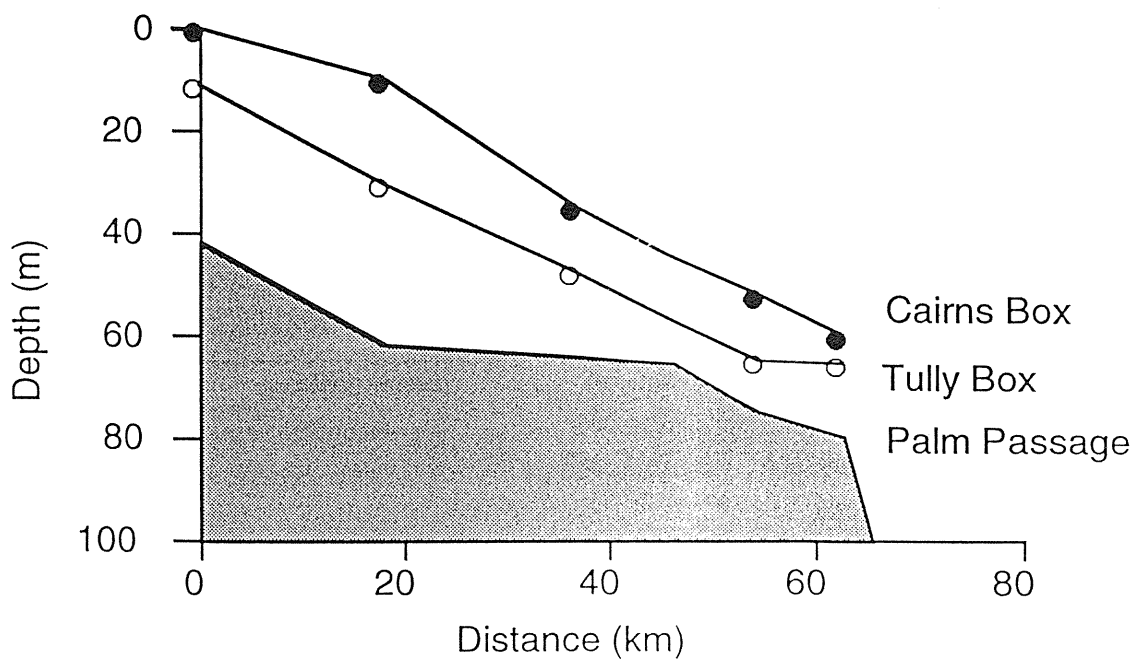


Figure 15. Mean cross-shelf bathymetric profiles for the Cairns and Tully boxes in comparison to the cross-shelf bathymetry down the central axis of Palm Passage.

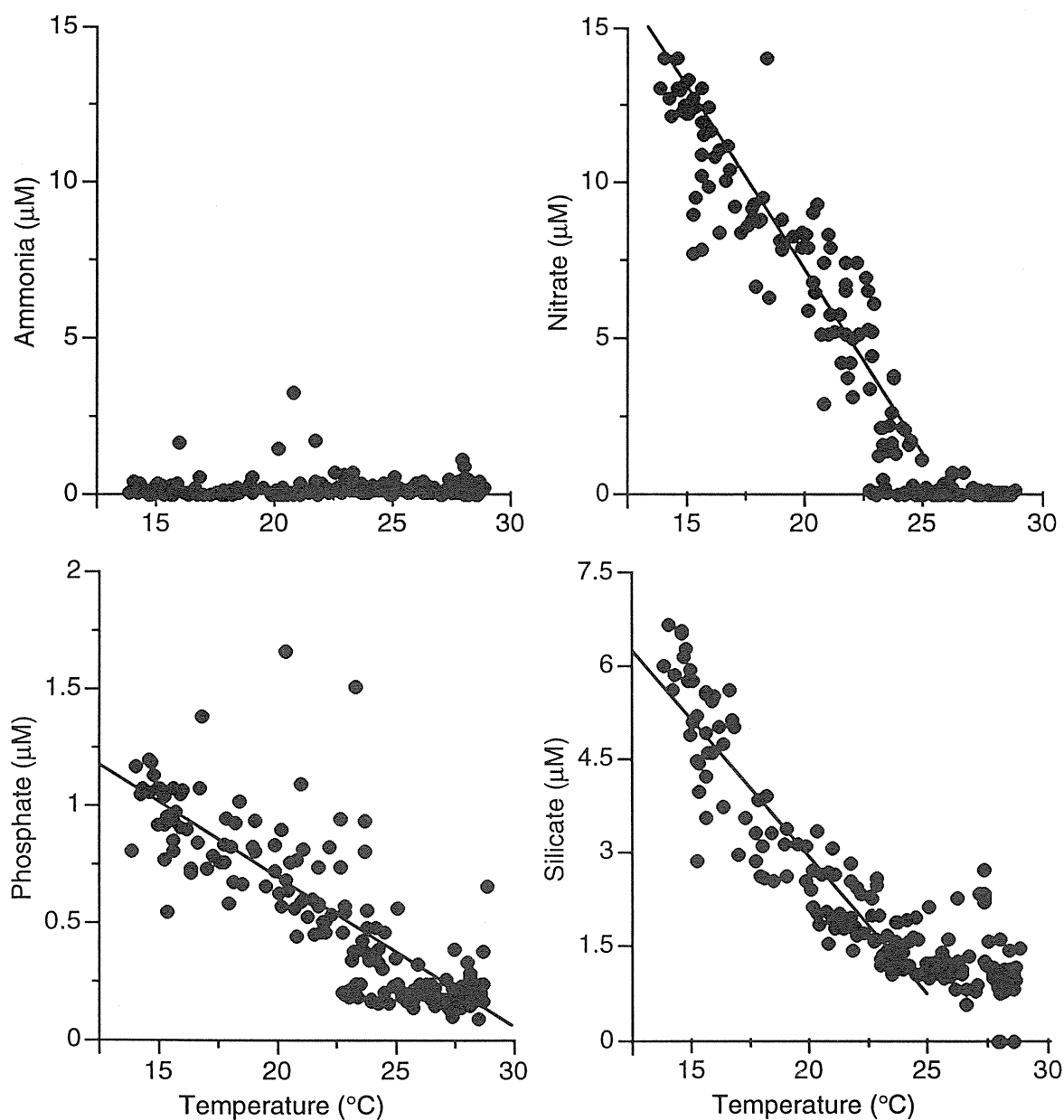


Figure 16. Temperature-inorganic nutrient relationships from stations in the East Australian Current during 1983. The linear regressions shown (for temperatures < 25°C) are: $\text{NO}_3 = 28.97 - 1.11 (T)$, $r^2 = 0.840$; $\text{PO}_4 = 1.95 - 0.06 (T)$, $r^2 = 0.484$; $\text{Si(OH)}_4 = 11.58 - 0.43 (T)$, $r^2 = 0.842$.

5.11 Moored Traps

The moored traps (Figure 17) were right cylinders 38 cm in diameter with a long tapering cone at the bottom to concentrate sedimented material into a small volume sample cup. The traps and cones were constructed of rolled sheet steel which was hot dip galvanized and covered with an electrostatically applied polyester paint (Powdercote). To reduce resuspension within individual traps, the cylindrical portion of the traps had a length:diameter ratio of 3 (Butman, 1986; Butman et al., 1986). Each individual mooring was comprised of paired traps in a rigid wood and aluminium frame which included built-in buoyancy to keep the traps floating upright when deployed. Trap moorings were anchored to the bottom with a 75 kg steel weight and plow anchor. A 14 mm nylon or polyester line extending to a surface buoy with a radar reflector was attached to the top of the trap frame.

The traps were recovered by positioning the research vessel above the deployed trap, grappling the surface line aboard and winching the trap smoothly to the surface with the ship's trawl winch capstan. Flapper doors in the side of the cylindrical portion of the trap allowed water above the cone to escape when the traps were hauled through the surface. The traps were placed on the deck in a vertical position for processing of the contents. Visual examination of the water remaining within the conical section of the trap indicated that appreciable resuspension of particulate material did **not** occur during recovery.

Moored trap deployments were nominally 24 hours in duration. Because of the short duration of the deployments, no preservatives were added to the collection cups. When the recovered trap was returned to the ship's deck, water remaining within the cone portion of each trap (ca. 44-50 l) was drained into a polyethylene drum and retained. The sample cup at the bottom of each trap and the small volume of water remaining at the bottom of the cones were then drained through a tap into a plastic beaker. The interior of each trap was washed with a fine high pressure spray of surface seawater into the beaker containing the concentrated sediment. The volume of water drained from each cone and the combined volume of sediment and trap washings for each trap were noted.

Duplicate aliquots of well mixed water from each of the drained cones and each of the combined sediment + washing samples were filtered onto pre-weighed, ashed (400°C) glass fibre filters (Whatman GF/A, 47 mm). Visually obvious live zooplankton ("swimmers") were removed during and after filtration. In most cases, two litres of drum water and 250-500 ml of the sediment + washings were filtered. The filtered material was usually a mixture of clay-like inorganic and gelatinous organic matter. The filters were stored frozen in ashed petri dishes, dried at 60°C and reweighed before analysis. The total amount of mass, carbon, nitrogen or phosphorus sedimented in each individual trap was ultimately calculated taking account of both the concentrated material in the cups and the incremental amount of dispersed suspended material within the water drained from the cones.

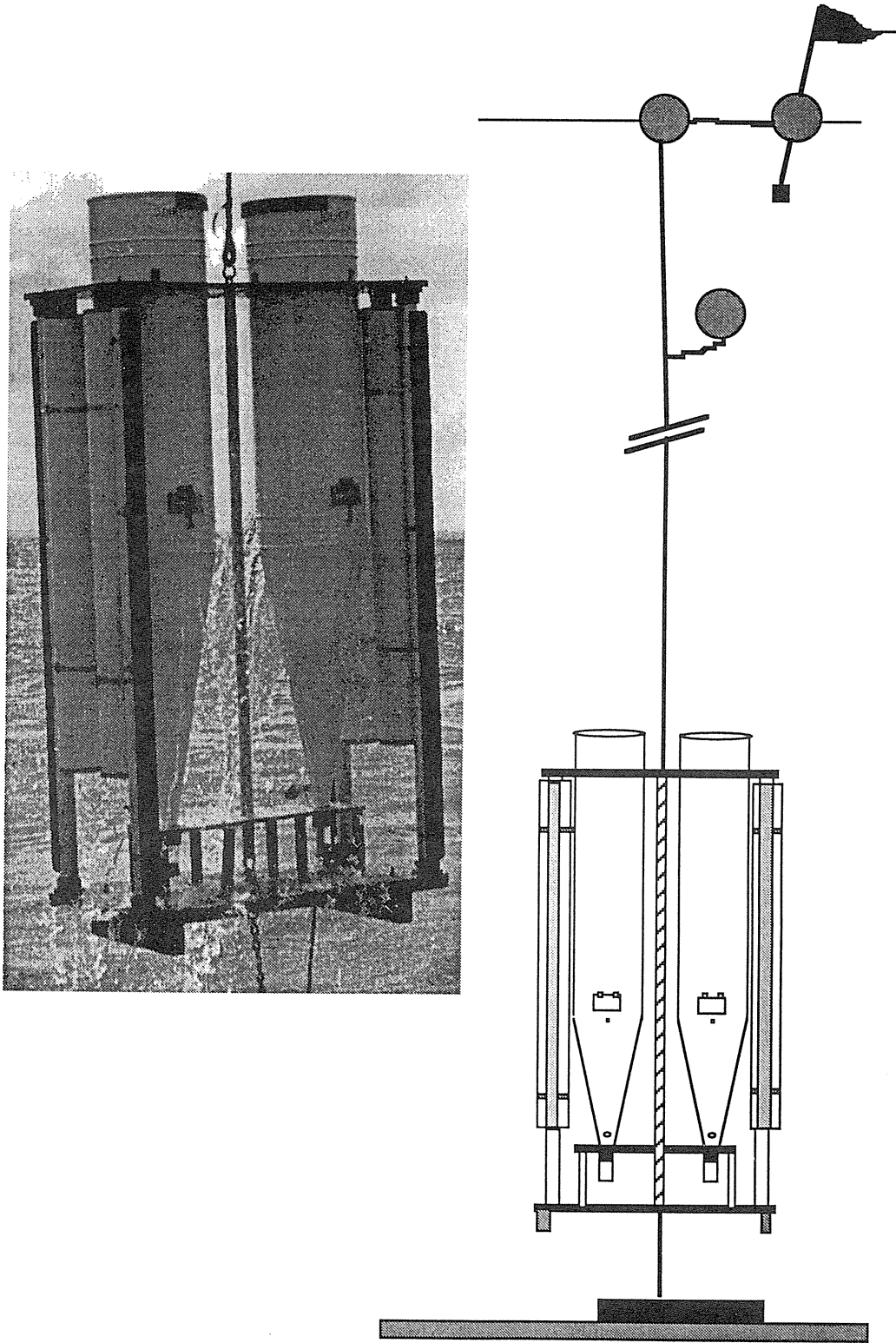


Figure 17. Moored sediment trap array used to collect sedimenting carbon, nitrogen and phosphorus in the Cairns and Tully boxes. Background: Schematic depiction of a trap mooring.

5.12 Drifter Traps

Twelve individual traps 80 mm in diameter and 800 mm in length were supported in a cross-shaped array constructed of PVC with stainless steel fittings (Figure 18). The trap tubes were constructed from acrylic tubing, with PVC bases and were covered with PVC baffles to retard the penetration of turbulence into the traps. No brine solutions or preservatives were put into the traps. Prior to each cruise, the traps were washed and acid-soaked and rinsed well with fresh seawater between deployments. The trap array was suspended from a string of floats to dampen vertical movements arising from wave motion. Depending upon water depth, the traps were suspended between 10 and 45 metres below the surface and generally 3-10 metres above the bottom. In all but one case, the drifting traps were deployed for 12 hours (ca. 0600-1800). Longer deployments were not carried out as they would have entailed tracking and vessel movements at night in either the unmarked reef matrix or in the main shipping channel when the trap marker buoy was poorly visible. Hydrocasts were made near the location of the trap at the time of trap deployments and recoveries. Occasional mid-day casts were also made. Water samples were collected at 3-6 metre depths for all dissolved and particulate nutrient species.

At the end of each deployment, after the floats and marker buoy supporting the traps were grappled on board the research vessel, the trap array was smoothly winched to the surface, and placed on the ship's deck. The contents of the traps were allowed to settle for at least an hour. Visual examination of the traps immediately after recovery indicated little, if any, resuspension within the traps had taken place. The supernatant layer above the sediment in each trap was gently siphoned off. Aliquots of supernatant were saved on a number of occasions to measure concentrations of particulate material in the supernatant. In most cases, these concentrations were similar to those in the water column. The remaining supernatant + sediment was then filtered onto pre-weighed, ashed glass-fibre filters (47 or 25 mm diameter, Whatman GF/C). Live zooplankton organisms, visible to the naked eye ("swimmers"), were removed during and after filtration. The filters were placed in acid-washed petri dishes and frozen for storage. Before analysis, the filters were dried to constant weight at 60°C.

Sedimented material collected on the filters was analysed in a variety of ways. In all cases, measured concentrations were corrected for amounts of suspended matter and particulate nutrients (C, N, P) that would have been present in the volume of water filtered. The total mass of material collected on the filters was determined gravimetrically from the difference between dried filter weights before and after filtration of the trap samples. A correction for salt in the water blotted into the filter material, but not sediment, was applied. *In situ* concentrations of particulate nutrients (PN, PP) and suspended solids were determined from the means of depth-weighted average concentrations in the water column at the time of trap deployment and recovery. When sedimented material was collected on 47 mm glass-fibre filters, the filters were cut in two pieces such that the filtered material was divided equally between the two halves. In the case of 25 mm filters, an entire filter was used for each individual analysis.

5.13 Carbon and Nitrogen Analyses of Trapped Material

Inorganic carbon was removed from filters or filter halves to be analysed for sedimented organic carbon and nitrogen by acidification with concentrated trace metal grade HCl (Baker Instra-analysed). The filters were poised on steel knife edges within individual petri dishes and small amounts of acid (100-500 µl) were carefully blotted onto the filters to minimize the likelihood that acid with re-dissolved material would drip or wick off the filters. After noticeable signs of CO₂ generation stopped, the filters, still poised on their knife edges, were re-dried at 60-80°C in an oven. The carbon and nitrogen content of the larger (47 mm) filter halves were determined with a LECO CHN analyzer. Carbon and nitrogen analyses of material collected on the smaller filters were carried out using an ANTEK Model 707 nitrogen analyzer

with a Rosemount non-dispersive CO₂ analyzer fitted to the instrument exhaust stream. The analog signal from the CO₂ detector was quantified with a Delta Data Systems peak digitizer fitted to a microcomputer. Both CHN analyzers were standardized against AR grade EDTA. Filter blanks were prepared by blotting 200-300 µl of concentrated HCl onto a combusted filter or half-filter, which was then dried and run in parallel with sample filters.

5.14 Phosphorus Analyses of Trapped Materials

Intact filters or half-filters were refluxed to dryness in 10% v/v HCl to remove inorganic carbon and convert polyphosphate and other (though perhaps not all; Froelich, 1988) mineral phase phosphorus to monomeric PO₄. Total organic and inorganic phosphorus in the residue was then digested and analysed as given above for total phosphorus in sediments.

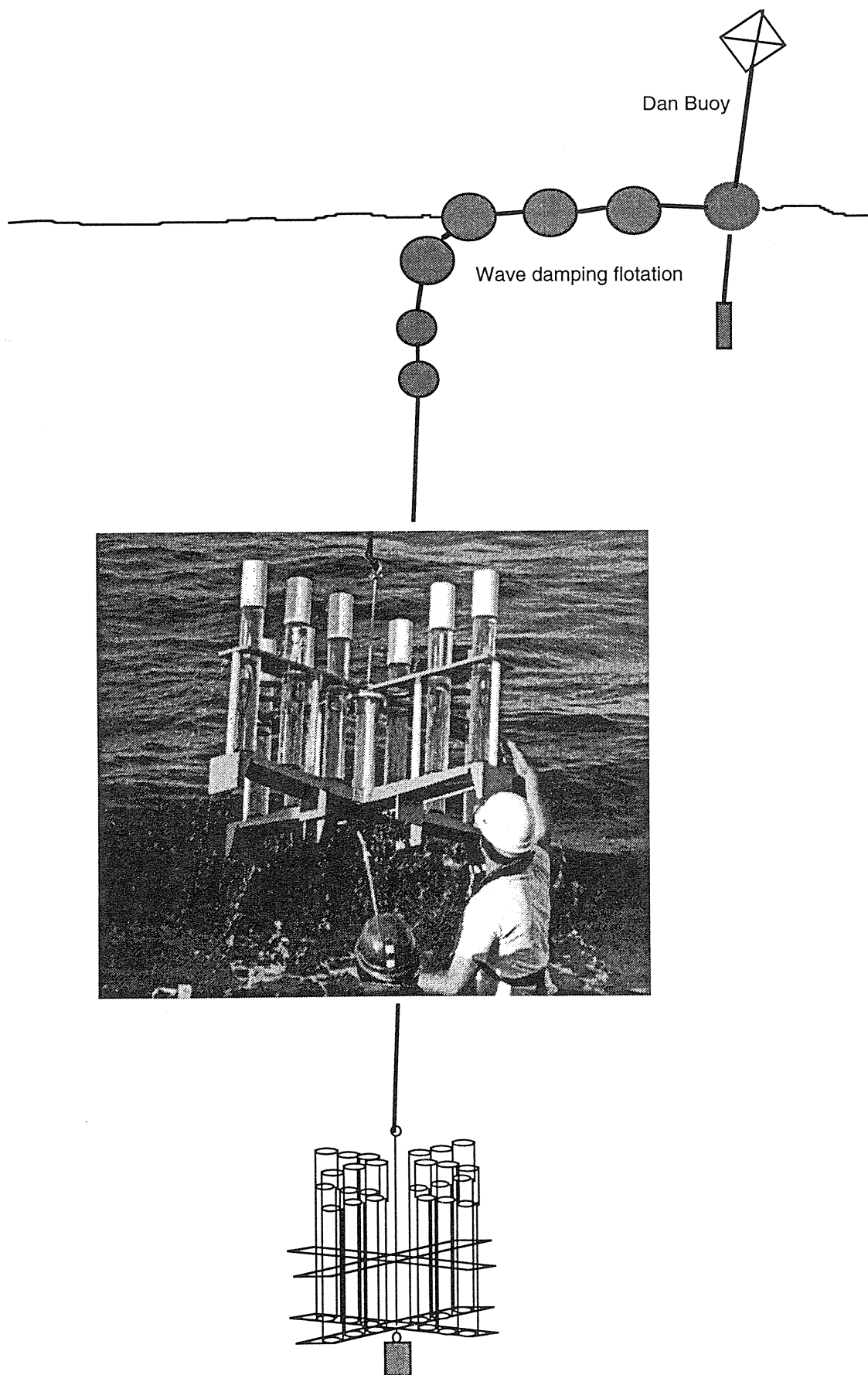


Figure 18. Free-drifting sediment trap array used to collect sedimenting carbon, nitrogen and phosphorus in the Cairns box. Background: Schematic depiction of deployed trap.

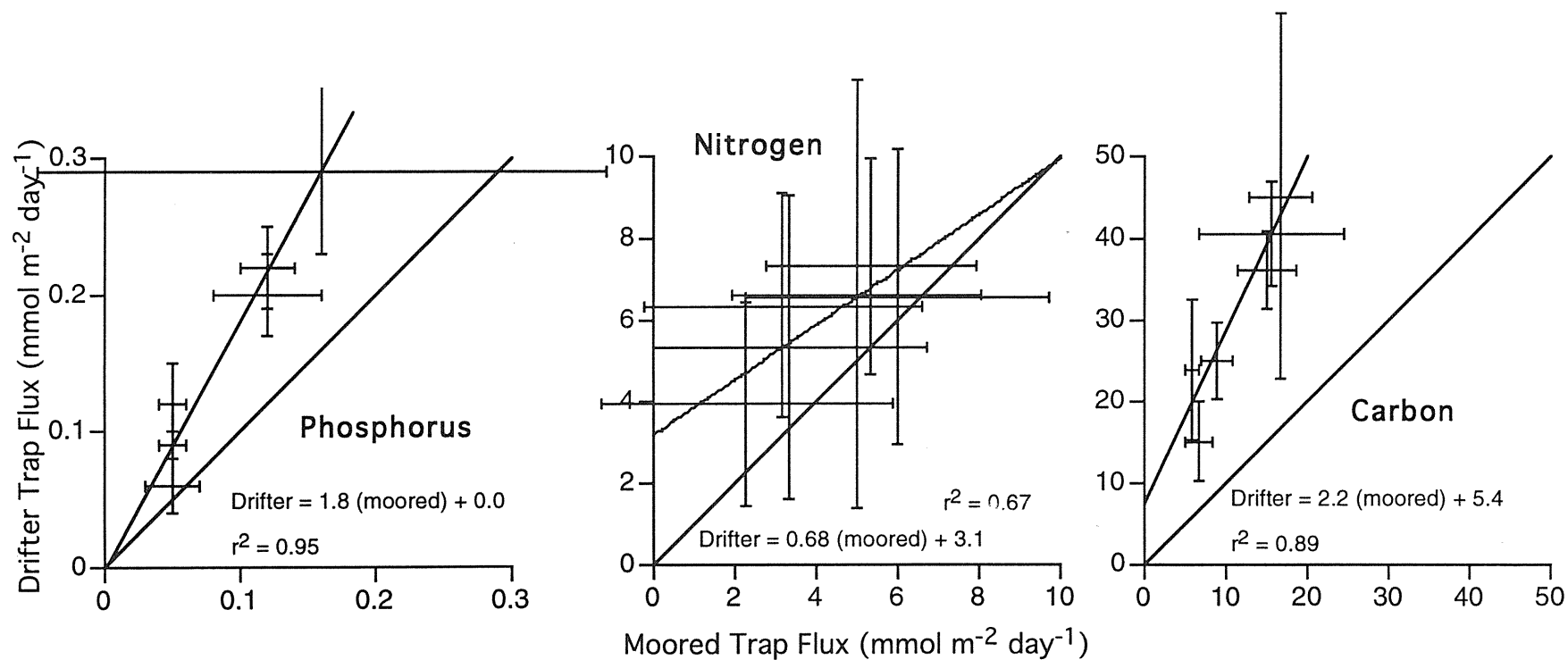


Figure 19. Comparisons between calculated sedimentation fluxes of particulate carbon, nitrogen and phosphorus using drifting and moored sediment traps in simultaneous deployments at the same site. Error bars = one standard deviation.

6. NUTRIENT STOCKS

Sampling in the Cairns box was carried out between February 1989 and July 1991 (CNS series). Two series of water samples were available for the Tully box, an initial series collected during February, 1987 (COT series) and a second series collected between October 1988 and November 1989 (FAM series). Depth-weighted mean water column concentrations of dissolved and particulate nutrients, plant pigments and suspended solids concentrations (where measured) in the two study boxes are summarized in Tables 5-8. As the water column was generally well mixed at most stations, the depth-weighted mean concentration is usually similar to both a simple arithmetic mean of station concentration data and near-surface concentrations. The station data are grouped by bathymetric depth bands and season.

The summer season (October-April) corresponds to the period of greatest rainfall, river runoff, shelfbreak upwelling activity and the occurrence of cyclones. South-easterly trade winds, which typify the winter (May-September) period, suppress shelfbreak upwelling activity and lead to active mixing of the water column at all locations across the shelf. South-easterly trade winds occur throughout the year, but are generally most intense during the July-September period.

The four depth bands selected roughly correspond to: inshore waters (< 10 m); the inshore-lagoon transition zone (10-20 m); the central GBR lagoon (20-30 m); and the outer-shelf reef matrix (> 40 m). Because of horizontal mixing, the segregation of individual stations into defined depth bands is somewhat arbitrary. Stations from the 31 to 40 m depth band were not included in the statistical calculations as this band encompasses a poorly defined transition between the open waters of the GBR lagoon and the outer-shelf reef matrix. Shelf stations located in depths exceeding 40 m are all clearly within the reef matrix and therefore provide a clearer contrast between the two hydrographic settings. To discount the importance of a small number of stations with high, outlying concentration values, the medians of the depth-averaged concentrations for each season and depth band are given as well.

The presence or absence of cross-shelf gradients (Figures 20-23) in nutrient and particulate concentrations varied between nutrient species, season and location. For the larger data set available for the Cairns box, statistically significant (1-way ANOVA, $p \leq 0.05$), season-independent cross-shelf gradients in depth-averaged water column concentrations were found for particulate nitrogen (PN), particulate phosphorus (PP), silicate, phytoplankton pigments (chlorophyll and phaeophytin) and suspended solids. Although concentrations were very low, a statistically significant cross-shelf gradient for nitrite was also found in winter samples. Ammonia, phosphate, DON and DOP, the principal pools of dissolved nitrogen and phosphorus did not show significant cross-shelf gradients.

In the case of the Tully box, fewer stations were occupied and for some nutrient or particulate species, data is not available for all depth bands in both of the seasonal periods. No suspended solids data is available for Tully box stations. Silicate was the only dissolved nutrient species in the Tully box data to have a statistically significant cross shelf concentration gradient in both seasons. Significant cross-shelf nitrite and DOP gradients were found in the summer, while significant cross-shelf ammonium, nitrite, PON, phosphate and PP gradients occurred during the winter.

It is not surprising that higher PN, PP and suspended solids concentrations occurred at shallow stations, given the inputs of sediment and wind-driven resuspension near the coast. Low suspended solid and particulate nutrient concentrations within the outer-shelf reef matrix reflect the greater importance of lateral exchange with adjacent low-nutrient oceanic waters.

Table 5. Summary statistics for dissolved and particulate water column nutrient concentrations in the Cairns box for the summer (October - April) season. Values are given as depth-weighted average concentrations over the full depth of the water column sampled. Italics = significant difference between winter-summer mean ($p < 0.05$). Bold = significant difference between Cairns-Tully box means ($p < 0.05$)

	NH ₄	NO ₂	NO ₃	TDN	DON	PON μmol l ⁻¹	PO ₄	TDP	DOP	POP	SiO	Chl μg l ⁻¹	Phaeo μg l ⁻¹	S.S. mg l ⁻¹
CNS - <=10 m Summer														
Mean	0.28	0.001	<i>0.03</i>	6.79	6.49	1.80	0.10	0.19	<i>0.09</i>	<i>0.13</i>	5.23	<i>0.61</i>	<i>0.25</i>	2.00
Std Dev	0.28	0.003	0.03	3.08	2.91	0.63	0.11	0.22	0.13	0.04	2.64	0.14	0.05	1.10
Coeff. Var.	98.6	282.3	75.3	45.3	44.9	35.0	109.1	120.0	133.8	33.7	50.5	22.1	20.7	54.8
n	17	17	17	16	16	17	17	16	16	17	17	17	17	16
Median	0.21	0.000	0.04	5.75	5.45	1.60	0.08	0.09	0.03	0.14	4.48	0.58	0.23	1.80
Maximum	0.81	0.010	0.08	14.50	13.64	3.66	0.50	0.87	0.37	0.19	12.55	0.84	0.35	5.39
Minimum	0.00	0.000	0.00	3.53	3.16	1.20	0.01	0.02	0.00	0.05	2.08	0.41	0.18	0.45
CNS - 11 to 20 m Summer														
Mean	<i>0.36</i>	0.004	0.04	6.40	5.99	1.15	<i>0.06</i>	0.18	0.13	<i>0.09</i>	3.73	<i>0.42</i>	0.20	<i>1.07</i>
Std Dev	0.29	0.008	0.04	3.50	3.40	0.38	0.03	0.20	0.19	0.03	2.13	0.13	0.08	0.50
Coeff. Var.	82.2	205.2	90.4	54.7	56.7	33.0	42.5	106.1	150.9	36.5	57.1	30.8	40.3	46.3
n	20	20	20	18	18	19	20	18	18	19	20	19	19	15
Median	0.29	0.000	0.04	5.14	4.69	1.10	0.07	0.13	0.06	0.08	3.86	0.40	0.18	1.06
Maximum	0.92	0.030	0.16	16.67	16.25	2.23	0.11	0.73	0.67	0.14	6.99	0.83	0.46	1.90
Minimum	0.04	0.000	0.00	3.18	3.07	0.44	0.02	0.03	0.00	0.04	0.53	0.19	0.09	0.27
CNS - 21 to 30 m Summer														
Mean	0.35	<i>0.000</i>	<i>0.04</i>	6.61	6.26	1.13	0.08	<i>0.14</i>	0.07	0.09	2.12	0.38	0.19	0.64
Std Dev	0.40	0.000	0.04	2.49	2.29	0.45	0.04	0.06	0.05	0.03	1.48	0.15	0.09	0.34
Coeff. Var.	114.7		100.2	37.6	36.5	39.7	52.4	40.3	77.3	32.5	69.9	39.2	45.9	52.2
n	20	20	20	18	18	19	20	18	18	20	20	20	20	9
Median	0.17	0.000	0.03	6.36	6.14	0.99	0.07	0.13	0.05	0.09	1.89	0.33	0.19	0.62
Maximum	1.22	0.000	0.20	10.03	9.71	2.73	0.17	0.28	0.20	0.15	4.58	0.68	0.38	1.28
Minimum	0.01	0.000	0.01	2.87	2.69	0.68	0.02	0.04	0.00	0.05	0.52	0.20	0.08	0.32
CNS - > 41 m Summer														
Mean	0.33	0.018	0.05	6.11	5.88	0.83	0.08	0.14	0.07	0.06	1.70	0.34	0.19	0.16
Std Dev	0.30	0.042	0.04	2.93	2.91	0.22	0.04	0.03	0.03	0.02	0.91	0.13	0.08	0.08
Coeff. Var.	90.4	235.8	75.2	48.0	49.4	26.3	51.7	22.1	48.2	35.9	53.5	38.5	41.7	50.1
n	17	17	17	11	11	17	17	11	11	17	17	17	17	4
Median	0.18	0.000	0.03	6.77	6.17	0.80	0.07	0.15	0.07	0.05	1.64	0.36	0.19	0.16
Maximum	0.95	0.170	0.13	12.25	11.93	1.19	0.17	0.18	0.12	0.10	3.61	0.56	0.36	0.25
Minimum	0.04	0.000	0.02	2.64	2.46	0.49	0.02	0.07	0.02	0.03	0.45	0.13	0.08	0.07

Table 6. Summary statistics for dissolved and particulate water column nutrient concentrations in the Cairns box for the winter (May - September) season. Values are given as the depth-weighted average concentrations over the full depth of the water column sampled. Bold means = significant difference between Cairns-Tully box means ($p < 0.05$)

	NH ₄	NO ₂	NO ₃	TDN	DON	PON μmol l ⁻¹	PO ₄	TDP	DOP	POP	SiO	Chl μg l ⁻¹	Phaeo μg l ⁻¹	S.S. mg l ⁻¹
CNS - <=10 m Winter														
Mean	0.40	0.003	0.06	6.34	5.87	1.67	0.10	0.15	0.06	0.19	6.69	0.77	0.34	3.47
Std Dev	0.31	0.009	0.05	2.86	2.83	0.54	0.03	0.07	0.06	0.09	3.31	0.33	0.18	1.98
Coeff. Var.	78.0	281.3	92.2	45.1	48.1	32.3	27.9	44.8	93.2	49.6	49.5	42.9	53.6	57.1
n	25	25	25	25	25	25	25	25	25	25	25	17	17	18
Median	0.26	0.000	0.04	5.87	5.00	1.63	0.10	0.13	0.05	0.17	4.94	0.70	0.28	2.99
Maximum	1.31	0.040	0.22	11.91	11.44	3.41	0.13	0.31	0.19	0.50	15.02	1.57	0.70	7.20
Minimum	0.11	0.000	0.00	2.90	2.62	0.73	0.04	0.03	0.00	0.06	3.42	0.35	0.11	0.59
CNS - 11 to 20 m Winter														
Mean	0.56	0.004	0.04	6.42	5.83	1.22	0.09	0.16	0.09	0.13	5.80	0.58	0.28	1.43
Std Dev	0.47	0.009	0.03	2.42	2.46	0.61	0.04	0.14	0.13	0.08	3.35	0.26	0.21	0.69
Coeff. Var.	83.6	224.9	87.3	37.7	42.3	49.9	43.2	85.8	149.3	64.3	57.8	44.7	75.5	48.4
n	50	50	50	49	49	50	50	49	49	50	50	36	36	32
Median	0.33	0.000	0.03	6.21	5.21	1.12	0.09	0.12	0.04	0.10	5.08	0.48	0.23	1.26
Maximum	1.80	0.050	0.16	12.21	12.01	4.43	0.25	0.57	0.50	0.43	17.78	1.68	1.38	3.29
Minimum	0.10	0.000	0.00	2.20	1.77	0.56	0.02	0.02	0.00	0.04	0.58	0.33	0.11	0.39
CNS - 21 to 30 m Winter														
Mean	0.39	0.006	0.08	5.24	4.73	1.09	0.09	0.10	0.03	0.08	3.79	0.59	0.27	0.88
Std Dev	0.28	0.007	0.08	1.40	1.33	0.27	0.03	0.06	0.05	0.02	3.27	0.21	0.11	0.28
Coeff. Var.	71.5	129.3	103.9	26.7	28.2	24.5	27.1	58.1	167.0	23.3	86.2	35.1	39.9	31.8
n	16	16	16	14	14	16	16	14	14	16	16	14	14	8
Median	0.33	0.000	0.06	5.69	4.99	1.06	0.10	0.08	0.01	0.08	2.62	0.58	0.26	0.86
Maximum	1.24	0.020	0.29	7.45	7.07	1.63	0.13	0.23	0.18	0.11	9.90	1.02	0.50	1.35
Minimum	0.11	0.000	0.00	2.97	2.66	0.74	0.05	0.03	0.00	0.05	0.71	0.30	0.11	0.60
CNS - >41 m Winter														
Mean	0.51	0.006	0.05	5.33	4.70	0.75	0.09	0.14	0.06	0.05	1.36	0.48	0.27	0.23
Std Dev	0.41	0.009	0.03	1.24	1.00	0.20	0.02	0.08	0.06	0.02	0.78	0.25	0.14	0.17
Coeff. Var.	80.6	162.0	72.1	23.3	21.2	27.0	19.9	54.8	108.5	42.0	56.9	53.4	52.0	70.9
n	21	21	21	19	18	20	21	19	18	21	21	11	11	10
Median	0.23	0.000	0.04	5.44	4.97	0.72	0.09	0.11	0.04	0.04	1.18	0.45	0.21	0.21
Maximum	1.27	0.030	0.14	7.49	6.18	1.20	0.12	0.27	0.19	0.08	3.76	1.11	0.63	0.52
Minimum	0.16	0.000	0.01	2.96	2.70	0.45	0.04	0.04	0.00	0.01	0.38	0.24	0.13	0.02

Table 7. Summary statistics for dissolved and particulate water column nutrient concentrations in the Tully box for the summer (October - April) season. Values are given as depth-weighted average concentrations over the full depth of the water column sampled. Italics = significant difference between winter-summer means ($p < 0.05$)

	NH ₄	NO ₂	NO ₃	TDN	DON	PON $\mu\text{mol l}^{-1}$	PO ₄	TDP	DOP	POP	SiO	Chl $\mu\text{g l}^{-1}$	Phaeo $\mu\text{g l}^{-1}$	S.S. mg l^{-1}
COT/FAM - <=10 m Summer														
Mean	0.16	0.050	0.10	0.31			0.10				9.71			
Std Dev	0.09	0.058	0.14	0.24			0.03				10.75			
Coeff. Var.	59.9	115.5	141.4	78.5			27.9				110.7			
n	4	4	4	4			4				4			
Median	0.17	0.050	0.05	0.32			0.10				5.49			
Maximum	0.24	0.100	0.30	0.53			0.12				25.34			
Minimum	0.04	0.000	0.00	0.06			0.06				2.53			
COT/FAM - 11-20 m Summer														
Mean	<i>0.19</i>	<i>0.006</i>	<i>0.04</i>	0.23	4.00	<i>1.37</i>	0.12		0.27	<i>0.10</i>	3.57	0.38	0.70	
Std Dev	0.25	0.025	0.06	0.28	0.49	0.27	0.05		0.06	0.03	1.60	0.16	0.95	
Coeff. Var.	134.3	400.0	165.1	118.6	12.3	19.6	41.6		20.7	31.6	44.9	41.5	136.1	
n	16	16	16	16	3	10	16		3	10	16	10	10	
Median	0.10	0.000	0.00	0.13	4.21	1.37	0.11		0.27	0.10	3.19	0.38	0.24	
Maximum	0.94	0.100	0.20	0.99	4.35	1.94	0.21		0.32	0.15	8.78	0.60	3.09	
Minimum	0.00	0.000	0.00	0.01	3.44	0.95	0.06		0.21	0.06	2.11	0.17	0.02	
COT/FAM - 21 to 30 m Summer														
Mean	0.19	0.000	0.03	0.22	3.70	1.21	0.12		0.22	<i>0.07</i>	2.09	0.35	<i>0.99</i>	
Std Dev	0.32	0.000	0.05	0.33	0.30	0.35	0.06		0.04	0.03	0.96	0.20	1.29	
Coeff. Var.	170.6		164.1	148.8	8.0	28.8	52.0		15.7	39.0	46.0	57.9	129.4	
n	14	14	14	14	3	10	14		3	10	14	10	10	
Median	0.05	0.000	0.00	0.08	3.68	1.16	0.11		0.22	0.07	1.63	0.32	0.41	
Maximum	1.12	0.000	0.10	1.19	4.00	1.88	0.26		0.26	0.12	4.02	0.70	3.97	
Minimum	0.00	0.000	0.00	0.01	3.41	0.68	0.06		0.19	0.04	0.84	0.14	0.02	
COT/FAM - > 41 m Summer														
Mean	<i>0.16</i>	<i>0.032</i>	0.09	<i>0.29</i>	4.55	<i>1.32</i>	<i>0.13</i>		0.35	0.08	<i>1.87</i>	0.38	0.90	
Std Dev	0.24	0.048	0.14	0.33	0.53	0.44	0.06		0.15	0.03	1.05	0.18	0.95	
Coeff. Var.	151.7	148.0	154.9	111.4	11.7	33.3	42.6		43.8	41.2	56.2	46.6	106.1	
n	28	28	28	28	6	21	28		6	21	28	21	21	
Median	0.09	0.000	0.00	0.14	4.65	1.20	0.12		0.31	0.08	1.50	0.36	0.51	
Maximum	1.02	0.100	0.60	1.13	5.29	2.59	0.23		0.64	0.13	4.26	0.70	3.32	
Minimum	0.00	0.000	0.00	0.06	3.79	0.90	0.06		0.23	0.04	0.75	0.15	0.11	

Table 8. Summary statistics for dissolved and particulate water column nutrient concentrations in the Tully box for the winter (May - September) season. Values are given as depth-weighted average concentrations over the full depth of the water column sampled.

	NH ₄	NO ₂	NO ₃	TDN	DON	PON μmol l ⁻¹	PO ₄	TDP	DOP	POP	SiO	Chl μg l ⁻¹	Phaeo μg l ⁻¹	S.S. mg l ⁻¹
COT/FAM - <= 10 m Winter														
Mean	1.17	0.175	0.35	1.71		2.46	0.14			0.30	29.26		0.02	
Std Dev	1.09	0.206	0.57	1.54		0.61	0.09			0.12	24.41		0.02	
Coeff. Var.	93.2	117.8	164.1	90.1		24.8	62.3			41.8	83.4		88.7	
n	4	4	4	4		4	4			4	4		4	
Median	0.89	0.150	0.10	1.70		2.19	0.13			0.27	18.80		0.02	
Maximum	2.61	0.400	1.20	3.08		3.37	0.25			0.46	65.53		0.03	
Minimum	0.30	0.000	0.00	0.35		2.08	0.06			0.20	13.91		0.00	
COT/FAM - 11 to 20 m Winter														
Mean	0.77	0.075	0.53	1.37		2.69	0.13			0.19	29.48		0.01	
Std Dev	0.65	0.096	0.61	1.40		0.18	0.07			0.06	11.49		0.01	
Coeff. Var.	83.9	127.7	116.8	102.1		6.5	57.1			34.9	39.0		102.9	
n	4	4	4	4		4	4			4	4		4	
Median	0.56	0.050	0.30	0.88		2.69	0.10			0.21	24.61		0.01	
Maximum	1.69	0.200	1.40	3.36		2.89	0.23			0.23	46.46		0.03	
Minimum	0.29	0.000	0.10	0.36		2.49	0.08			0.09	22.26		0.00	
COT/FAM - 21 to 30 m Winter														
Mean	0.32	0.000	0.06	0.38		1.18	0.11			0.11	4.74	0.26	0.00	
Std Dev	0.11	0.000	0.05	0.11		0.31	0.03			0.03	2.73	0.04	0.00	
Coeff. Var.	33.5		82.8	27.9		26.5	26.9			24.0	57.7	14.7	27.6	
n	8	8	8	8		12	8			12	8	4	8	
Median	0.30	0.000	0.10	0.36		1.27	0.11			0.11	4.75	0.27	0.00	
Maximum	0.49	0.000	0.10	0.54		1.69	0.15			0.15	7.62	0.30	0.01	
Minimum	0.16	0.000	0.00	0.21		0.70	0.07			0.07	1.89	0.22	0.00	
COT/FAM - > 41 m Winter														
Mean	0.42	0.000	0.07	0.51		0.89	0.08			0.07	1.29	0.25	0.74	
Std Dev	0.22	0.000	0.07	0.21		0.24	0.01			0.02	1.35	0.04	1.56	
Coeff. Var.	53.5		96.4	41.4		26.5	17.1			23.9	104.3	17.6	211.1	
n	10	10	10	10		16	10			16	10	8	10	
Median	0.32	0.000	0.10	0.44		0.91	0.08			0.07	0.98	0.25	0.00	
Maximum	0.92	0.000	0.20	0.98		1.18	0.11			0.10	5.09	0.31	4.08	
Minimum	0.27	0.000	0.00	0.33		0.57	0.07			0.04	0.44	0.16	0.00	

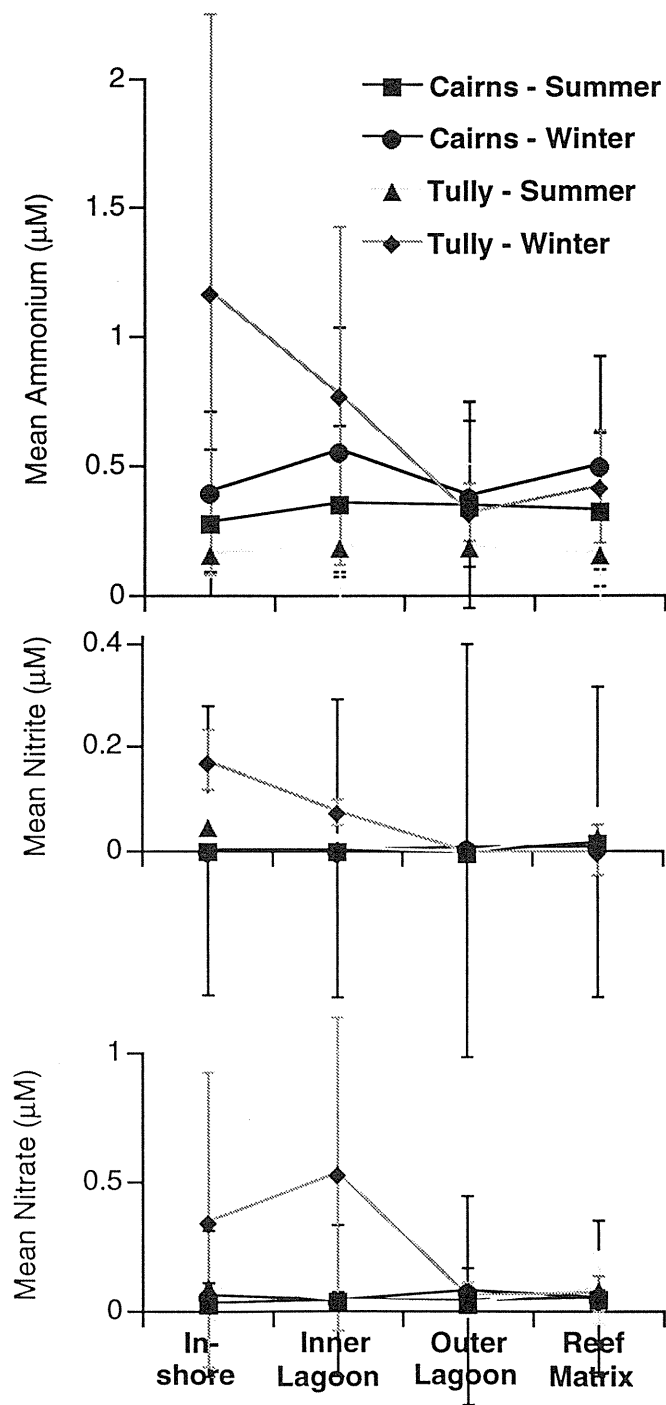


Figure 20. Cross-shelf gradients and seasonal changes in depth-weighted mean water column concentrations (± 1 standard deviation) of ammonium (Top), nitrite (Middle) and nitrate (Bottom) in the Cairns and Tully boxes.

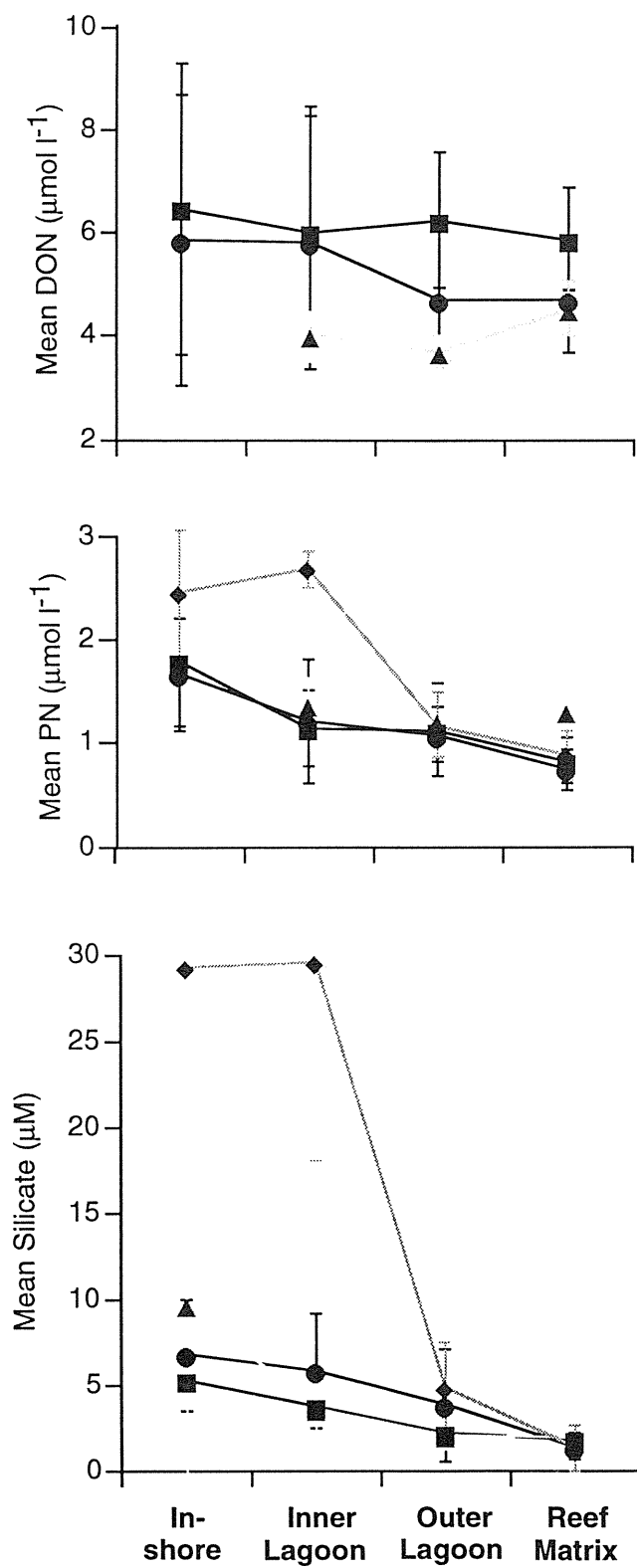


Figure 21. Cross-shelf gradients and seasonal changes in depth-weighted mean water column concentrations (± 1 standard deviation) of DON (Top), PN (Middle) and silicate (Bottom) in the Cairns and Tully boxes. Symbols are as given in Figure 20.

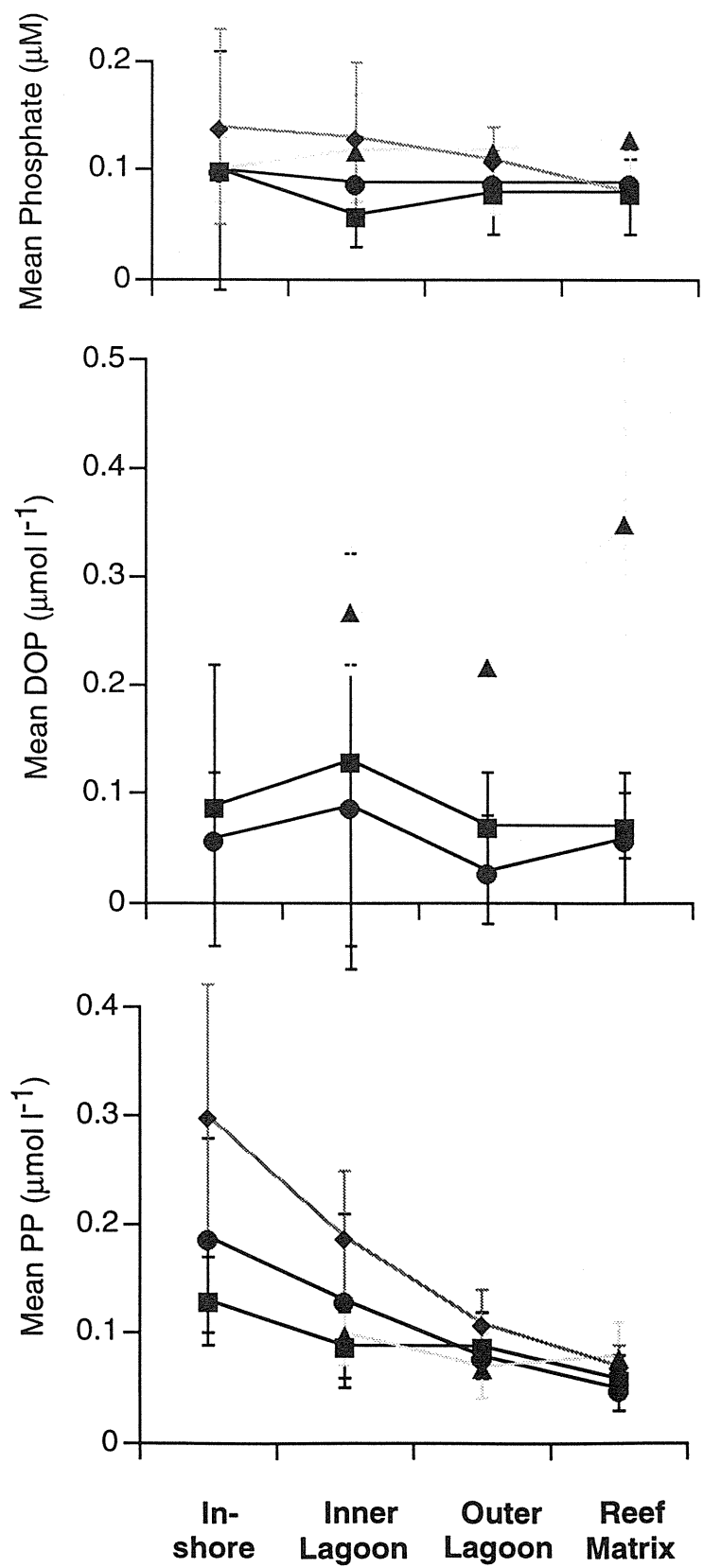


Figure 22. Cross-shelf gradients and seasonal changes in depth-weighted mean water column concentrations (± 1 standard deviation) of phosphate (Top), DOP (Middle) and PP (Bottom) in the Cairns and Tully boxes. Symbols are as given in Figure 20.

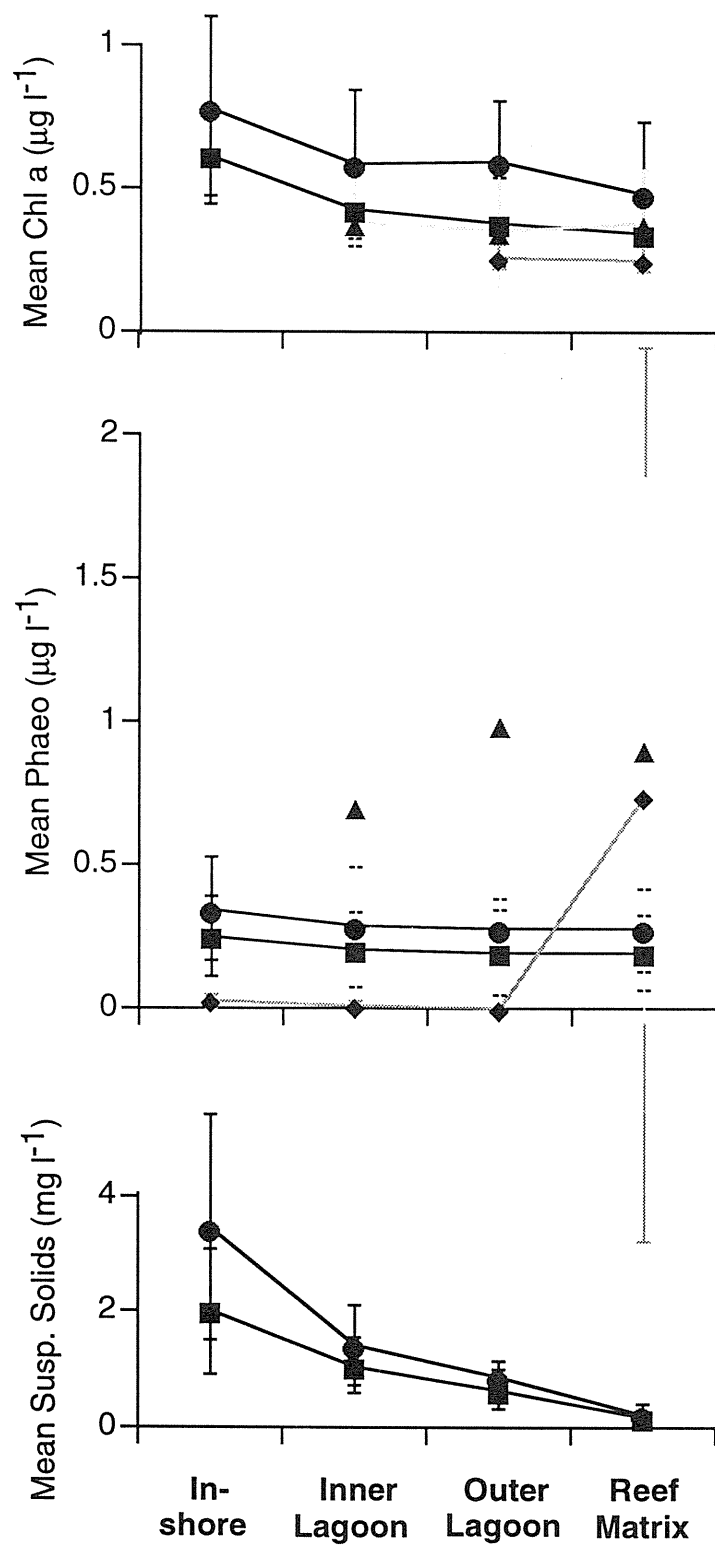


Figure 23. Cross-shelf gradients and seasonal changes in depth-weighted mean water column concentrations (± 1 standard deviation) of chlorophyll *a* (Top), phaeophytin (Middle) and suspended solids (Bottom) in the Cairns and Tully boxes. Symbols are as given in Figure 20.

Tables 9-12 present calculated seasonal estimates of integrated stocks of individual nutrient species within each of the depth bands, total stocks within each of the two boxes and the distributions of nutrient stocks between the four depth bands. Despite the general occurrence of higher concentrations of most nutrient species in the two shallowest depth bands, most of the nutrient, suspended particle and pigment stocks, resided in the larger volumes of water seaward of the 30 m isobath. This trend was least pronounced in the case of suspended solids, where resuspension processes near the coast result in elevated nearshore concentrations.

Tables 13-16 give the estimates of total shelf nutrient stocks per linear metre of coastline within each of the two boxes. With the exception of DON and suspended solids, shelf stocks of most nutrient species were on the order of several 1's to several 10's of kilomoles per metre of coastline. These estimates provide a basis for normalizing inputs and sinks of nutrients which must be averaged over longer sections of the coast.

Dissolved organic nitrogen (DON) was, by a large margin, the largest pool of water column nitrogen, comprising 78-81 percent of the total water column stock. The composition and activity of this heterogeneous pool of nitrogen is virtually unknown. Particulate nitrogen (PN) is the next largest pool, ranging between 14 and 21 percent of total water column nitrogen. Ammonium was the principal form of inorganic nitrogen in central GBR waters, with contributions to total shelf stocks ranging between 1.5 and 6.3 percent. Nitrate and nitrite were, in all cases, trivial contributors to total shelf nitrogen stocks.

Phosphorus was more equally divided between dissolved inorganic, dissolved organic and particulate pools in both the Cairns and Tully boxes. Dissolved inorganic stocks ranged between 23 and 49 percent of total phosphorus. Dissolved organic phosphorus ranged between 15 and 60 percent of total phosphorus, while particulate phosphorus varied between 16 and 36 percent of total phosphorus. The greatest discrepancy from this general pattern occurred during summer in the samples collected off Dunk Island, where 60 percent of the total water column phosphorus was apparently present as DOP and only 16 percent as PP. Unfortunately, insufficient winter data is available to assess whether this distribution between phosphorus species is a persistent feature in the Tully box or is ephemeral.

The relationship of measured PN and PP concentrations to phytoplankton biomass (as chlorophyll) was highly variable (Figure 24). In both cases, statistical correlations between either PN or PP and chlorophyll were weak. The intercepts of geometrical mean slope functional regressions (Ricker, 1973, hereafter GM regression) of PN on chlorophyll were not statistically different from zero, indicating that most of the particulate nitrogen in the water column was associated with, or derived from, algal material. However, the slopes of both the PN-chl and PP-chl functional regressions (1.9 and $0.21 \text{ mmol mg}^{-1}$, respectively) are considerably higher than the ratios expected for living phytoplankton (0.5 to 1 and 0.01 - 0.1 mmol mg^{-1} ; Perry, 1976; Goldman, 1980), clearly indicating that most of the PN and PP in GBR shelf waters is in the form of detritus.

Correlations between PN or PP and suspended solids were less well defined (Figure 25). In the case of PN, the intercept of the GM regression was considerably greater than zero, clearly indicating a poor association between PN and inorganic suspended materials. The intercept of the functional PP vs. suspended solids relationship did not greatly differ from zero, suggesting that most of the PP not tied up in phytoplankton biomass is bound to inorganic particles. Phosphorus is known to be strongly bound to regional soil (Moody and Chapman, 1991) and marine sediment particles (Entsch et al., 1983; Alongi, 1989) and to be enriched in carbonate sediments in particular (Entsch et al., 1983). Step-wise regressions of PN and PP on suspended solids and chlorophyll concentrations indicate that fluctuations in these two variables collectively account for only 44 and 33 percent of the variances in PN and PP concentrations, respectively. In single variable regressions, fluctuations in suspended solids concentrations

account for 30 and 18 percent of the variance in PN and PP, respectively, with chlorophyll alone accounting for 31 and 16 percent. The high level of scatter in the individual relationships precludes the use of functional relationships between PN, PP, chlorophyll and suspended solids based on field data for predicting phytoplankton biomass.

The mean N/P ratio in pooled particulate matter taken from the GM regressions slope (7.53) is approximately half of the value expected for phytoplankton with a Redfield composition (N/P = 16) (Figure 26). Collectively, the high P/chl ratio (from the GM regression slope) and low particulate N/P ratio are indicative of dilution of the water column particulate phosphorus pool with phosphorus adsorbed to or incorporated in inorganic particles.

Table 9. Distribution of shelf nutrient stocks within long-shelf depth bands in the Cairns box during summer (October - April). Concentrations used are median concentrations from Table 5.

Depth Band Volume (km ³)	Median concentration (μM)*				Stock in depth band (kmol)				kmol Total Stock	Percentage of total stock in depth bands			
	<10 m	10-20 m	20-30 m	30+ m	<10 m	10-20 m	20-30 m	30+ m		<10 m	10-20 m	20-30 m	30+ m
	1.9	10.9	20.4	149									
NH ₄	0.21	0.29	0.17	0.18	399.0	3106.5	3366.0	26820.0	33692	1.2	9.2	10.0	79.6
NO ₂	0.000	0.000	0.000	0.000	0.0	0.0	0.0	0.0	0	0	0	0	0
NO ₃	0.04	0.04	0.03	0.03	76.0	436.0	612.0	4470.0	5594	1.4	7.8	10.9	79.9
TDN	5.75	5.14	6.36	4.81	10915.5	55971.5	129642.0	715945.0	912474	1.2	6.1	14.2	78.5
DON	5.45	4.69	6.14	4.68	10355.0	51121.0	125154.0	696575.0	883205	1.2	5.8	14.2	78.9
PON	1.60	1.10	0.99	0.91	3040.0	11990.0	20196.0	135590.0	170816	1.8	7.0	11.8	79.4
PO ₄	0.08	0.07	0.07	0.06	152.0	708.5	1428.0	8940.0	11229	1.4	6.3	12.7	79.6
TDP	0.09	0.13	0.13	0.15	171.0	1362.5	2652.0	22350.0	26536	0.6	5.1	10.0	84.2
DOP	0.03	0.06	0.05	0.07	57.0	599.5	1020.0	10430.0	12107	0.5	5.0	8.4	86.2
POP	0.14	0.08	0.09	0.06	266.0	872.0	1734.0	8940.0	11812	2.3	7.4	14.7	75.7
SiO	4.48	3.86	1.89	2.06	8512.0	42019.5	38454.0	306940.0	395926	2.1	10.6	9.7	77.5
Chlorophyll	0.58	0.40	0.33	0.31	1102.0	4360.0	6732.0	46190.0	58384	1.9	7.5	11.5	79.1
Phaeophytin	0.23	0.18	0.19	0.17	437.0	1962.0	3774.0	25330.0	31503	1.4	6.2	12.0	80.4
Susp. Solids	1.80	1.06	0.62	0.25	3420.0	11554.0	12648.0	37250.0	64872	5.3	17.8	19.5	57.4
Total dissolved N					475.0	3542.5	3978.0	31290.0					
Total N					13870.0	66653.5	149328.0	863455.0					
Total dissolved P					323.0	2071.0	4080.0	31290.0					
Total P					589.0	2943.0	5814.0	40230.0					

* Pigment concentrations are in μg per litre and suspended solids concentrations are in mg per litre

Table 10. Distribution of shelf nutrient stocks within long-shelf depth bands in the Cairns box during winter (May - September). Concentrations used are median concentrations from Table 6.

Depth Band Volume (km ³)	Median concentration (µM)*				Stock in depth band (kmol)				kmol Total Stock	Percentage of total stock in depth bands			
	<10 m 1.9	10-20 m 10.9	20-30 m 20.4	30+ m 149	<10 m	10-20 m	20-30 m	30+ m		<10 m	10-20 m	20-30 m	30+ m
NH ₄	0.26	0.33	0.33	0.44	494.0	3542.5	6630.0	65560.0	76227	0.6	4.6	8.7	86.0
NO ₂	0.000	0.000	0.000	0.000	0.0	0.0	0.0	0.0	0	0	0	0	0
NO ₃	0.04	0.03	0.06	0.07	76.0	327.0	1122.0	10430.0	11955	0.6	2.7	9.4	87.2
TDN	5.87	6.21	5.69	6.26	11153.0	67689.0	116076.0	932740.0	1127658	1.0	6.0	10.3	82.7
DON	5.00	5.21	4.99	5.29	9500.0	56789.0	101796.0	787465.0	955550	1.0	5.9	10.7	82.4
PON	1.63	1.12	1.06	0.86	3097.0	12153.5	21624.0	128140.0	165015	1.9	7.4	13.1	77.7
PO ₄	0.10	0.09	0.10	0.09	190.0	981.0	1938.0	13410.0	16519	1.2	5.9	11.7	81.2
TDP	0.13	0.12	0.08	0.12	247.0	1308.0	1530.0	17880.0	20965	1.2	6.2	7.3	85.3
DOP	0.05	0.04	0.01	0.03	95.0	436.0	204.0	4470.0	5205	1.8	8.4	3.9	85.9
POP	0.17	0.10	0.08	0.06	323.0	1090.0	1632.0	8940.0	11985	2.7	9.1	13.6	74.6
SiO	4.94	5.08	2.62	1.41	9386.0	55317.5	53346.0	210090.0	328140	2.9	16.9	16.3	64.0
Chlorophyll	0.70	0.48	0.58	0.35	1330.0	5232.0	11730.0	52150.0	70442	1.9	7.4	16.7	74.0
Phaeophytin	0.28	0.23	0.26	0.20	532.0	2452.5	5202.0	29800.0	37987	1.4	6.5	13.7	78.4
Susp. Solids	2.99	1.26	0.86	0.36	5671.5	13734.0	17442.0	53640.0	90488	6.3	15.2	19.3	59.3
Total dissolved N					570.0	3869.5	7752.0	75990.0					
Total N					13167.0	72812.0	131172.0	991595.0					
Total dissolved P					437.0	2289.0	3468.0	31290.0					
Total P					760.0	3379.0	5100.0	40230.0					

* Pigment concentrations are in µg per litre and suspended solids concentrations are in mg per litre

Table 11. Distribution of shelf nutrient stocks within long-shelf depth bands in the Tully box during summer (October - April). Concentrations used are median concentrations from Table 7.

Depth Band Volume (km ³)	Median concentration (µM)*				Stock in depth band (kmol)				kmol	Percentage of total stock in depth bands			
	<10 m 1.5	10-20 m 8.5	20-30 m 31	30+ m 267	<10 m	10-20 m	20-30 m	30+ m		<10 m	10-20 m	20-30 m	30+ m
NH4	0.17	0.10	0.05	0.09	255.0	807.5	1395.0	24030.0	26488	1.0	3.0	5.3	90.7
NO2	0.050	0.000	0.000	0.000	75.0	0.0	0.0	0.0	75	100.0	0.0	0.0	0.0
NO3	0.05	0.00	0.00	0.00	75.0	0.0	0.0	0.0	75	100.0	0.0	0.0	0.0
TDN	0.32	0.13	0.08	0.14	472.5	1062.5	2480.0	37380.0	41395	1.1	2.6	6.0	90.3
DON		4.21	3.68	4.65	0.0	35785.0	114080.0	1240215.0	1390080	0.0	2.6	8.2	89.2
PON		1.37	1.16	1.20	0.0	11602.5	35960.0	320400.0	367963	0.0	3.2	9.8	87.1
PO4	0.10	0.11	0.11	0.12	150.0	935.0	3410.0	30705.0	35200	0.4	2.7	9.7	87.2
TDP													
DOP		0.27	0.22	0.31	0.0	2295.0	6820.0	81435.0	90550	0.0	2.5	7.5	89.9
POP		0.10	0.07	0.08	0.0	807.5	2015.0	21360.0	24183	0.0	3.3	8.3	88.3
SiO	5.49	3.19	1.63	1.45	8235.0	27072.5	50375.0	385815.0	471498	1.7	5.7	10.7	81.8
Chlorophyll		0.38	0.32	0.36	0.0	3187.5	9765.0	96120.0	109073	0.0	2.9	9.0	88.1
Phaeophytin		0.24	0.41	0.51	0.0	2044.3	12679.0	136437.0	151160	0.0	1.4	8.4	90.3
Susp. Solids													
Total dissolved N					405.0	807.5	1395.0	24030.0					
Total N					405.0	48195.0	151435.0	1584645.0					
Total dissolved P					150.0	935.0	3410.0	30705.0					
Total P					150.0	1742.5	5425.0	52065.0					

* Pigment concentrations are in µg per litre and suspended solids concentrations are in mg per litre

Table 12. Distribution of shelf nutrient stocks within long-shelf depth bands in the Tully box during winter (May - September). Concentrations used are median concentrations from Table 6.

Depth Band Volume (km ³)	Median concentration (µM)*				Stock in depth band (kmol)				kmol	Percentage of total stock in depth bands			
	<10 m	10-20 m	20-30 m	30+ m	<10 m	10-20 m	20-30 m	30+ m		<10 m	10-20 m	20-30 m	30+ m
	1.9	10.9	20.4	149									
NH ₄	0.89	0.56	0.30	0.32	1681.5	6049.5	6120.0	47680.0	61531	2.7	9.8	9.9	77.5
NO ₂	0.150	0.050	0.000	0.000	285.0	545.0	0.0	0.0	830	34.3	65.7	0.0	0.0
NO ₃	0.10	0.30	0.10	0.10	190.0	3270.0	2040.0	14900.0	20400	0.9	16.0	10.0	73.0
TDN													
DON													
PON	2.19	2.69	1.27	0.91	4161.0	29321.0	25806.0	134845.0	194133	2.1	15.1	13.3	69.5
PO ₄	0.13	0.10	0.11	0.08	247.0	1035.5	2142.0	11920.0	15345	1.6	6.7	14.0	77.7
TDP													
DOP													
POP	0.27	0.21	0.11	0.07	503.5	2289.0	2142.0	10430.0	15365	3.3	14.9	13.9	67.9
SiO ₂	18.80	24.61	4.75	0.98	35710.5	268194.5	96798.0	145275.0	545978	6.5	49.1	17.7	26.6
Chlorophyll			0.27	0.25									
Phaeophytin	0.02	0.01	0.00	0.00	32.3	92.7	81.6	596.0	803	4.0	11.5	10.2	74.3
Susp. Solids													
Total dissolved N					2156.5	9864.5	8160.0	62580.0					
Total N					6317.5	39185.5	33966.0	197425.0					
Total dissolved P					247.0	1035.5	2142.0	11920.0					
Total P					750.5	3324.5	4284.0	22350.0					

* Pigment concentrations are in µg per litre and suspended solids concentrations are in mg per litre

Table 13. Calculated stocks of nutrients per metre of coastline within the Cairns box during summer. Linear distance along coast (16° 5'S - 16° 52.5'S) - 88 km.

	kmol	kmol m ⁻¹	Metric tons	Metric tons per metre of Coastline
NH ₄	33692	0.383	472.02	0.0054
NO ₂	0	0.000	0.00	0.0000
NO ₃	5594	0.064	78.37	0.0009
TDN	912474	10.369	12783.76	0.1453
DON	883205	10.036	12373.70	0.1406
PON	170816	1.941	2393.13	0.0272
PO ₄	11229	0.128	157.31	0.0018
TDP	26536	0.302	371.76	0.0042
DOP	12107	0.138	169.61	0.0019
POP	11812	0.134	165.49	0.0019
SiO	395926	4.499	5546.92	0.0630
	kg	kg m ⁻¹	Metric tons	Metric tons per metre of Coastline
Chlorophyll	58384	0.663	58.38	0.0007
Phaeophytin	31503	0.358	31.50	0.0004
Susp. Solids	64872	0.737	64872.00	0.7372

Table 14. Calculated stocks of nutrients per metre of coastline within the Cairns box during winter. Linear distance along coast (16° 5'S - 16° 52.5'S) - 88 km.

	kmol	kmol m ⁻¹	Metric tons	Metric tons per metre of Coastline
NH ₄	76227	0.866	1067.93	0.0121
NO ₂	0	0.000	0.00	0.0000
NO ₃	11955	0.136	167.49	0.0019
TDN	1127658	12.814	15798.49	0.1795
DON	955550	10.859	13387.26	0.1521
PON	165015	1.875	2311.85	0.0263
PO ₄	16519	0.188	231.43	0.0026
TDP	20965	0.238	293.72	0.0033
DOP	5205	0.059	72.92	0.0008
POP	11985	0.136	167.91	0.0019
SiO	328140	3.729	4597.23	0.0522
	kg	kg m ⁻¹	Metric tons	Metric tons per metre of Coastline
Chlorophyll	70442	0.800	70.44	0.0008
Phaeophytin	37987	0.432	37.99	0.0004
Susp. Solids	90488	1.028	90487.50	1.0283

Table 15. Calculated stocks of nutrients per metre of coastline within the Tully box during summer. Linear distance along coast (16° 52.5'S - 17° 55'S) - 116 km.

	kmol	kmol m ⁻¹	Metric tons	Metric tons per metre of Coastline
NH ₄	26488	0.228	371.09	0.0032
NO ₂	75	0.001	1.05	0.0000
NO ₃	75	0.001	1.05	0.0000
TDN				
DON	1390080	11.983	19475.02	0.1679
PON	367963	3.172	5155.15	0.0444
PO ₄	35200	0.303	493.15	0.0043
TDP				
DOP	90550	0.781	1268.61	0.0109
POP	24183	0.208	338.80	0.0029
SiO	471498	4.065	6605.68	0.0569
	kg	kg m ⁻¹	Metric tons	Metric tons per metre of Coastline
Chlorophyll	109073	0.940	109.07	0.0012
Phaeophytin	151160	1.303	151.16	0.0017
Susp. Solids				

Table 16. Calculated stocks of nutrients per metre of coastline within the Tully box during winter. Linear distance along coast (16° 52.5'S - 17° 55'S) - 116 km.

	kmol	kmol m ⁻¹	Metric tons	Metric tons per metre of Coastline
NH ₄	61531	0.530	862.05	0.0074
NO ₂	830	0.007	11.63	0.0001
NO ₃	20400	0.176	285.80	0.0025
TDN				
DON				
PON	194133	1.674	2719.80	0.0234
PO ₄	15345	0.132	214.98	0.0019
TDP				
DOP				
POP	15365	0.132	215.26	0.0019
SiO	545978	4.707	7649.15	0.0659
	kg	kg m ⁻¹	Metric tons	Metric tons per metre of Coastline
Chlorophyll	803	0.007	0.80	0.0000
Phaeophytin		0.000	0.00	0.0000
Susp. Solids				

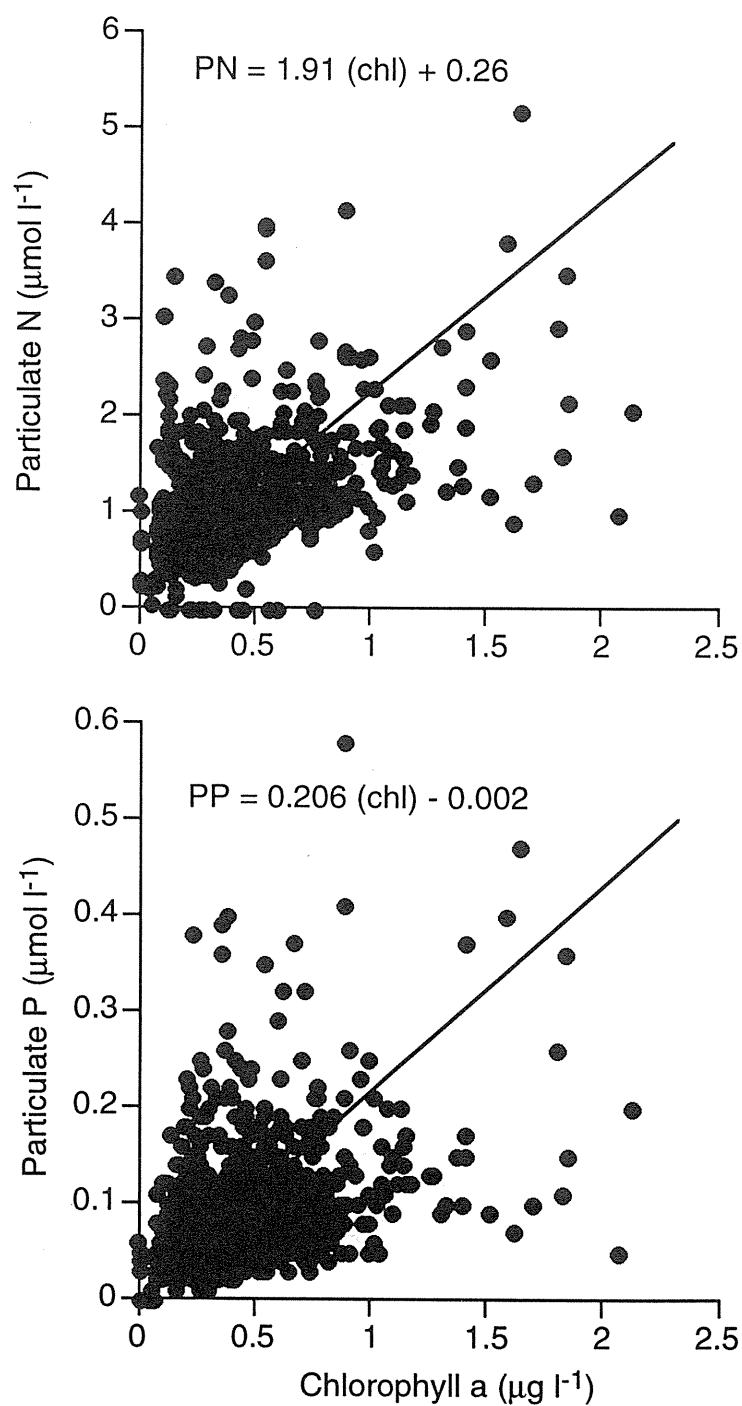


Figure 24. Relationships between depth-weighted mean water column stocks of PN and PP and stocks of chlorophyll *a* in waters of the Cairns and Tully boxes. The regression lines shown are GM functional regressions (Ricker, 1973).

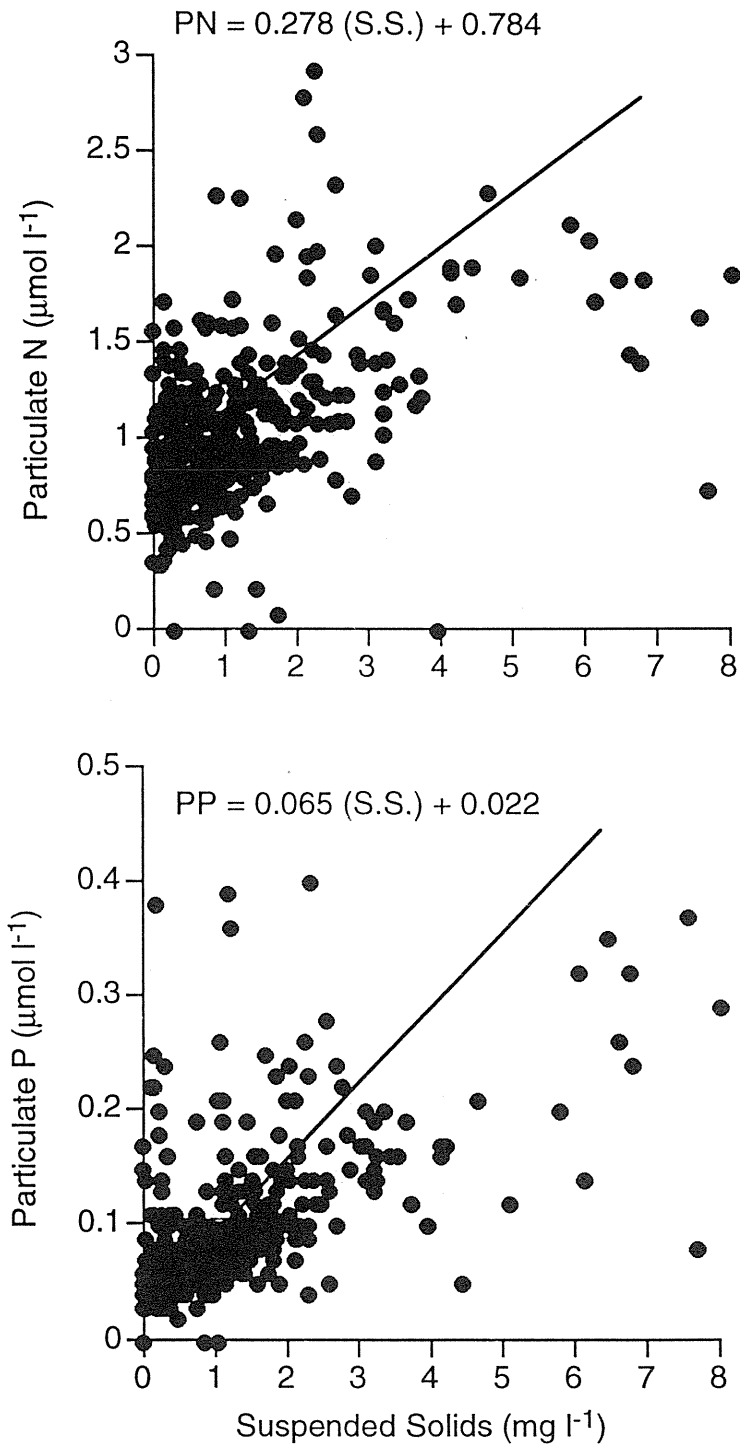


Figure 25. Relationships between depth-weighted mean water column stocks of PN and PP and stocks of suspended solids in waters of the Cairns and Tully boxes. The regression lines shown are GM functional regressions (Ricker, 1973).

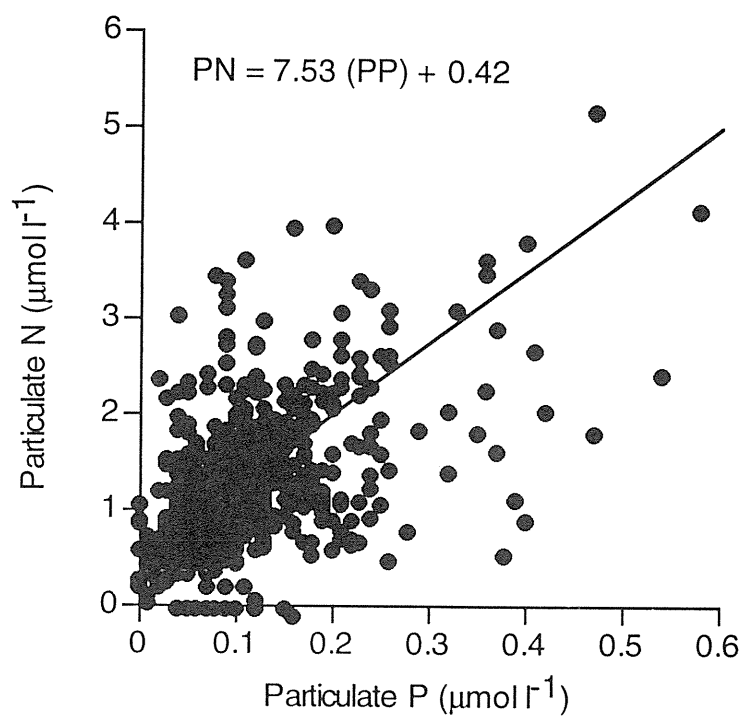


Figure 26. Relationships between depth-weighted mean water column stocks of PN and PP in the Cairns and Tully boxes. The regression lines shown are GM functional regressions (Ricker, 1973).

7. TEMPORAL AND SPATIAL VARIABILITY OF NUTRIENT SPECIES IN THE CAIRNS AND TULLY BOXES

One of the factors affecting our perception of nutrient levels and water quality in GBR waters, and the estimation of system fluxes, is the spatial and temporal variability in the components of interest. This variability can be partitioned between sampling and subsampling processes, analytical methodologies, spatial variations in concentration arising out of physical and biological processes affecting nutrient sources and sinks and temporal variations in those processes. As part of the ongoing program of oceanographic and geochemical studies being carried out in the central GBR, a number of hydrographic stations within each box were repeatedly occupied. This repeat sampling allows us to develop a quantitative understanding about spatial and temporal variability in dissolved and particulate nutrient concentrations.

Along the southern boundary of the Tully box, hydrographic stations were occupied at each of the sediment trap deployment sites when traps were deployed and recovered (FAM stations). This data set gives an indication of nutrient variability related to cross-shelf location (4 sites), seasonal changes (5 times), and day-to-day fluctuations (each station occupied once per day for 4 days per seasonal trip). Sampling along this transect was carried out during September, 1989; February, 1990; May, 1990; August, 1990 and November, 1991. For statistical analysis, the nutrient concentration data are dealt with as depth-weighted mean water column concentrations.

To specifically investigate levels of spatial and temporal variability in dissolved and particulate nutrient concentrations within coastal waters of the Cairns box, a transect of eleven stations between Cape Tribulation and Green Island (Figure 5; Table 17) were occupied ten times between February, 1989 and July, 1991. The transect will continue to be occupied, but only samples and data for the period indicated have been analysed to date. For brevity, the data are reported as depth weighted mean water column concentrations.

Table 17. Locations of longshore transect stations between Cape Tribulation and Green Island.

Station	Latitude	Longitude	Depth (m)	Site Name
1	16° 7.1'S	145° 28.9'E	17	Cape Tribulation
2	16° 14.3'	145° 30.8'	21	Snapper Island
3	16° 19.2'	145° 28.2'	12	Daintree River
4	16° 24.7'	145° 30.5'	16	Port Douglas
5	16° 39.9'	145° 42.1'	20	Double Island
6	16° 47.8'	145° 44.6'	9	Yorkey's Knob
7	16° 49.5'	145° 47.4'	9	Cairns Airport
8	16° 51.0'	145° 50.0'	8	Cairns Fairlead
9	16° 49.3'	145° 52.8'	14	Mission Bay
10	16° 47.8'	145° 55.1'	30	Shipping Channel
11	16° 46.6'	145° 57.1'	38	Green Island

On each cruise, all stations on the transect were occupied on a single day, proceeding from north to south. The transect consists of nine stations situated in close proximity to the coastline between Cape Tribulation and Cape Grafton. The two final stations of the transect were located in deeper waters of the shipping channel seaward of Cape Grafton (28-30 m depth) and near Green Island (34-36 m depth). The coastal stations generally lie outside of the nearshore zone of wave forced sediment resuspension, as suggested by water column turbidity. The northernmost three stations are situated downcurrent of the Daintree River as its outflow moves northward along the coast. Likewise, stations between Yorkey's Knob and Port Douglas are

directly affected by outflow from the Barron River. Distinct low salinity waters or plumes were not evident visually, though salinities tended to be slightly lower inshore.

Figures 27-32 summarize the temporal and spatial changes in depth-weighted mean water column nutrient and particulate concentrations measured at the Cairns box transect stations over a 30-month period. Overall means and standard deviations of the depth-weighted mean water column concentrations for the individual cruises are summarized in Table 18. The results of analyses of variance of the transect data (2-way fixed effect: Cruise, Station; Super Anova, Abacus Software) are summarized in Table 19.

Spatial (longshore) and temporal (cruise-to-cruise) variability varied considerably between individual nutrient and particulate species. Stocks of all species exhibited highly significant between-cruise variability. Significant between-station variability was observed for NO_3 , DON, PN, PP, Si, Chl *a*, phaeophytin and suspended solids. However, spatial patterns of nutrient concentration changed considerably between individual cruises. With the exception of consistently lower water column nutrient concentrations in the mid-shelf waters near Cape Grafton and Green Island, no clear-cut recurrent patterns of nutrient concentration were evident for individual nutrient species. It should be noted that the chemical and statistical analysis of the samples and data from this exercise is incomplete and more interesting patterns or trends may emerge with more concentrated and sophisticated analysis.

Because of the often long intervals (up to 6 months) between cruises, it is not possible to attribute the observed temporal changes solely to seasonal factors. Rather, it is likely that the observed between-cruise differences reflect local responses to short-term events, such as wind mixing or resuspension in coastal waters. With the exception of DON and DOP, no distinct temporal trends in mean water column concentrations of any nutrient or particulate species were observed over the 30-month period examined to date (Figure 33). This is a rather short interval, so the absence of a distinct temporal trend is not surprising. DON and DOP concentrations (which were analysed simultaneously on the same samples) exhibited a simultaneous increase and decrease over time. If the initial and final mean concentrations are compared, little net change is apparent.

The limited set of results from this monitoring exercise clearly illustrate that the detection of trends in water quality parameters in coastal waters of the GBR region will require a long-term (>10 year) commitment to monitoring programs. It is unlikely that sampling programs of short duration, no matter how they are designed to resolve sampling and spatial variability, will be able to detect real temporal changes in water quality parameters.

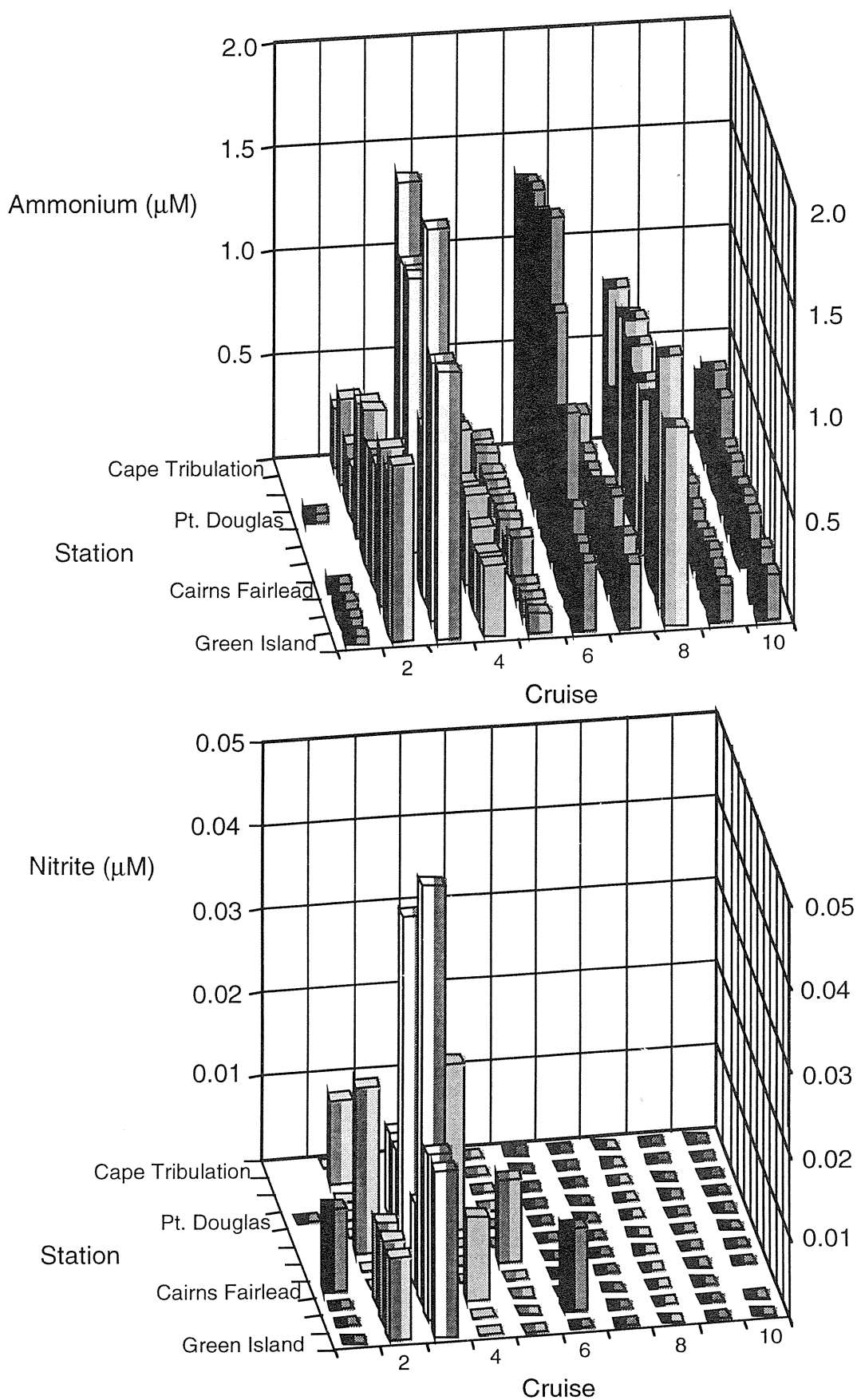


Figure 27. Depth-weighted mean water column concentrations of ammonium (Top) and nitrite (Bottom) along a transect between Cape Tribulation and Green Island, sampled ten times between February 1989 and July 1991.

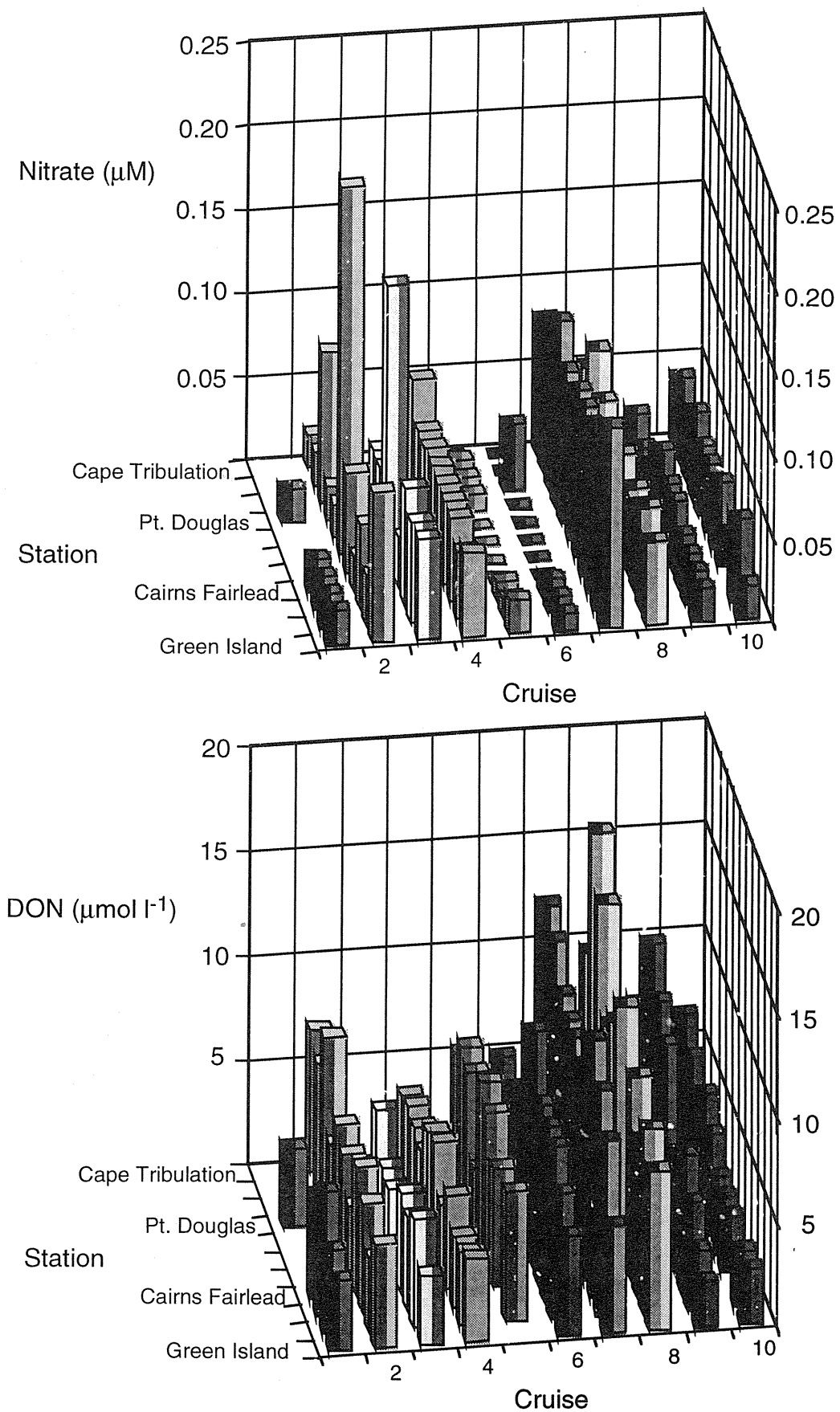


Figure 28. Depth-weighted mean water column concentrations of nitrate (Top) and dissolved organic nitrogen (Bottom) along a transect between Cape Tribulation and Green Island, sampled ten times between February 1989 and July 1991.

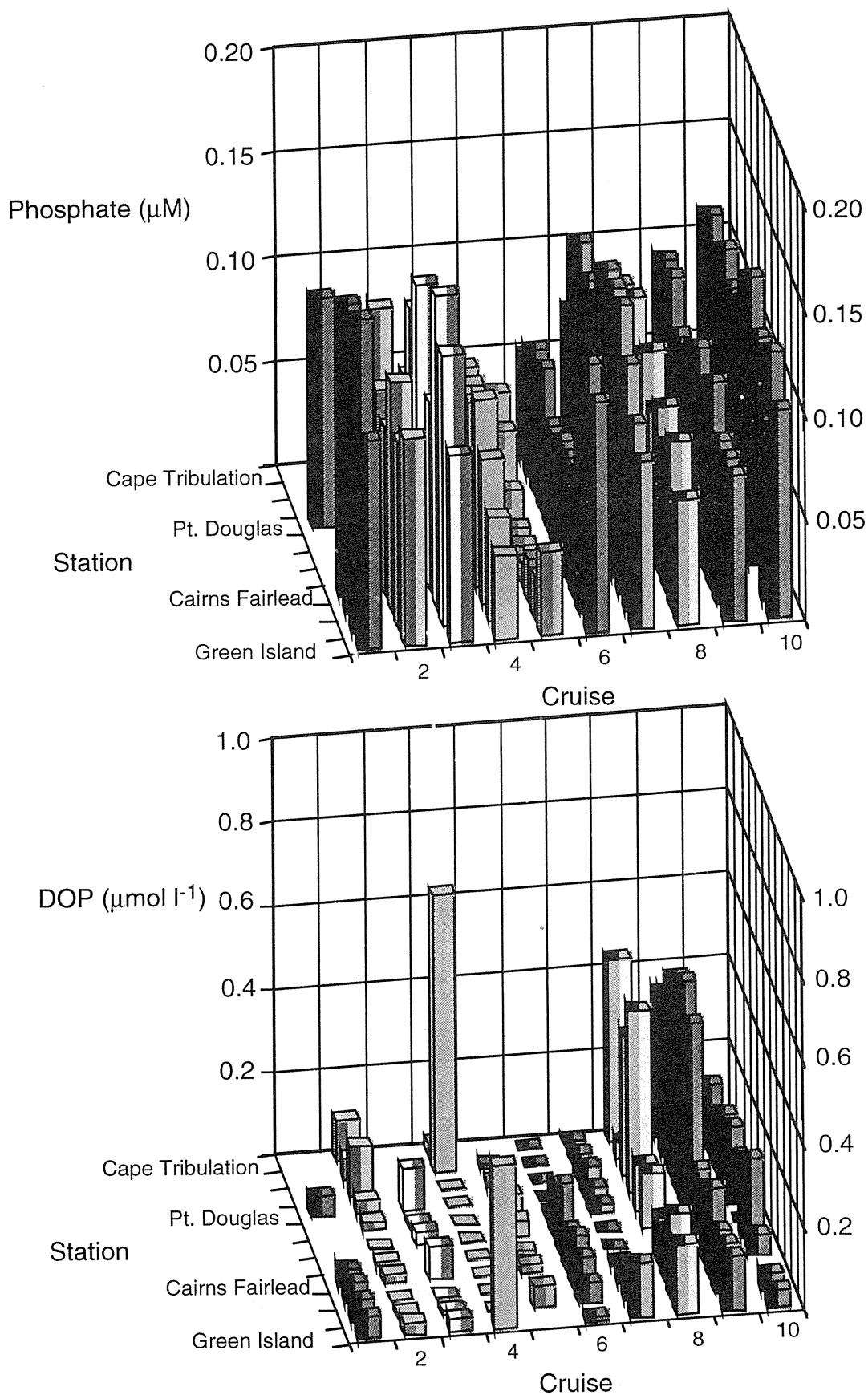


Figure 29. Depth-weighted mean water column concentrations of phosphate (Top) and dissolved organic phosphorus (Bottom) along a transect between Cape Tribulation and Green Island, sampled ten times between February 1989 and July 1991.

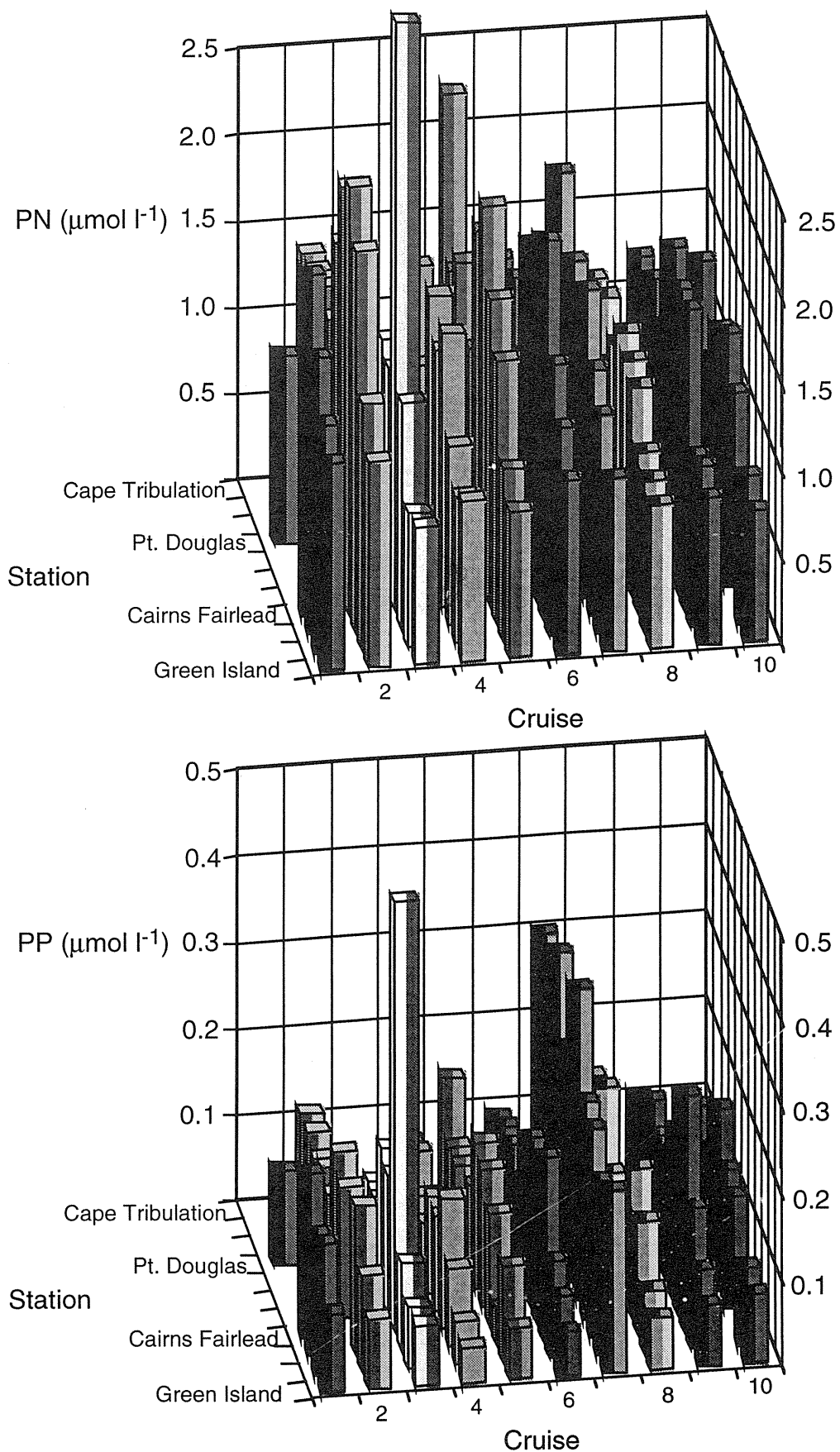


Figure 30. Depth-weighted mean water column concentrations of particulate nitrogen (Top) and particulate phosphorus (Bottom) along a transect between Cape Tribulation and Green Island, sampled ten times between February 1989 and July 1991.

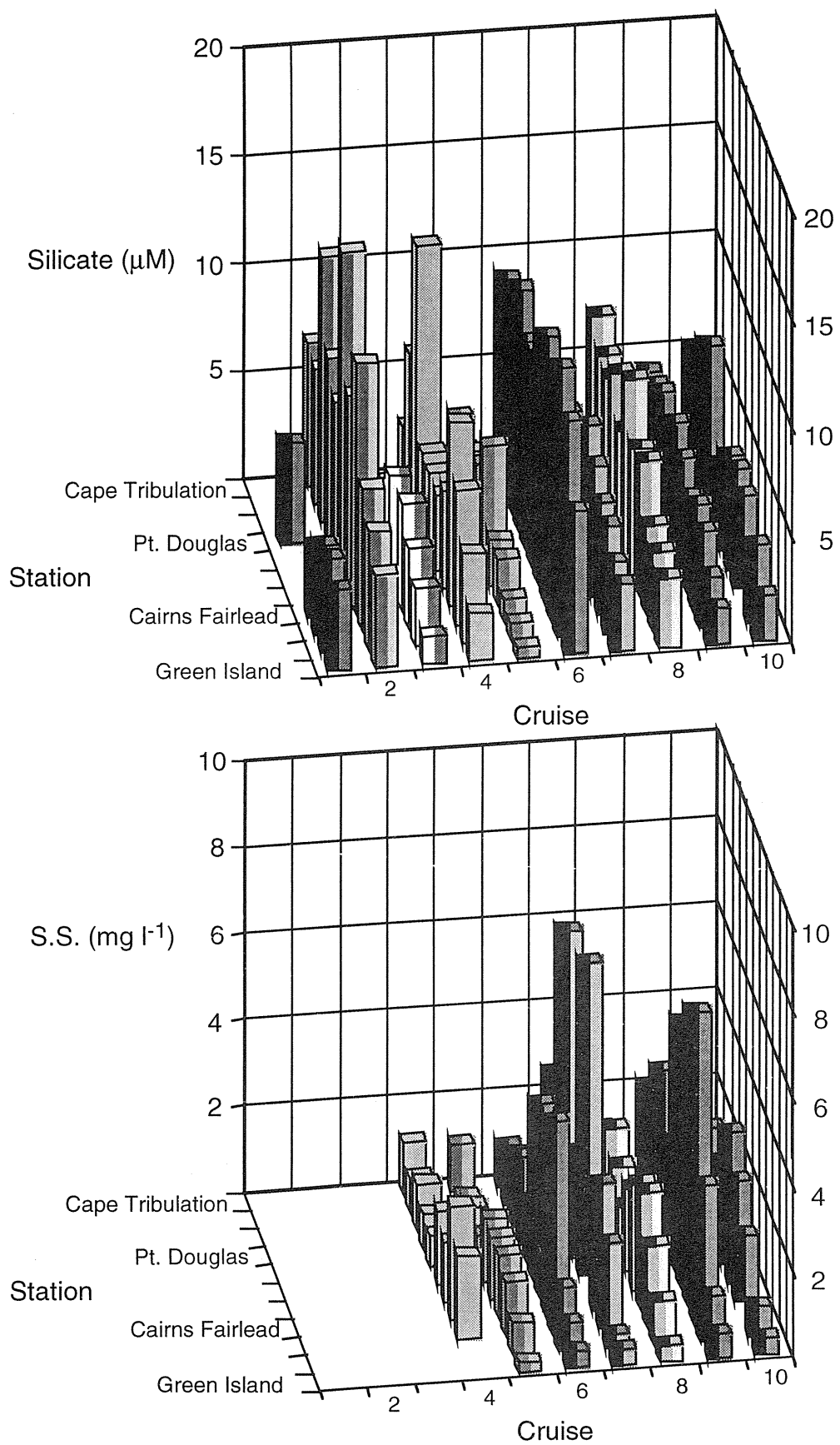


Figure 31. Depth-weighted mean water column concentrations of silicate (Top) and suspended solids (Bottom) along a transect between Cape Tribulation and Green Island, sampled ten times between February 1989 and July 1991.

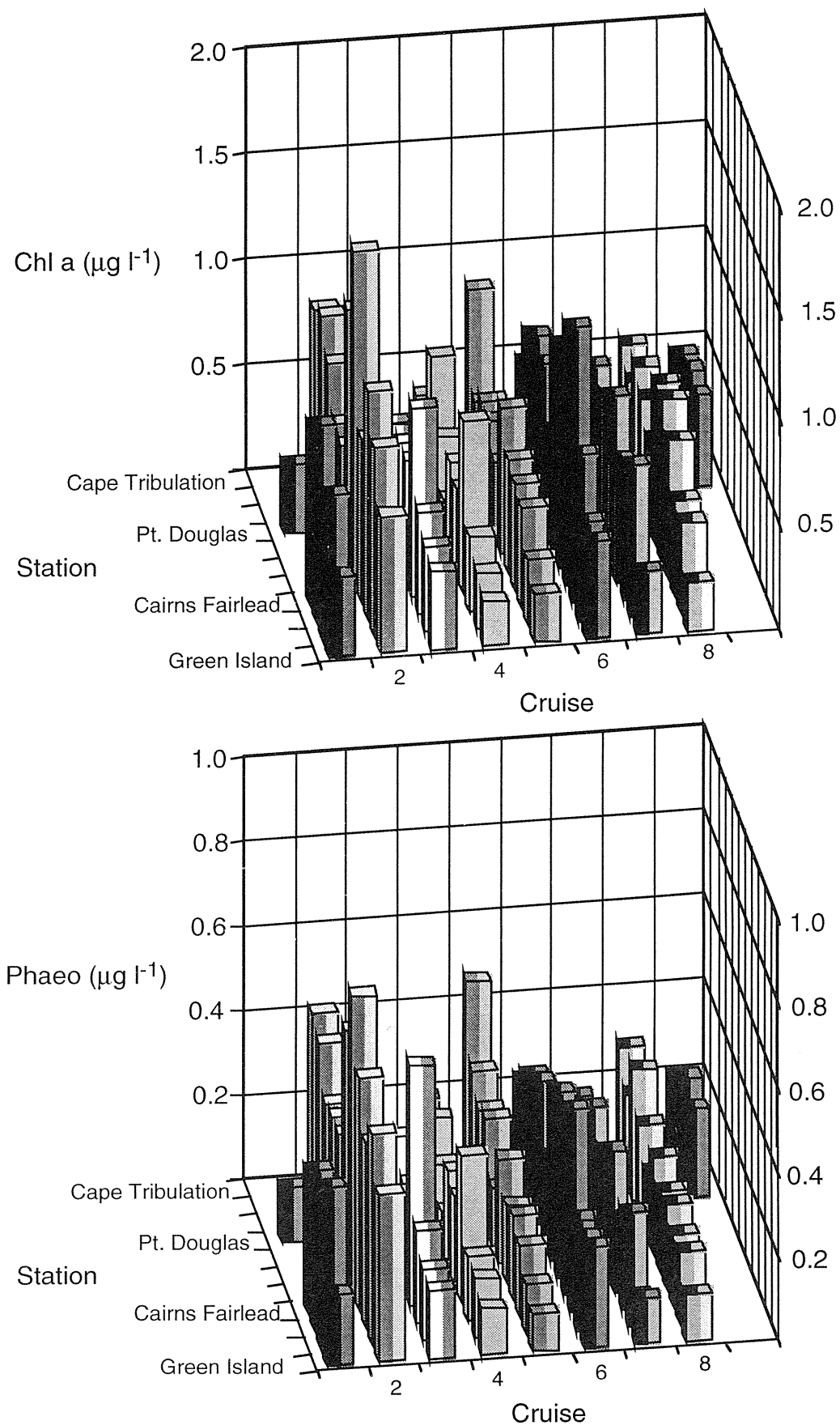


Figure 32. Depth-weighted mean water column concentrations of chlorophyll (Top) and phaeophytin (Bottom) along a transect between Cape Tribulation and Green Island, sampled ten times between February 1989 and July 1991.

Table 18. Overall station means and standard errors for water column variables measured at transect stations between Cape Tribulation and Cape Grafton. *** = significant difference at $p < 0.001$, * = significant difference at $0.01 < p < 0.05$

	NH ₄		NO ₂		NO ₃		DON		PN μmol l ⁻¹		PO ₄		DOP		POP		SiO		Chl μg l ⁻¹		Phaeo μg l ⁻¹		S.S. mg l ⁻¹	
Sta.	mean	s.e.	mean	s.e.	mean	s.e.	mean	s.e.	mean	s.e.	mean	s.e.	mean	s.e.	mean	s.e.	mean	s.e.	mean	s.e.	mean	s.e.	mean	s.e.
1	0.42	0.15	0.001	0.001	0.03	0.01	7.17	1.09	1.25	0.15	0.064	0.011	0.15	0.07	0.13	0.03	5.0	0.8	0.54	0.07	0.28	0.04	1.47	0.23
2	0.45	0.14	0.001	0.001	0.03	0.01	7.45	1.49	1.02	0.10	0.074	0.008	0.16	0.09	0.12	0.02	5.1	0.8	0.50	0.07	0.24	0.03	1.08	0.16
3	0.46	0.15	0.000	0.000	0.05	0.01	7.66	1.36	1.42	0.08	0.075	0.008	0.14	0.06	0.14	0.03	7.5	1.3	0.59	0.04	0.26	0.02	2.42	0.78
4	0.47	0.16	0.001	0.001	0.03	0.01	6.09	0.74	1.08	0.08	0.071	0.008	0.13	0.06	0.11	0.02	4.6	0.8	0.44	0.02	0.20	0.02	1.46	0.21
5	0.60	0.17	0.003	0.002	0.03	0.01	6.12	0.84	1.06	0.12	0.076	0.010	0.09	0.05	0.11	0.02	4.8	0.6	0.38	0.04	0.16	0.03	1.08	0.17
6	0.54	0.15	0.007	0.005	0.07	0.03	6.53	1.04	1.63	0.09	0.090	0.013	0.05	0.02	0.17	0.03	6.8	1.2	0.76	0.10	0.32	0.05	3.56	0.83
7	0.34	0.08	0.001	0.001	0.04	0.01	5.12	0.98	1.68	0.14	0.080	0.014	0.05	0.03	0.15	0.02	5.8	1.1	0.75	0.15	0.29	0.07	2.50	0.43
8	0.40	0.08	0.002	0.001	0.03	0.01	6.24	0.82	1.86	0.22	0.086	0.012	0.06	0.02	0.21	0.04	5.9	1.0	0.76	0.09	0.35	0.06	3.19	0.70
9	0.53	0.19	0.008	0.005	0.04	0.01	5.97	0.76	1.35	0.14	0.086	0.013	0.05	0.02	0.12	0.02	5.0	1.0	0.59	0.08	0.23	0.03	1.85	0.30
10	0.48	0.14	0.004	0.002	0.04	0.01	5.06	0.70	0.96	0.10	0.092	0.012	0.06	0.02	0.09	0.01	4.0	0.8	0.45	0.08	0.22	0.05	0.72	0.11
11	0.46	0.13	0.003	0.002	0.05	0.01	4.18	0.55	0.94	0.50	0.079	0.008	0.11	0.04	0.08	0.02	2.9	0.6	0.35	0.05	0.17	0.04	0.38	0.04
Cruise	***		***		***		***		***		***		***		***		***		***		***		***	
Station					*		*		***						***		***		***		***		***	

Table 19. Summary of ANOVAs for significance of variability related to cruises and stations on the transect between Cape Tribulation and Green Island. The comparison was run as a 2-way analysis with Cruise and Station as fixed factors. The data was not transformed.

Variable	Cruise		Station	
	F	p	F	p
Ammonia	27.39 (9,79)	<.001	0.39 (10,79)	0.945
Nitrite	11.32 (9,79)	<.001	1.05 (10,79)	0.407
Nitrate	13.11 (9,79)	<.001	2.35 (10,79)	<.001
DON	15.28 (9,75)	<.001	2.28 (10,75)	0.021
PN	4.80 (9,79)	<.001	9.52 (10,79)	<.001
Phosphate	19.45 (9,79)	<.001	1.394 (10,79)	0.199
DOP	5.66 (9,75)	<.001	1.05 (10,75)	0.410
PP	9.15 (9,78)	<.001	5.83 (10,78)	<.001
Silicate	22.52 (9,79)	<.001	5.63 (10,79)	<.001
Chlorophyll	8.11 (8,63)	<.001	6.70 (10,63)	<.001
Phaeophytin	11.76 (8,63)	<.001	4.306 (10,63)	<.001
Suspended Solids	5.76 (6,55)	<.001	7.37 (10,55)	<.001

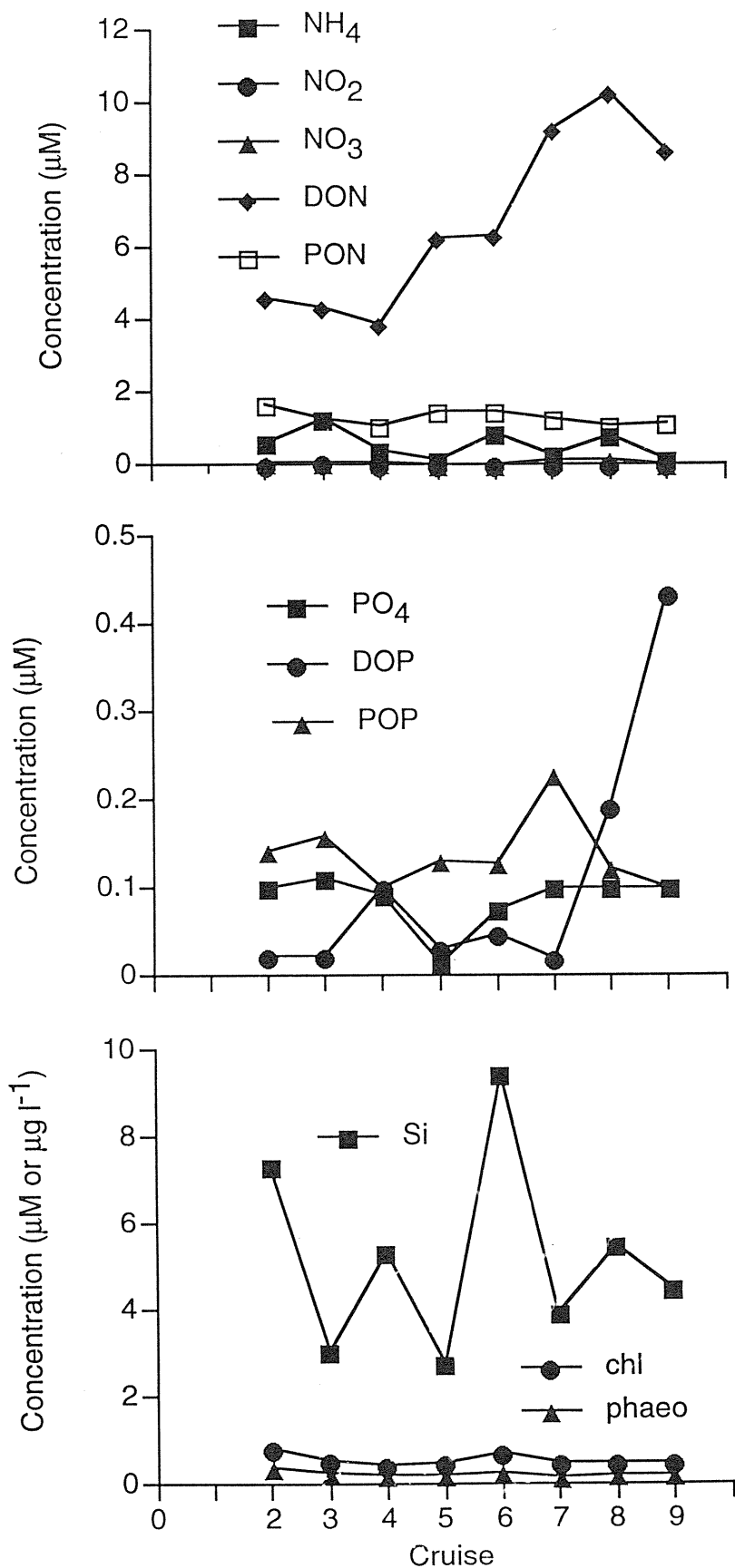


Figure 33. Cruise means for depth-weighted mean water column concentration of (Top) nitrogen species, (Middle) phosphorus species and (Bottom) silicate and pigments on the 11 station Cairns box transect.

8. RIVER INPUTS OF NUTRIENTS

Discharges from rivers (Figure 6) constitute the major pathway for the transport of terrestrial and anthropogenic nutrients to waters of the central GBR. While watershed areas, daily flows and annual discharges from most of these rivers are reasonably well characterized (Table 3), relatively little is known regarding the temporal dynamics of nutrient speciation concentration variability and delivery in or from particular watersheds. Sampling to quantify nutrient fluxes from the major north Queensland rivers was initiated in 1987 (Table 20), with the sampling network being progressively expanded and temporally intensified since then.

Table 20. River sampling sites, sampling frequencies and analyses carried out.

River	Site	Frequency	Started	DIN	DON	PN/PP	S.S.	Chl
Barron	Lower	3 mo.	1989	+	+	+	+	1
	Estuarine	3 mo.	1989	+	+	+	+	1
Mulgrave	Lower	3 mo.	1988	+	+	+	+	1
	Estuarine	3 mo.	1988	+	+	+	+	1
Russell	Lower	3 mo.	1988	+	+	+	+	1
No. Johnstone	Lower	3 mo.	1988	+	+	+	+	1
So. Johnstone	Lower	Daily 1	1987	+	+	+	1	1
Tully	Upper	Monthly +	1987	+	+	+		
	Lower	Monthly +	1987	+	+	+	1	1
	Boulder Ck.	Monthly +	1987	+	+	+		
	Jarra Ck.	Monthly +	1987	+	+	+		
	White's X	Monthly +	1987	+	+	+		
	Banyan Ck.	Monthly +	1987	+	+	+	1	1
Murray	Lower	3 mo.	1987	+	+	+		
	Estuarine	3 mo.	1987	+	+	+		
Herbert	Yamani Falls	Daily 2	1989	+	+	+	+	+
	Abergowrie	Daily 2	1989	+	+	+	+	+
	Lower	Daily 2	1987	+	+	+	+	+

Seasonal flow patterns in all of the rivers sampled (e.g. Figure 34 Bottom) are characterized by substantial short-term variability associated with large and small flood events. The largest seasonal flow events are usually associated with the occurrence of cyclones or the monsoonal depressions following a cyclone. The intensity of seasonal flow variability from a particular watershed depends in turn on whether the cyclone directly affected that watershed and the amount of rainfall associated with particular storms. Over multi-decadal time periods, the frequency of cyclonic storms is highly variable and likely coupled to processes like ENSO (Lough, 1993).

Seasonal flow dynamics in the So. Johnstone River, as revealed by frequent, often daily sampling, were quite different, even though a tropical cyclone (Ivor - March 24, 1990; Joy - December 25, 1990) occurred both years. Cyclone Ivor crossed the coast near Cooktown (15°S), then degenerated into a tropical depression which moved southward. The resulting rainfall produced a maximum instantaneous flow exceeding 800 m³ sec⁻¹. With several small peaks, river flow then declined progressively over the remainder of the 1989-90 wet season. In contrast, Cyclone Joy was the first major storm of the 1990-91 wet season. After striking the coast near Cairns, most of the rainfall was delivered by an extended monsoonal depression. As a result, there was no single massive flood event in the South Johnstone River catchment associated with Cyclone Joy. Overall flow peaked during February. The 1991-92 summer

season (not shown) was characterized by El Nino conditions and no pronounced rainfall or floods occurred.

The most comprehensive nutrient sampling in any north Queensland river was carried out in the South Johnstone River between December, 1990 and December, 1991 (Figures 34, 35). Water samples were collected for dissolved and particulate nutrient determinations on a daily to sub-weekly basis by Queensland Department of Primary Industries personnel stationed at the township of South Johnstone, which is located in the lower catchment. During periods of high flow, water samples were often collected several times daily. Sampling in other rivers was less frequent (Table 20). The high frequency sampling in the South Johnstone River revealed two seasonal patterns of variation in both dissolved and particulate nutrient concentrations: high short-term (day-to-day) variability during the summer season associated with equally short-term fluctuations in river height (=water flow) and longer periods of relatively low, but stable nutrient concentrations during dry season low-flow conditions.

Correlations between water column nutrient concentrations and contemporaneous flow rates in the So. Johnstone River for individual nutrient species were variable (Figure 36). Particulate nitrogen (PN) and phosphorus (PP) concentrations were positively correlated with river flow rates. As suspended solids concentrations were also positively related to flow rate (due to increased erosion within the catchment), PN and PP were clearly and significantly related to the amount of suspended sediment in the river. As a result, peaks of both PN and PP concentration and flux were closely associated with seasonal flood events (Figures 34, 35). Noticeable peaks in concentration of both PN and especially PP were associated with the first flood event of the wet season, as material accumulated in watershed soils and tributary sediments over the course of the dry season was flushed into the main stem of the river. In 1990, the maximum fluxes of PN and PP were clearly associated with the major flood associated with Cyclone Ivor which came late in the wet season. During the winter dry seasons, concentrations of both PN and PP in river waters remained low and stable. There is some indication that both DIN and PN stocks within the watershed were progressively exhausted over the course of the wet season.

In contrast, silicate concentrations in So. Johnstone River water were inversely related to discharge (Figure 37), indicating stable input fluxes of dissolved silicate to the river and dilution during high flow events.

Temporal relationships between concentrations of dissolved constituents (NH_4 , NO_2 , NO_3 , DON, PO_4 , DOP) and contemporaneous, unlagged, river flow rates were less straightforward. Concentrations of dissolved inorganic nitrogen (DIN) in So. Johnstone River waters went through a broad seasonal high during the summer wet season (ca. $25\text{--}35\ \mu\text{mol N l}^{-1}$), with a considerable amount of short-term variability (Figure 34). Concentrations of nitrate were positively correlated with flow rate, but for other dissolved species, there were no statistical significant correlations between instantaneously measured flow rate and dissolved concentrations (Figure 36). A particularly high concentration of DIN (ca. $75\ \mu\text{mol N l}^{-1}$, dominated by nitrate), leading to a concurrently high watershed flux rate, was measured during the first flush event of the 1990-91 wet season associated with Cyclone Joy. A similar first flush event, though of considerably smaller magnitude, occurred at the beginning of the 1991-92 wet season. Following the January seasonal maximum, DIN concentrations declined progressively over the course of the dry season to low, end of season levels (ca. $2\text{--}3\ \mu\text{mol N l}^{-1}$).

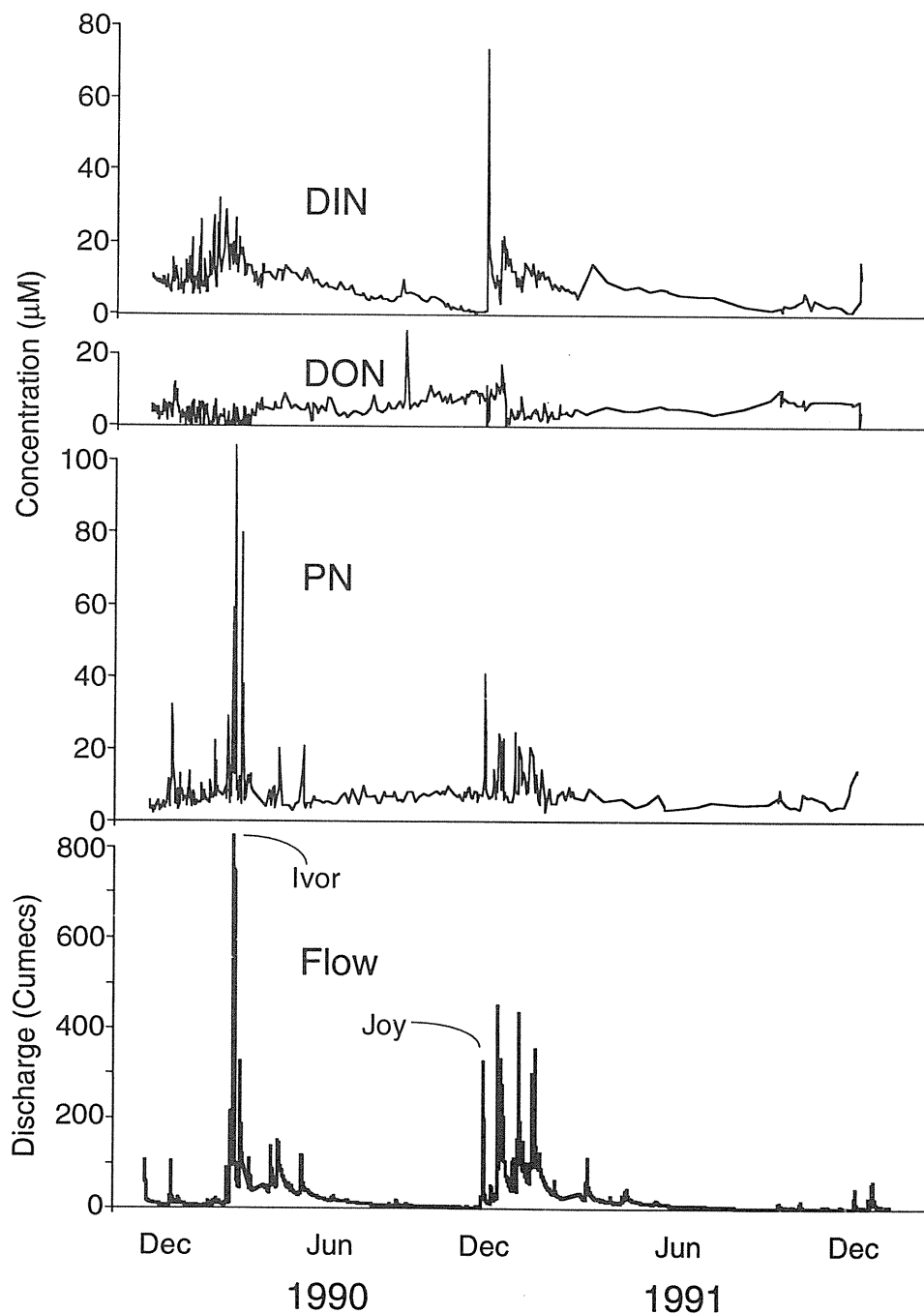


Figure 34. Temporal changes in concentrations of dissolved inorganic nitrogen ($\text{NH}_4+\text{NO}_2+\text{NO}_3$), dissolved organic nitrogen (DON) and particulate nitrogen (PN) in the lower South Johnstone River during 1990 and 1991 in relation to the temporal pattern of discharge at South Johnstone.

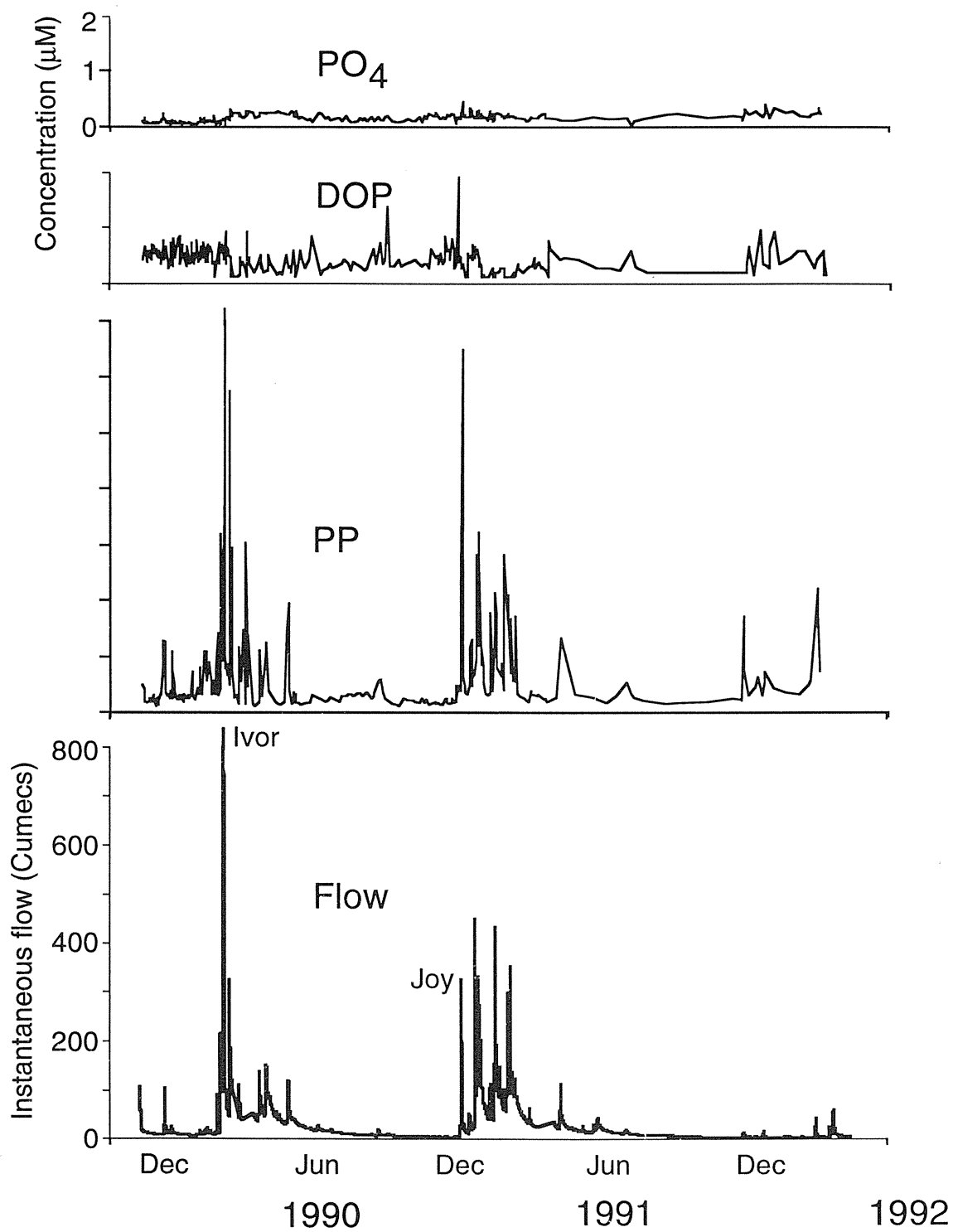


Figure 35. Temporal changes in concentrations of dissolved inorganic phosphorus (PO_4), dissolved organic phosphorus (DOP) and particulate phosphorus (PP) in the lower South Johnstone River during 1990 and 1991 and their relation to discharge measured at South Johnstone.

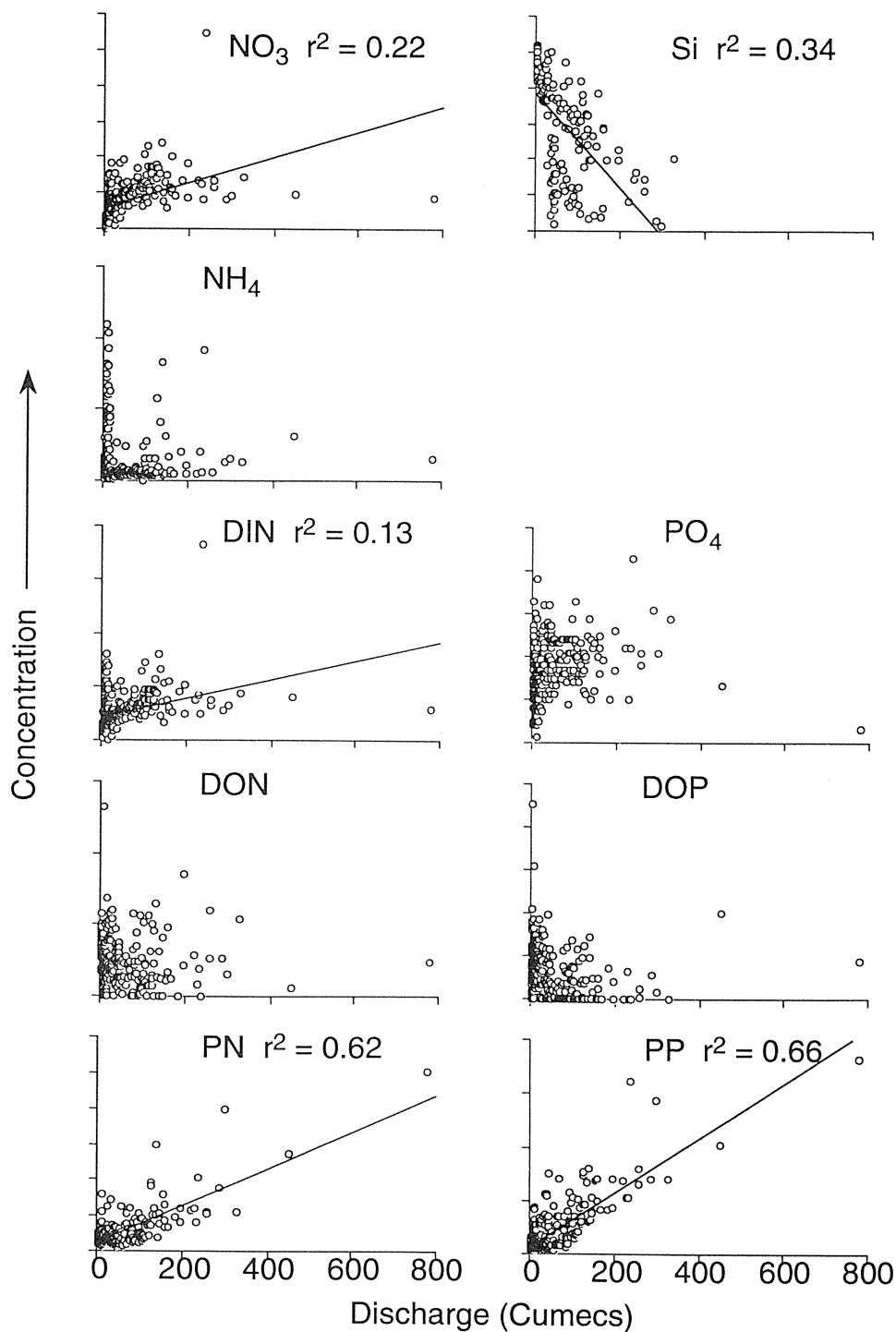


Figure 36. Scatter plots showing relationships between measured water column concentrations of individual nutrient species and the contemporaneous discharge rate of the South Johnstone River as measured at South Johnstone. Fitted linear lines indicate significant correlations.

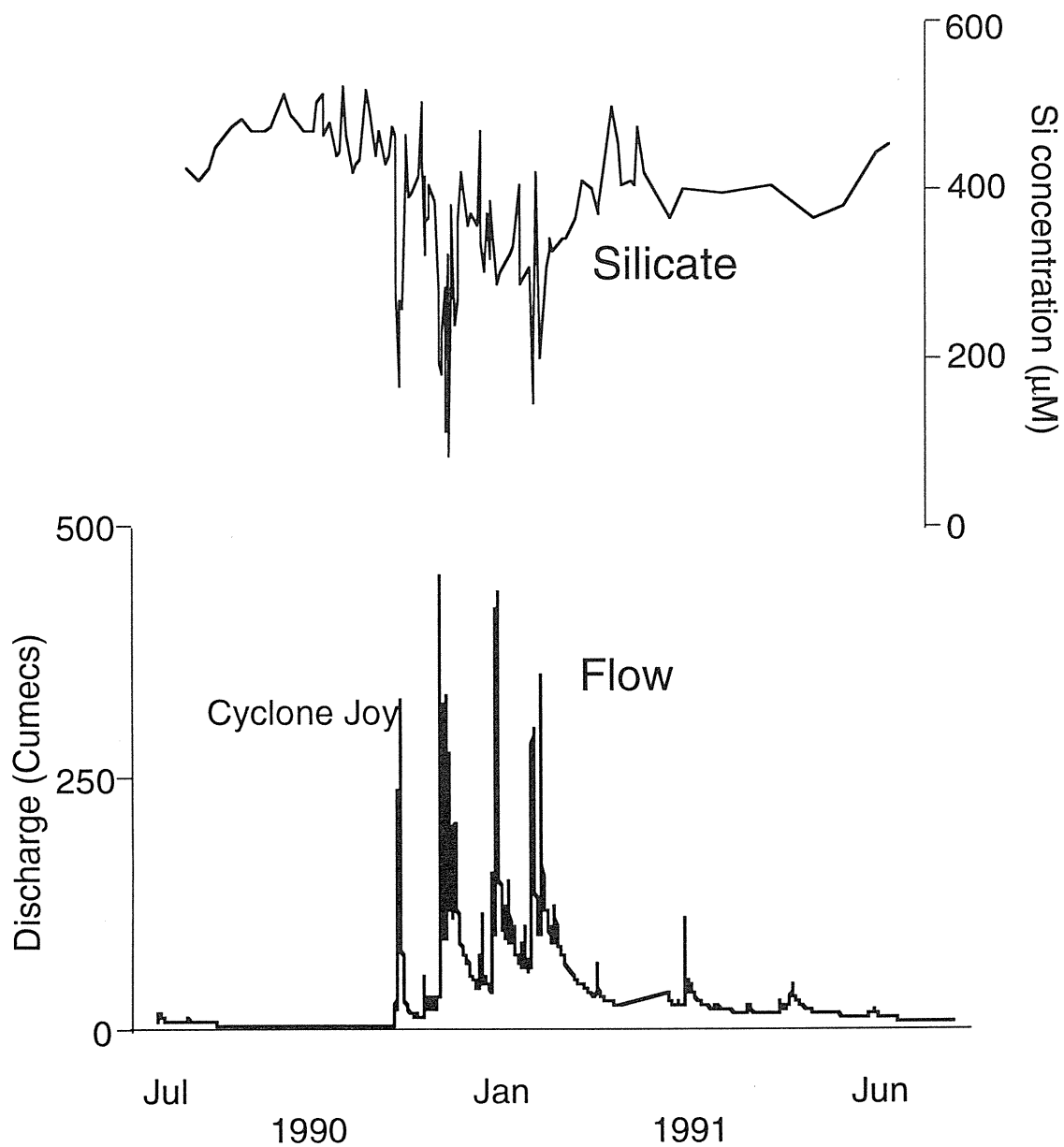


Figure 37. Temporal changes in concentrations of dissolved silicate [$\text{Si}(\text{OH})_4$] in the lower South Johnstone River during 1990 and 1991 and their relation to discharge measured at South Johnstone. Silicate concentrations measured prior to July, 1990 are considered unreliable.

Compared to DIN and PN, concentrations of dissolved organic nitrogen (DON) in the So. Johnstone River fluctuated within a fairly narrow range ($0\text{--}20\ \mu\text{mol N l}^{-1}$) over the period of intensive sampling. Following a broad seasonal low during the summer wet seasons, DON concentrations in So. Johnstone River waters tended to increase gradually over the duration of the dry season. While there is no statistical correlation between contemporaneous river discharge rates and DON concentrations, the general pattern was of declining DON concentrations in relation to increasing river discharge is suggestive of dilution during the wet season, and during high flow events. A particular example is the first flush flood associated with Cyclone Joy (December, 1990).

Dissolved phosphorus (PO_4 , DOP) concentrations in the So. Johnstone River were low and consistent throughout 1990 and much of 1991 (Figure 35). In contrast to the pattern observed for nitrogen, peaks or dilution troughs of dissolved organic and inorganic phosphorus were not associated with flood events. No statistical correlation between concentrations of dissolved phosphorus species and river flow rate was observed.

With the exception of brief periods during flood events, total water-borne nitrogen concentrations in the So. Johnstone River were on the order of $20\ \mu\text{mol N l}^{-1}$ and were relatively constant over the two-year period (Figure 38 Top). The balance between individual nitrogen species in the river water shifted on a short-term basis, though collectively, DIN and DON contributed similar proportions of the total annual export: 55 and 38 percent, respectively (Figure 38 Middle). PN was a major contributor to total export (ca. 43%). The temporal pattern of cumulative nitrogen export from the watershed was characterized by one to several abrupt steps in integrated discharge associated with individual flood events. A significant proportion of the annual discharge flux (ca. 25,000 kmol nitrogen or 340 metric tonnes) occurred during high-flow periods only a few days in duration (Figure 38 Bottom).

The temporal pattern of phosphorus export from the So. Johnstone River (Figure 39 Top) was similar to that observed for nitrogen. Unlike nitrogen, phosphorus fluxes were overwhelmingly dominated (81%) by particulate phosphorus (Figure 39 Middle). Integrated annual export of phosphorus was on the order of 2.26 kmol (35 metric tonnes; Figure 39 Bottom).

Several conclusions can be drawn from the results of the high frequency nutrient sampling program carried out in the So. Johnstone River. The first and most obvious is that most of the nitrogen and phosphorus export from the watershed occurs within one or a small number of discrete events during the wet season which are usually only a few days in duration. Any effort to quantify nutrient export from the watershed must be structured to catch and resolve these events. Sampling programs structured around regular collections at intervals of several days to weeks will almost surely miss the important export events. This makes it difficult to confidently estimate nutrient exports from other north Queensland rivers where intensive day-to-day sampling is lacking. All such estimates (including those made herein) should therefore be treated with the appropriate degree of caution. Sampling programs designed to estimate annual discharge from particular watersheds should be seasonally stratified, with high frequency sampling during the summer wet season to resolve brief discharge and export events, particularly floods associated with cyclonic storms and monsoonal depressions, with a relaxation to more infrequent sampling during the dry season, when events are largely absent and nutrient concentrations fairly constant.

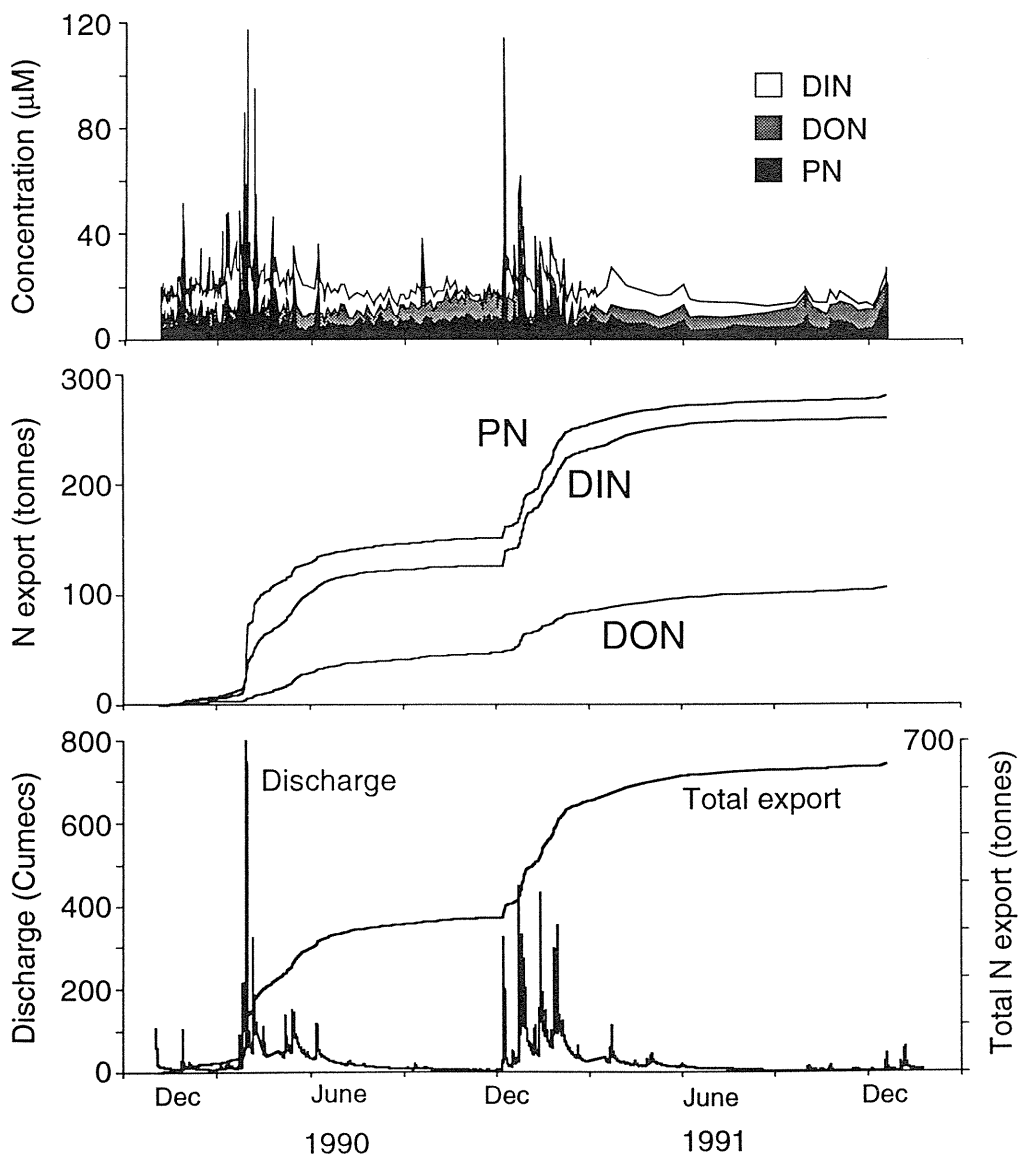


Figure 38. Top: Relative contributions of dissolved and particulate nitrogen species to total water-borne nitrogen concentrations and fluxes in the So. Johnstone River. Middle: Cumulative export of dissolved and particulate nitrogen from the So. Johnstone River. Bottom: Cumulative export of total nitrogen from the So. Johnstone River in relation to discharge measured at South Johnstone.

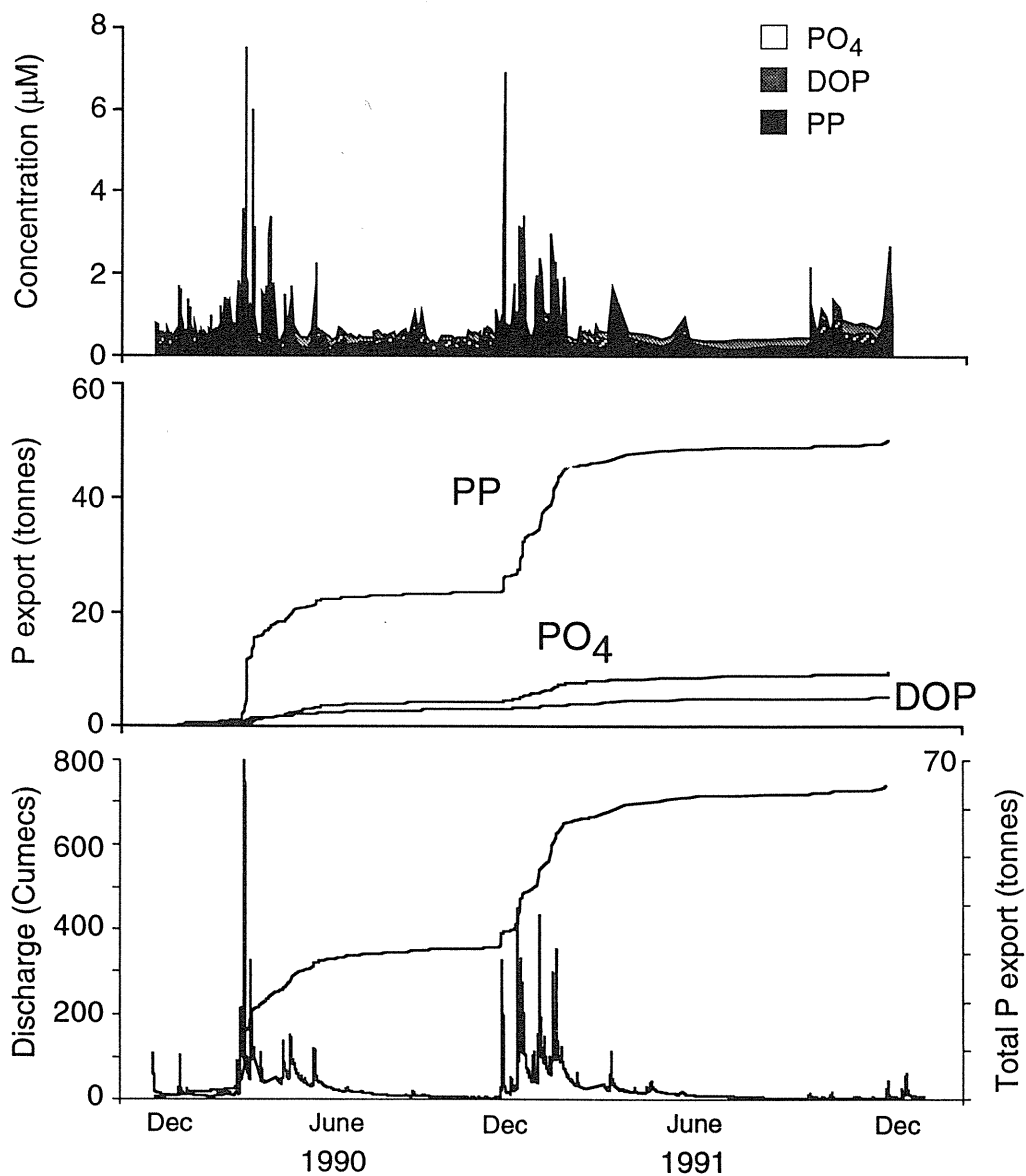


Figure 39. Top: Relative contributions of dissolved and particulate phosphorus species to total water-borne phosphorus concentrations and fluxes in the So. Johnstone River. Middle: Cumulative export of dissolved and particulate phosphorus from the So. Johnstone River. Bottom: Cumulative export of total phosphorus from the So. Johnstone River in relation to discharge measured at South Johnstone.

A second important conclusion, as noticed elsewhere, is that a significant fraction (ca. 80%) of the total flux of phosphorus from north Queensland rivers occurs in particulate form. A smaller but significant proportion (~40%) of total nitrogen is exported in particulate form. The transport of particulate material is concentrated during flood events, especially the large floods associated with cyclones. Efforts to resolve nutrient export must therefore include analyses of nutrients in the particulate fraction, using modern instrumental methods appropriate for those analyses. It should be noted, however, that no measurements have been published to date regarding nutrient transport in sediment bedload.

With the exception of PN, PP and silicate, concentrations of all the soluble nutrient species measured were uncorrelated with instantaneous flow rates. This indicates that modelling of soluble nutrient exports from watersheds on the basis of flow records will not be a straightforward process and will need to incorporate more elaborate functional parameterizations of watershed nutrient behaviour.

Despite the obvious differences between the temporal patterns of flow over the two years of intensive nutrient monitoring of the So. Johnstone River, integrated annual nitrogen and phosphorus exports for the two years. Both wet seasons contained a single cyclone, though the magnitude of the associated flood event was quite different. Analyses have not been carried out on all of the nutrient samples from the El Nino 1991-92 wet season, which lacked a major flood event in order to make a comparison with riverine exports under dry conditions. Given the considerable variability of flow in all north Queensland rivers, it is therefore still uncertain to what extent total annual nutrient export is related to average discharges over long periods.

8.1 Longitudinal Variations of Nutrient Concentrations within Catchments

8.1.1 Herbert River

Dissolved and particulate nutrient concentrations were measured at three sites along the Herbert River between December 1989 and February 1992 (Figures 40-42): Yamani Falls - a mid-catchment site situated just below the Yamani Falls National Park and above the sugar-cane dominated coastal floodplain; Abergowrie, a lower-catchment site in the upper portion of the floodplain with extensive sugar-cane culture surrounding; and at the John Row Bridge, a lower catchment site nearer to the mouth of the river. A considerable amount of grazing and some alluvial mining activity occurs within the Herbert River catchment above the Yamani Falls site. Sampling was largely carried out at weekly to monthly intervals; some daily sampling was carried out during flood events.

As in the South Johnstone River, PN, PP and suspended solids concentrations peaked during early season high flow periods. At other times, water-borne concentrations of PN, PP and suspended solids were low and stable, with little or no difference between concentrations measured at upper and lower catchment sites. Interestingly, peaks in PN and PP did not occur during the large late-summer flow peak of 1991, suggesting possible exhaustion of mobile PN and PP stocks within the watershed. This effect, however, requires corroboration. During flood peak events, there were no clear longitudinal trends in concentrations of particulate materials. The highest concentrations of PN, PP or suspended solids were sometimes measured at the Yamani Falls site, sometimes at Abergowrie or John Row Bridge.

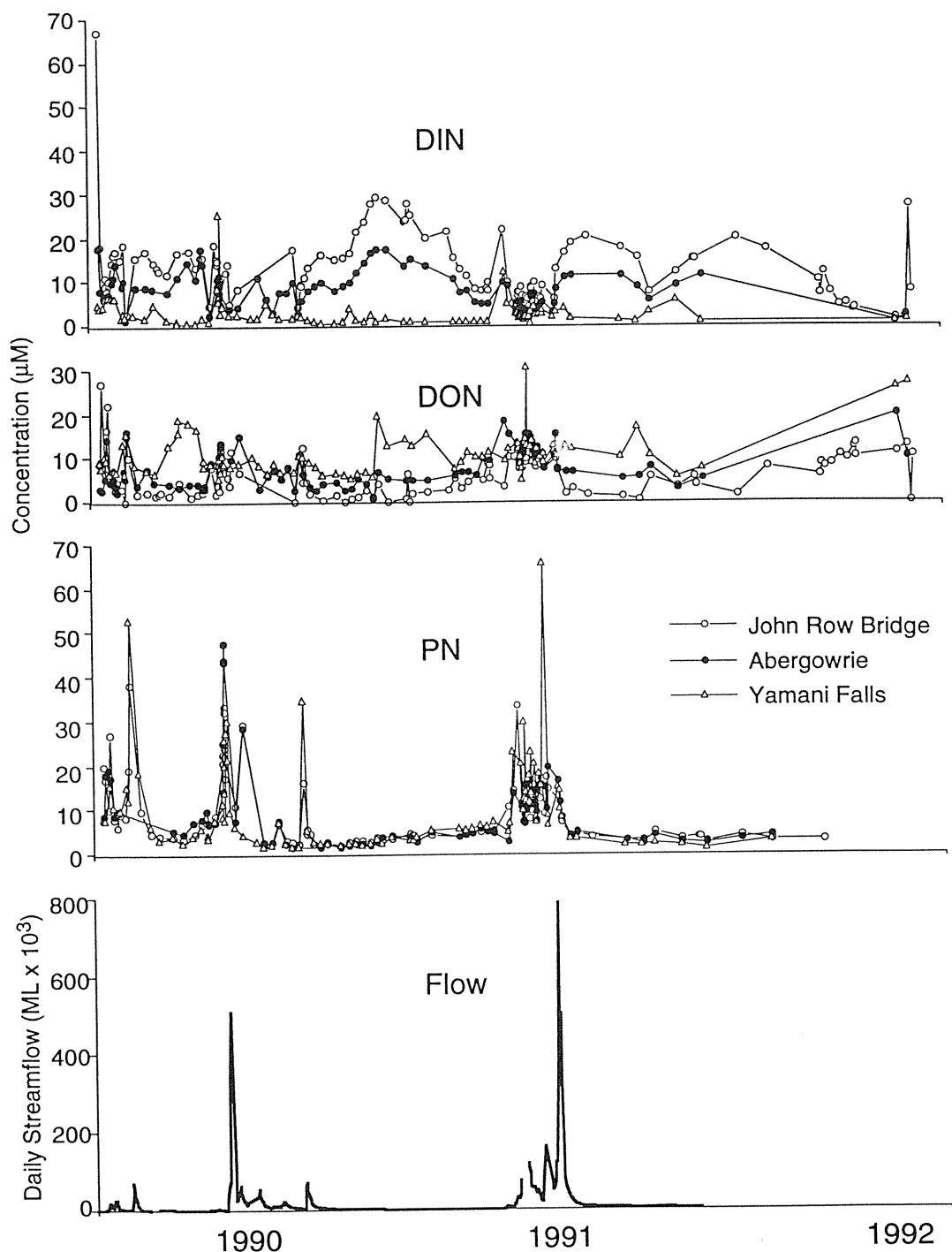


Figure 40. Temporal and longitudinal changes in concentrations of water-borne dissolved and particulate nitrogen in the Herbert River (1990-1992). The Yamani Falls sampling site is located above sugar-cane cultivation activity. The John Row Bridge site is located within the agricultural area of the lower catchment. The Abergowrie site is between the two.

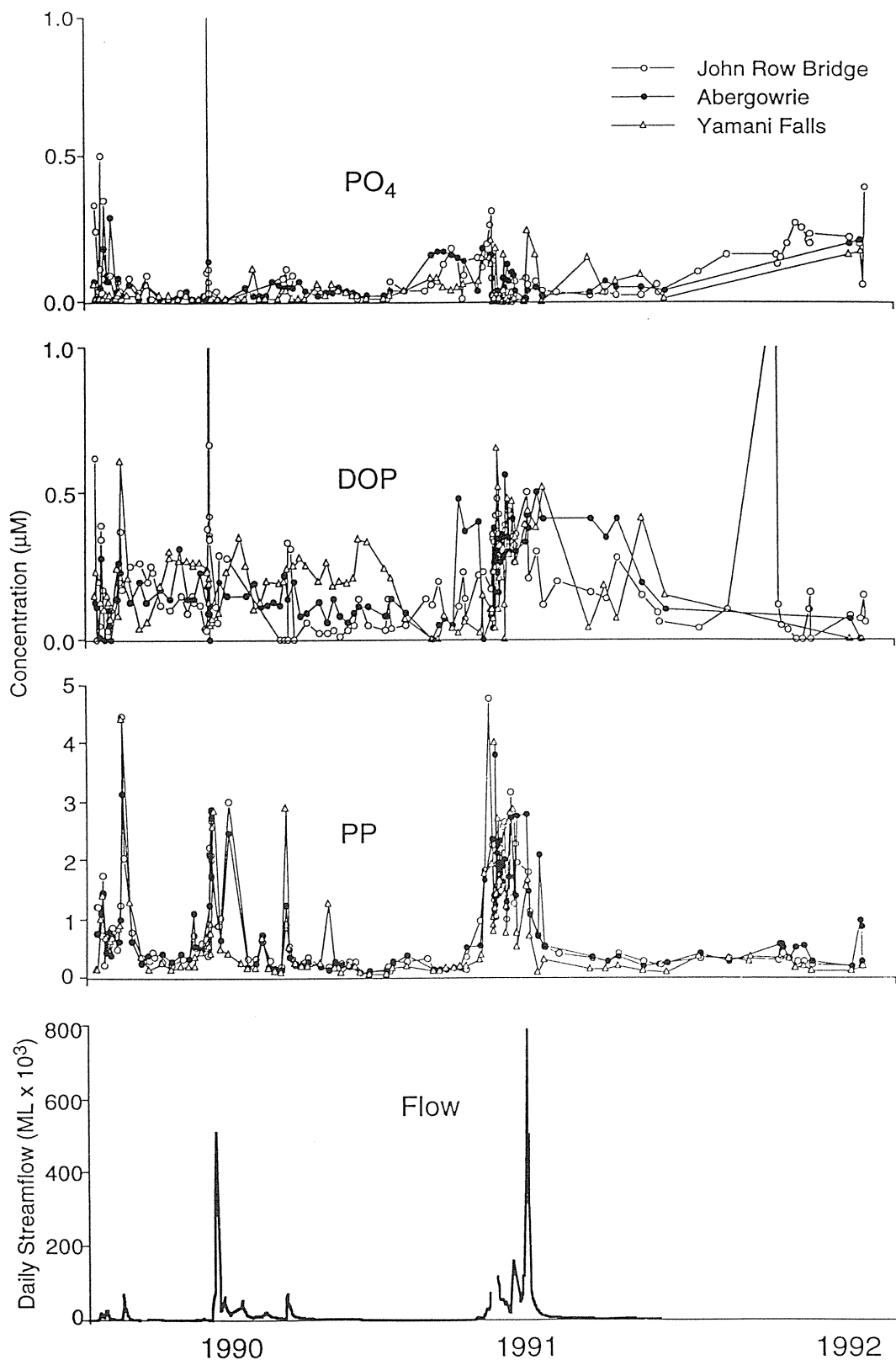


Figure 41. Temporal and longitudinal changes in concentrations of water-borne dissolved and particulate phosphorus in the Herbert River (1990-1992). The Yamani Falls sampling site is located above sugar-cane cultivation activity. The John Row Bridge site is located within the agricultural area of the lower catchment. The Abergowrie site is located between the two.

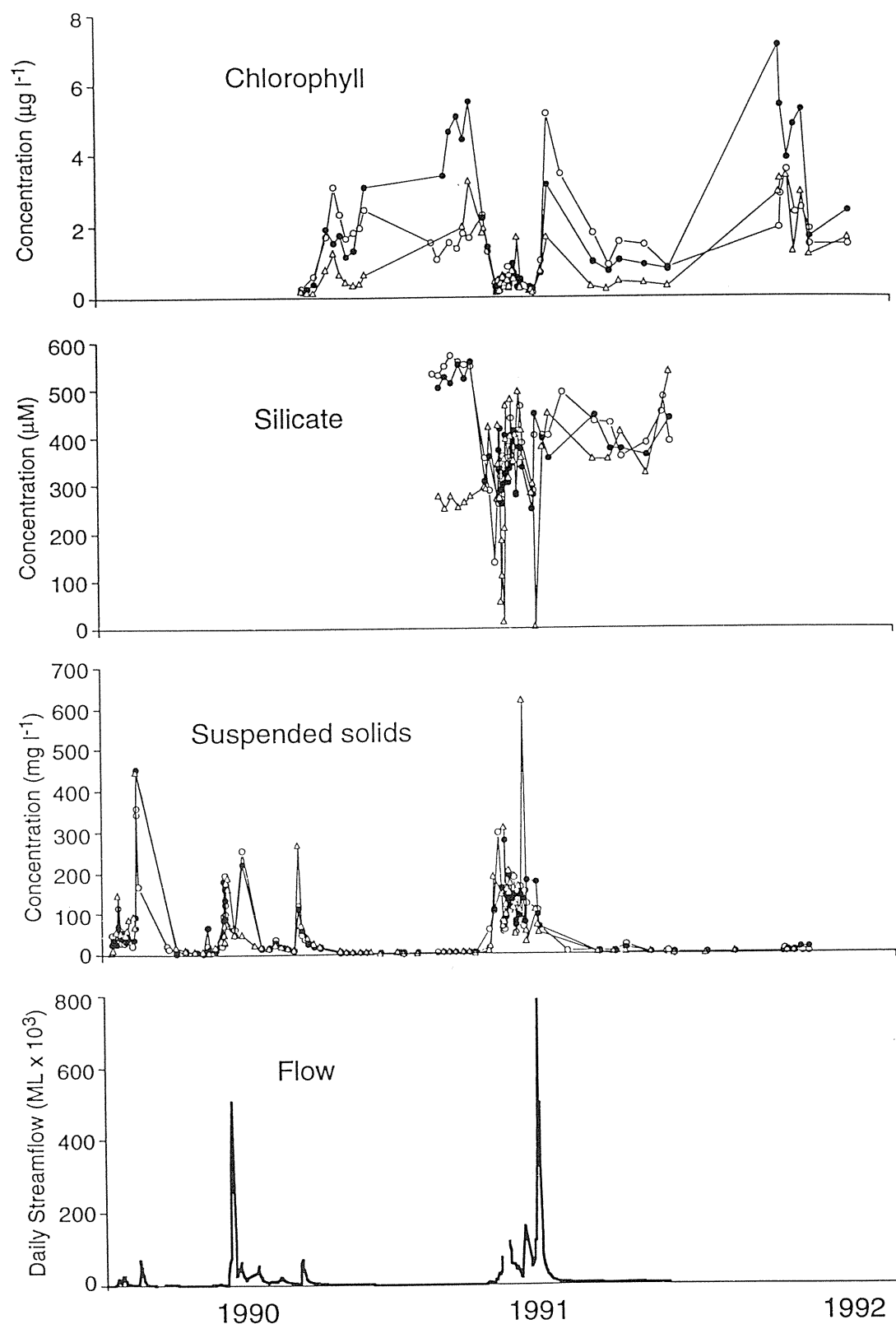


Figure 42. Temporal and longitudinal changes in concentrations of water-borne chlorophyll, dissolved silicate and suspended solids in the Herbert River (1990-1992). The Yamani Falls sampling site is located above sugarcane cultivation activity. The John Row Bridge site is located within the agricultural area of the lower catchment. The Abergowie site is between the two.

In contrast to particulate nutrients and suspended solids, soluble organic and inorganic nitrogen species (Figure 40 Top, Middle) exhibited a clear upstream-downstream trend in concentration. Concentrations of dissolved inorganic nitrogen increased downstream from the Yamani Falls site through the lower catchment. DIN concentrations at Yamani Falls were usually close to detection limits during low-flow periods, rising only moderately during brief flood events. It is interesting to note that concentrations of DIN decreased during larger flood events and the longer 1990-91 wet season monsoon, indicating dilution of input sources. Concentrations of DIN rebounded strongly once the wet seasons were finished. In contrast to the So. Johnstone River, DIN concentrations broadly peaked in the June-July period and then declined progressively until the start of the next wet season. Measured concentrations of DON were highest at the uppermost site, Yamani Falls, declining steadily downstream. At present, it is not possible to resolve the extent to which the downstream decline in DON concentrations reflects dilution of the main stream water with tributary or ground waters with a lower DON concentration, or mineralization of the DON within the river system.

Dissolved organic and inorganic phosphorus concentrations in the Herbert River exhibited no clearcut longitudinal trends. Likewise, no consistent seasonal trends were apparent. A general increase in PO_4 concentrations at all sites was observed during 1992. Reasons for this increase are unknown at this time. A brief peak in DIP, PO_4 and DOP (Figure 41) coincided with the intense flood associated with Cyclone Ivor (24 March 1990). However, Cyclone Joy (December 1990) did not produce a flood of similar size and no peaking in concentrations was observed. It should be noted that the Cyclone Joy flood was sampled on a 2-3 day interval. A brief high period of nutrient export may have been missed.

Concentrations of chlorophyll in Herbert River waters (Figure 42 Top) were highly variable. Chlorophyll concentrations were very low during the wet season of 1990-91, most likely reflecting dilution and short residence times of planktonic algae within the river. High turbidity during floods would also inhibit phytoplankton growth.

Silicate concentrations in the Herbert River (Figure 42 Middle) increased downstream. Sharp drops in concentration at the Yamani Falls site during flood peaks indicate dilution of soluble Si inputs to the river from the upper catchment. Dilution-related drops in lower catchment silicate concentrations were much smaller than measured at Yamani Falls, suggesting higher weathering rates or other sources of Si in the lower catchment.

Not surprisingly, suspended solids concentrations in the Herbert River (Figure 42 Bottom) were correlated with flow rates, reflecting erosion and runoff within the catchment. On a pairwise basis, there was no statistical difference between concentrations of suspended solids sampled contemporaneously at the upper and lower catchment sites, indicating that the source of much of the suspended material lay above Yamani Falls. Concentrations of particulate phosphorus and nitrogen (Figure 43) were significantly correlated with suspended solids concentrations. The phosphorus content of suspended material at the John Row Bridge site in the lower catchment was approximately 24 percent higher than measured at Yamani Falls.

Table 21 summarizes mean values for all of the nutrient and particulate species measured in the Herbert River samples. In paired comparisons between concentrations measured at Yamani Falls and the John Row Bridge, statistically significant longitudinal differences were observed for NO_2 , NO_3 , DON, PO_4 , PP, Si(OH)_4 and phaeophytin. Only DON and suspended solids exhibited higher mean concentrations upriver.

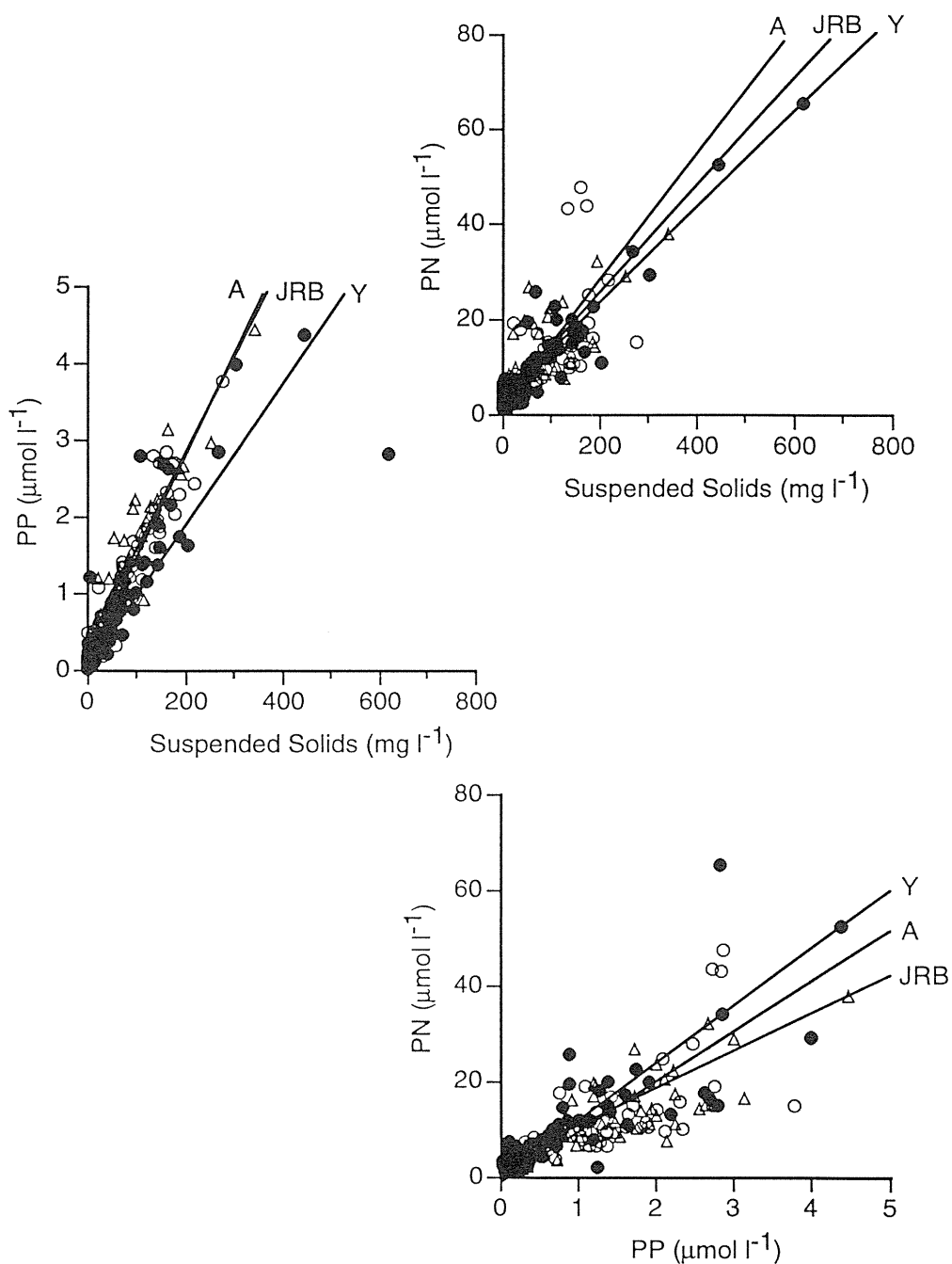


Figure 43. Functional relationships between particulate nitrogen, particulate phosphorus and suspended solids concentrations at three sites in the Herbert River. The regression lines shown are GM functional regressions (Ricker, 1973) with outliers excluded.

Table 21. Summary statistics for concentrations of dissolved nutrients and particulate matter measured contemporaneously at three sites in the Herbert River. The value of p gives the probability of significance for a paired t-test of the differences between concentrations measured at Yamani Falls and the John Row Bridge. Negative p values indicate higher downstream values.

Nutrient		No. Paired Obs.	Yamani Falls		Abergowrie		John Row Bridge		p
			Mean	1 S.D.	Mean	1 S.D.	Mean	1 S.D.	
NH ₄	μmol l ⁻¹	80	1.01	0.79	0.85	0.73	1.25	3.17	-0.481
NO ₂	"	80	0.05	0.05	0.08	0.06	0.16	0.59	-0.100
NO ₃	"	80	1.60	2.91	7.06	3.84	11.36	6.60	0.000
DON	"	76	10.85	4.75	8.26	4.26	6.67	4.79	0.000
PON	"	65	9.52	9.72	10.15	9.55	9.50	7.06	0.815
PO ₄	"	80	0.04	0.06	0.06	0.06	0.09	0.17	-0.024
DOP	"	80	0.20	0.14	0.19	0.13	0.22	0.23	-0.506
POP	"	76	0.77	0.91	0.98	0.91	1.00	0.92	-0.038
Si(OH) ₄	"	33	321	127	378	79	388	87	-0.009
Chl a	μg l ⁻¹	38	0.62	0.64	1.05	1.21	1.04	1.02	0.384
Phaeo	"	38	1.00	0.94	1.51	0.71	1.35	0.49	-0.005
S.S.	mg l ⁻¹	71	72.0	104.0	71.6	80.2	63.0	68.2	-0.191

8.1.2 Tully River

Dissolved and particulate nutrients were sampled at a number of sites in the Tully River catchment from late 1987 through to the present (Figure 44, 45). Analysis of the full suite of samples has not been completed, but enough have been analyzed to show that clear longitudinal trends in concentrations of some nutrient. The description herein will be restricted to data from a site near the Koombooloomba Dam at the top of the agriculturalized lower catchment and a lower catchment site located at the Bruce Highway bridge. The upper catchment of the Tully River is dominated by rainforest, grazing land and recreational/rural development. Agricultural activity in the coastal floodplain is characterized by extensive planting of sugar-cane.

Nitrate (NO₃) concentrations were consistently higher at the highway bridge sampling site. Concentrations of NO₃ at the Koombooloomba Dam site were similar to concentrations measured at the Yamani Falls site on the Herbert River. Distinct peaks in NO₃ concentrations were associated with the first flood peak events of the wet season in four of the five years sampled. On a seasonal basis, nitrate concentrations were highest during the wet season, declining over the course of the dry season as flow diminished. Sampling during the 1988-89 wet season commenced just before the first flush event. Small peaks in nitrate concentration were observed in the upper catchment samples, but the major DIN inputs to the river are clearly from the lower catchment. In the samples analysed, no clear or consistent longitudinal trend is apparent in either the DON or PN data from the main stem of the Tully River.

No clear upstream-downstream changes in soluble phosphorus speciation or concentrations were observed in the Tully River data. With one exception, peaks of particulate phosphorus concentration at the highway bridge site were associated with flood events. Corresponding increases in the upper-catchment samples were only observed once. Peaks of PP occurred in the initial flood samples of each wet season when the sampling program was able to catch the first flood event. Similar DOP increases were not observed. The absence of peaks in the time series of samples collected just below the Koombooloomba Dam is not unexpected as the large volume of water in the dam would damp out fluctuations in dissolved and particulate nutrient concentrations.

8.2 Inter-River Comparisons

Contemporaneous measurements of a range of nutrient species in the major rivers between and including the Herbert and Barron Rivers from 1989 to the present (Figures 46-49) do not show any short-term secular trend in either dissolved or particulate nutrient concentrations. However, systematic differences between nutrient concentrations under low-flow conditions in rivers can be discerned (Table 22). The comparison is restricted to samples collected during normal low or moderate-flow conditions in all rivers. For the short period considered, this is not surprising. The observed variability within individual rivers and between rivers reflects the lack of synchrony between the sampling dates and flow dynamics in individual rivers.

Table 22. Summary statistics for four water quality constituents sampled contemporaneously in eight north Queensland rivers between 1989 and 1991. Between-river comparisons were done by 1-way ANOVA.

River	NO ₃ μM			PO ₄ μM			PP μmol l ⁻¹			Susp. Solids mg l ⁻¹		
	Mean	Std. Dev.	n.	Mean	Std. Dev.	n.	Mean	Std. Dev.	n.	Mean	Std. Dev.	n.
Barron	4.20	2.34	9	0.09	0.05	3	0.39	0.31	10	15.9	18.8	12
Mulgrave	4.07	3.27	22	0.74	2.45	19	0.22	0.11	23	2.7	1.1	14
Russell	5.17	2.40	23	0.14	0.15	21	0.28	0.31	23	3.6	2.9	16
North Johnstone	5.04	3.66	25	0.23	0.24	23	0.38	0.37	26	4.6	2.6	17
South Johnstone	8.09	4.51	28	0.25	0.24	28	0.58	0.60	28	8.7	10.8	17
Tully	11.26	5.09	26	0.16	0.20	26	0.35	0.23	28	9.9	9.9	16
Murray	5.31	3.20	21	0.33	0.39	20	0.35	0.20	25	10.6	5.1	17
Herbert	9.27	6.27	27	0.26	0.36	27	0.67	0.90	29	58.2	87.3	18
p < 0.0001			p < 0.45			p < 0.01			p < 0.0001			

Nitrate concentrations in the rivers flowing into or affecting the Tully box were significantly higher than found in the Barron River. The highest NO₃ concentrations were measured in the Herbert, Tully and So. Johnstone Rivers which have the most extensive plantings of sugar cane in the lower catchment. With the exception of the Murray River, relatively little difference was observed between dissolved inorganic phosphorus concentrations in the rivers examined. Reasons for the high mean concentration of nitrate recorded for the Mulgrave River are unknown. Despite this high value, differences between mean concentrations in these rivers are not statistically significant. In contrast, significant between-river differences in the mean concentrations of PP and suspended solids were calculated. The highest PP and suspended solids concentrations were measured in the Herbert River, the largest of the rivers sampled and the one with the greatest flow variability.

8.3 Estuarine Processes

Estuaries are the primary zone of mixing between fresh and salt waters. During low-flow periods, the estuarine mixing zone of most north Queensland rivers largely lie in the lower reaches of the river. During flood events, however, salt water is displaced from the lower river and the various biological and chemical processes occurring under estuarine conditions take place within or at the periphery of the emergent river plume. A variety of biological and chemical processes take place within estuaries which directly affect nutrient concentration and speciation. Their magnitude depends upon both the amounts of materials flowing through the

estuary and the residence times for fresh and salt waters within the estuarine zone. Some important processes affecting river-borne nutrients include: desorption of ionic species from particles (e.g. phosphorus); biological uptake (nitrogen, phosphorus, silicate); adsorption/precipitation in high ionic strength seawater (a number of trace metals); biologically mediated precipitation or sedimentation of organic matter (e.g. humic acids); and the mineralization of organic matter by biological communities (e.g. benthic denitrification).

A detailed description of estuarine transformations occurring in all rivers discharging into the central GBR is beyond the scope of the present study. To gauge the extent to which estuarine processes might affect estimates of riverine nutrient fluxes based on samples collected in the freshwater sections of rivers, longitudinal sampling was carried out in the estuary of the Murray River on four occasions between September 1987 and August 1988 (Figures 50-52). This limited data set illustrates levels of spatial heterogeneity (lateral, vertical, longitudinal) likely to be found within estuaries adjacent to the central GBR. On individual trips, water samples were collected at four or five sites within the estuary. The downstream (most saline) site was located at the river mouth, while the upstream station was located in low-salinity water. Water samples were collected at two depths (surface and bottom). At four sites, replicate sampling was also carried out at three locations across the estuary to assess lateral variability.

Longitudinal gradients of total dissolved nitrogen ($= \text{NH}_4 + \text{NO}_2 + \text{NO}_3 + \text{DON}$) within the Murray River estuary were relatively small (Figure 50 left) on the four dates sampled. The small number of sampling dates precludes generalizations about seasonal or event-related temporal variability. Changes in nutrient concentrations down the longitudinal axis of the estuary reflect both the concentration gradient between the river system and sea and the residence times of water masses within the estuarine section of the river in relation to the magnitude of biological rate processes. Ammonia concentrations (Figure 52 left) did not vary greatly along the axis of the estuary. Nitrate concentrations (Figure 51 left) declined dramatically, reflecting dilution of river-borne nitrate with low nitrate coastal seawater and some (unknown) degree of biological uptake. The lack of a large change in ammonium concentrations may in part be due to mineralization processes within the estuary.

Total dissolved phosphorus concentrations ($= \text{PO}_4 + \text{DOP}$) increase down the axis of the estuary in response to two processes: mineralization of organic phosphorus in river water and the physical desorption of inorganic phosphorus with increasing salinity (e.g. Fox et al., 1986; Froelich, 1988). Silicate concentrations (Figure 52 right) declined toward the mouth of the estuary (increasing salinity), reflecting dilution within the estuary.

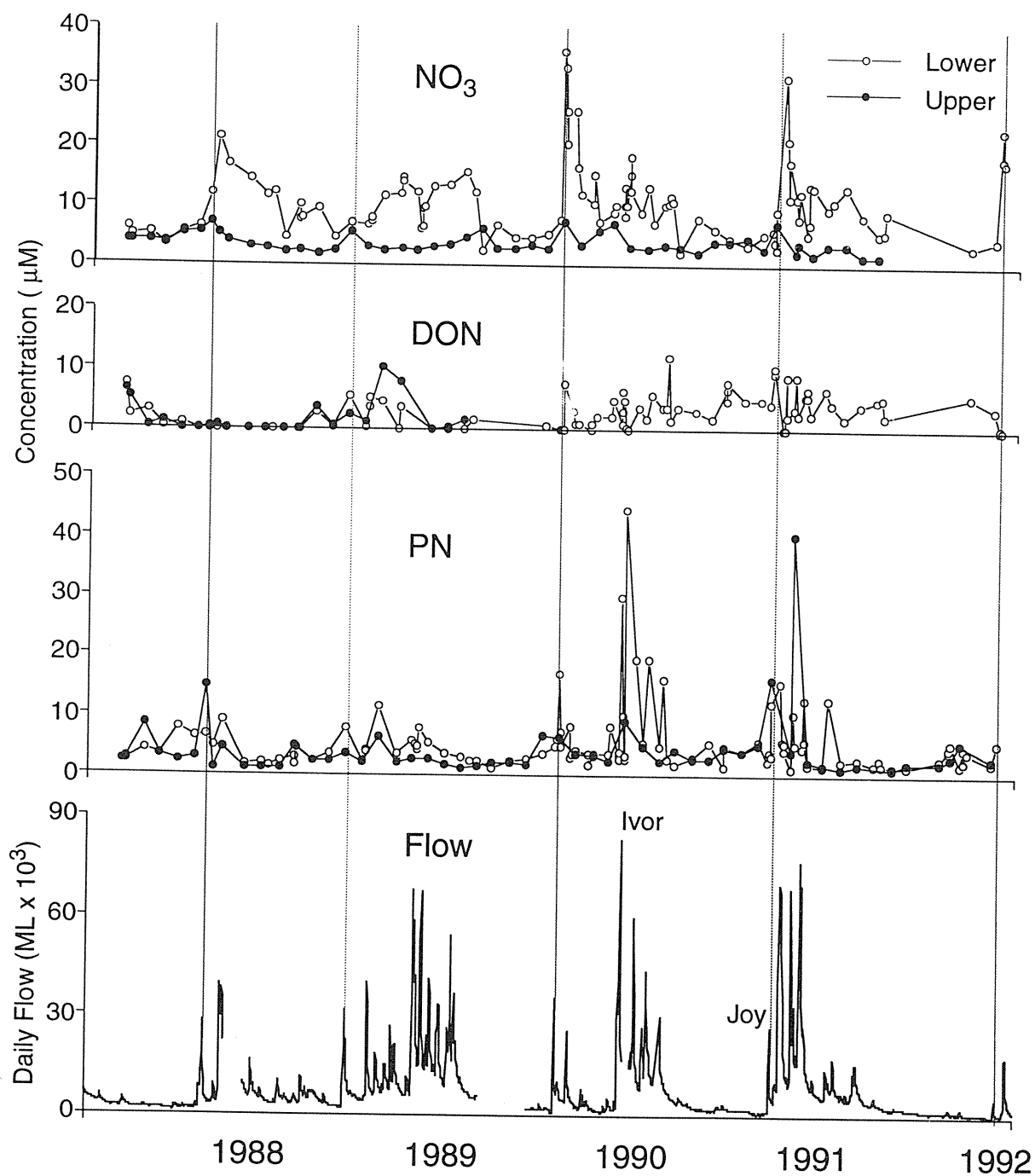


Figure 44. Temporal and longitudinal changes in concentrations of water-borne nitrogen in relation to daily flow in the Tully River (1988-1992) at sites near the Koombooloomba Dam and the Bruce Highway bridge. Vertical dotted lines identify the first flood event of each wet season. Flood peaks associated with Cyclones Ivor and Joy are identified.

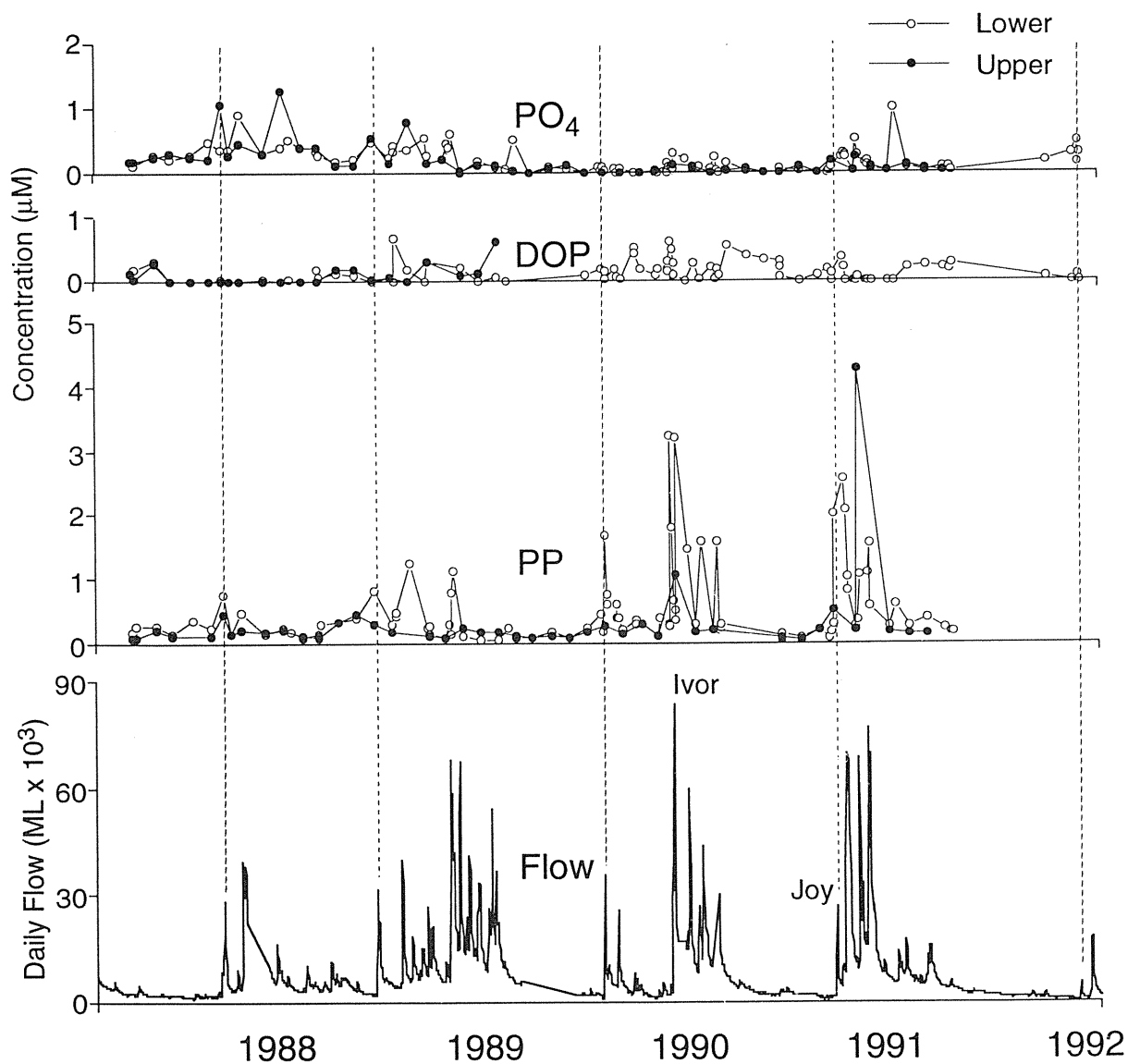


Figure 45. Temporal and longitudinal changes in concentrations of water-borne phosphorus in relation to daily flow in the Tully River (1988-1992) at sites near the Koombbooloomba Dam and the Bruce Highway bridge. Vertical dotted lines identify the first flood event of each wet season. Flood peaks associated with Cyclones Ivor and Joy are identified

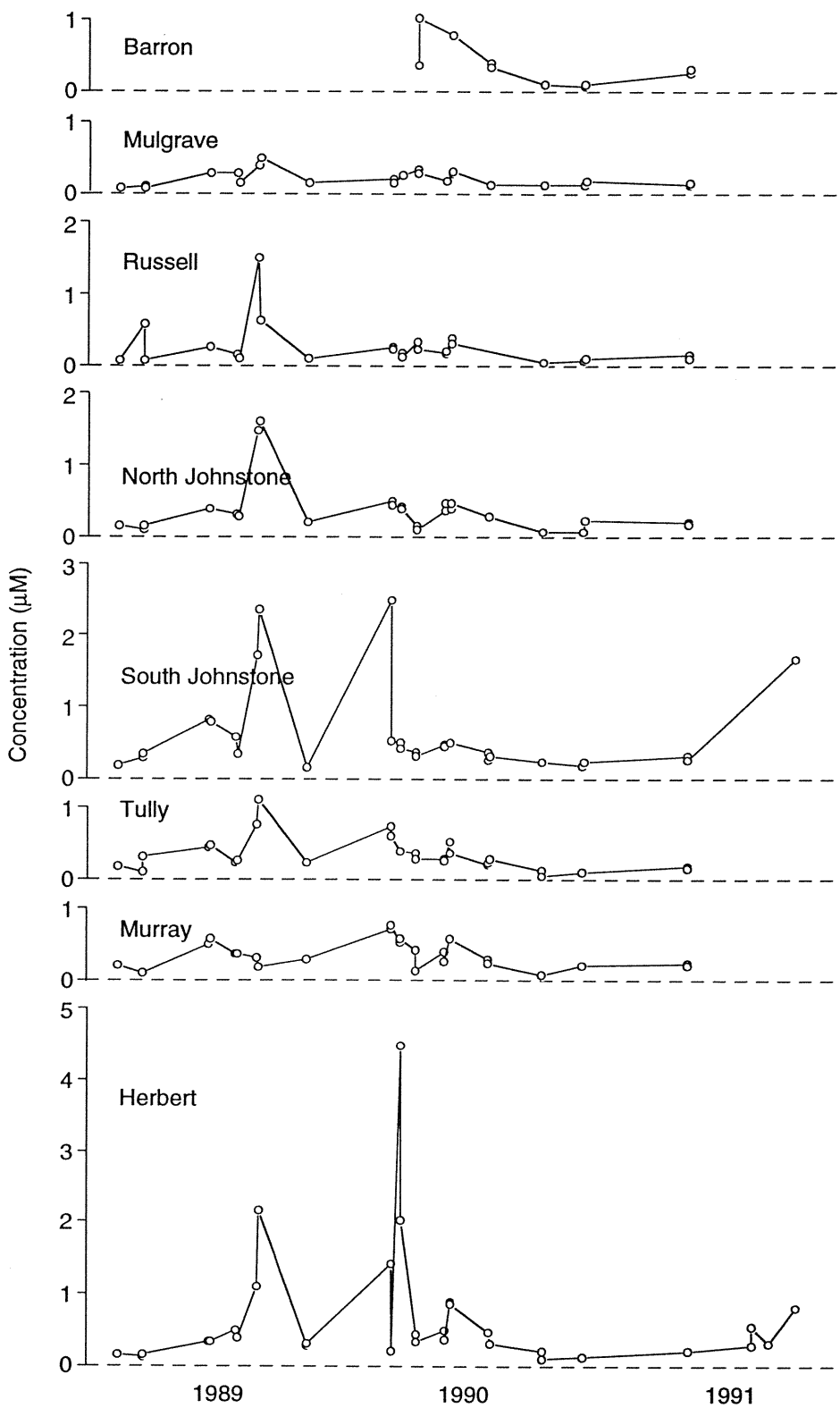


Figure 46. Concentrations of particulate phosphorus measured contemporaneously at lower catchment sites under low-flow conditions in eight north Queensland rivers between 1989 and 1992.

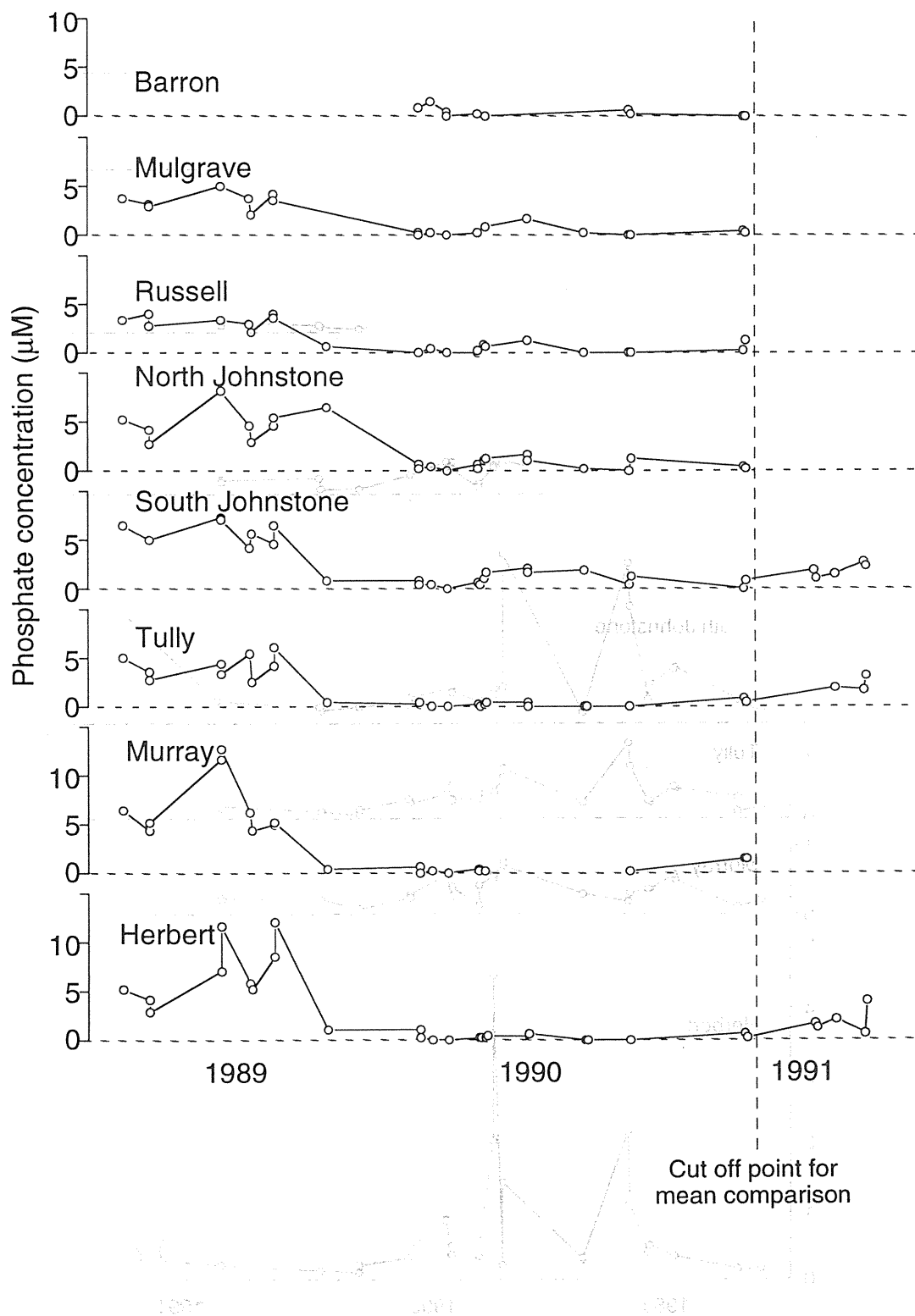


Figure 47. Concentrations of phosphate measured contemporaneously at lower catchment sites under low-flow conditions in eight north Queensland rivers between 1989 and 1992.

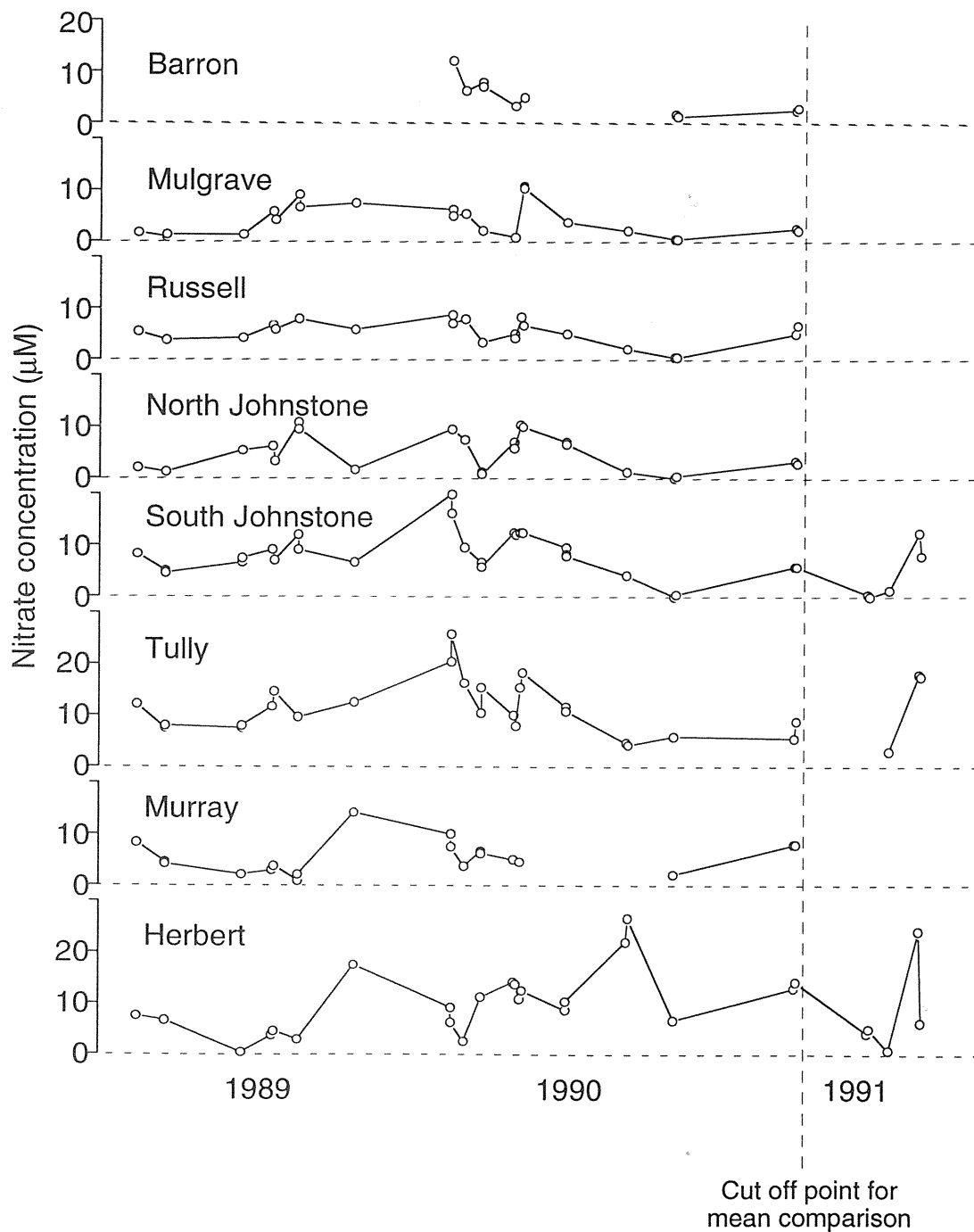


Figure 48. Concentrations of nitrate measured contemporaneously at lower catchment sites under low-flow conditions in eight north Queensland rivers between 1989 and 1992.

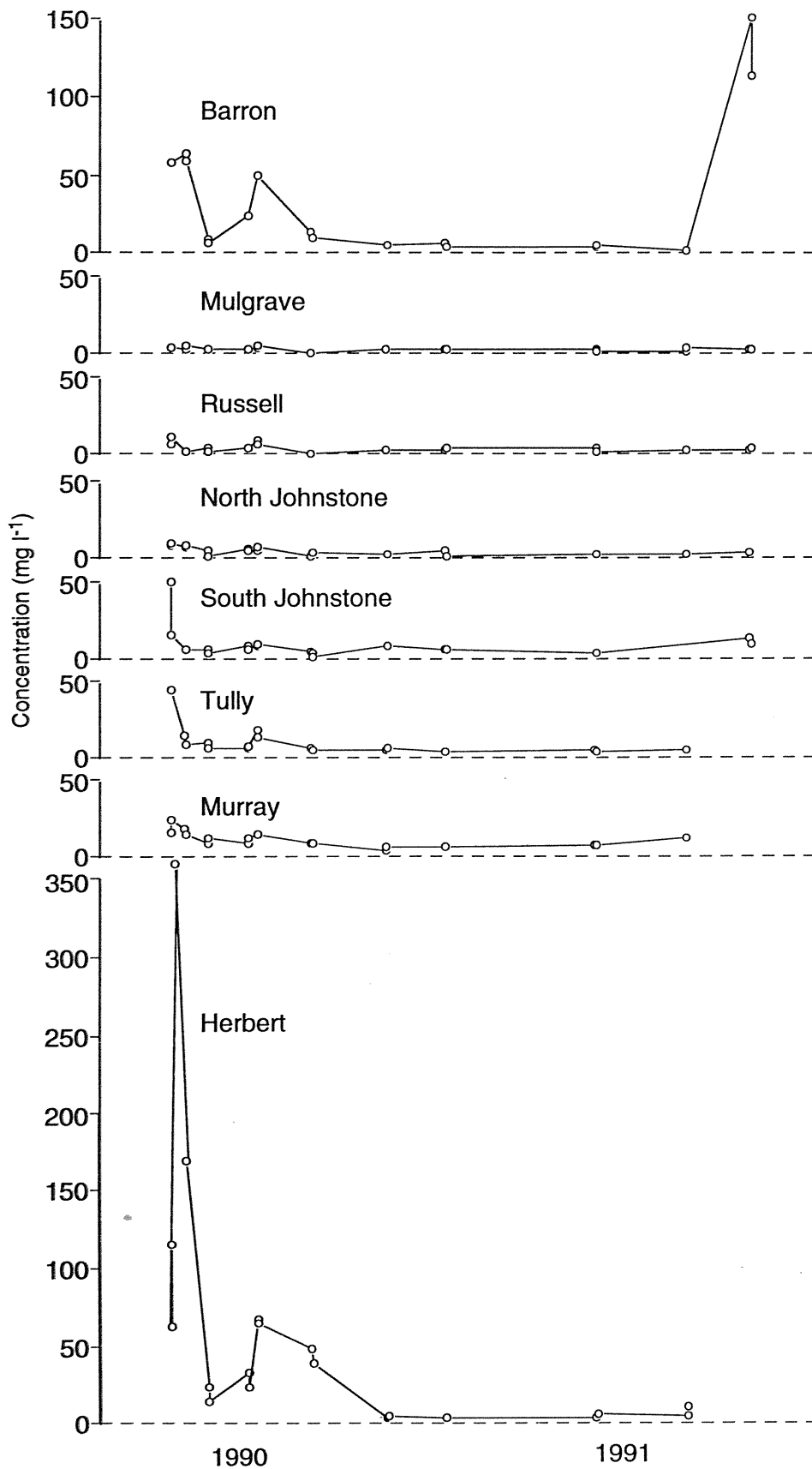


Figure 49. Concentrations of suspended solids measured contemporaneously at lower catchment sites under low-flow conditions in eight north Queensland rivers between 1989 and 1992.

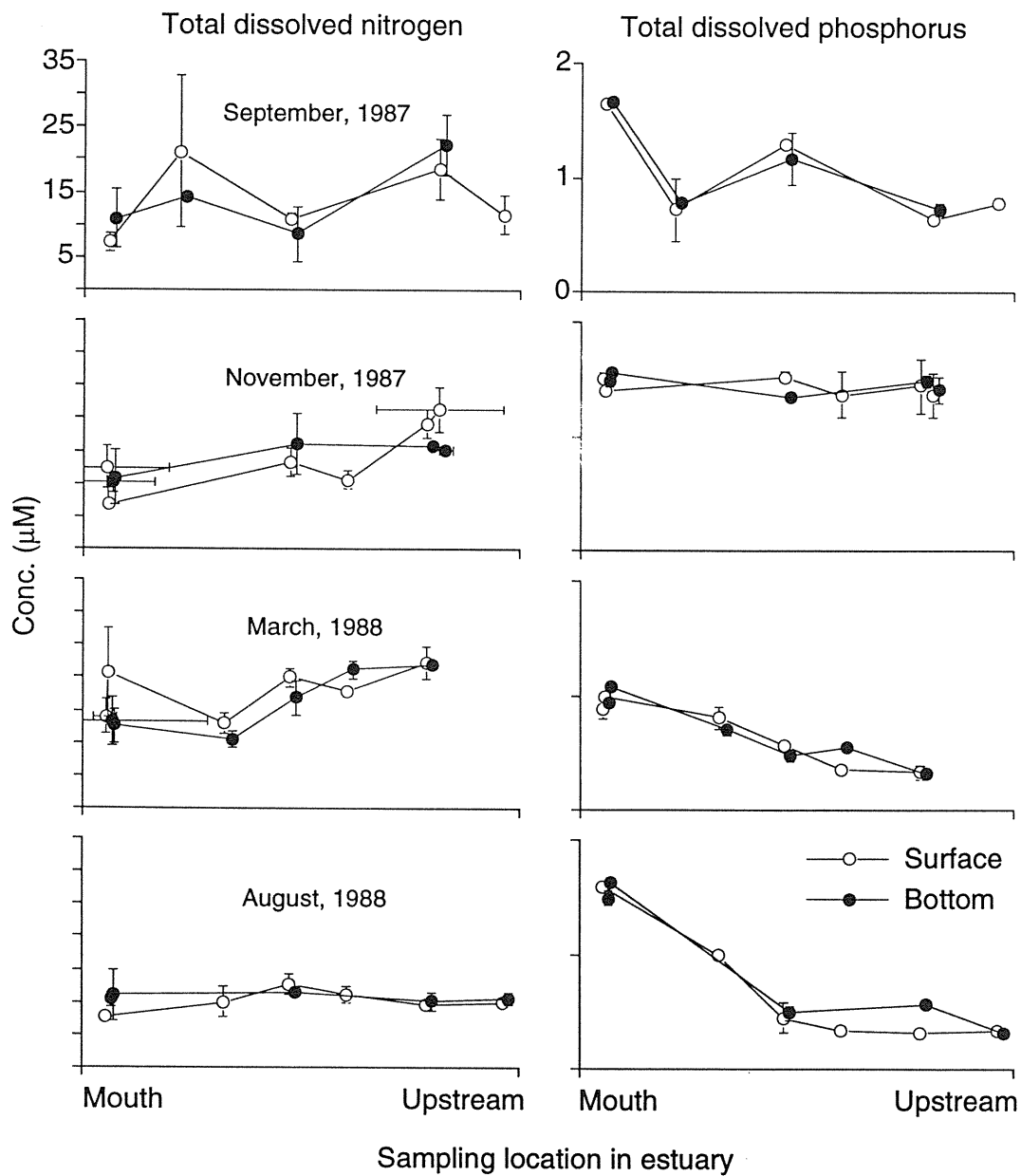


Figure 50. Longitudinal, cross-axial and vertical variability in total dissolved nitrogen (DIN+DON) and total dissolved phosphorus (DIP+DOP) concentrations in the estuarine section of the Murray River. The error bars shown represent 1 standard deviation about the mean for samples collected at three cross-axial stations for a particular depth.

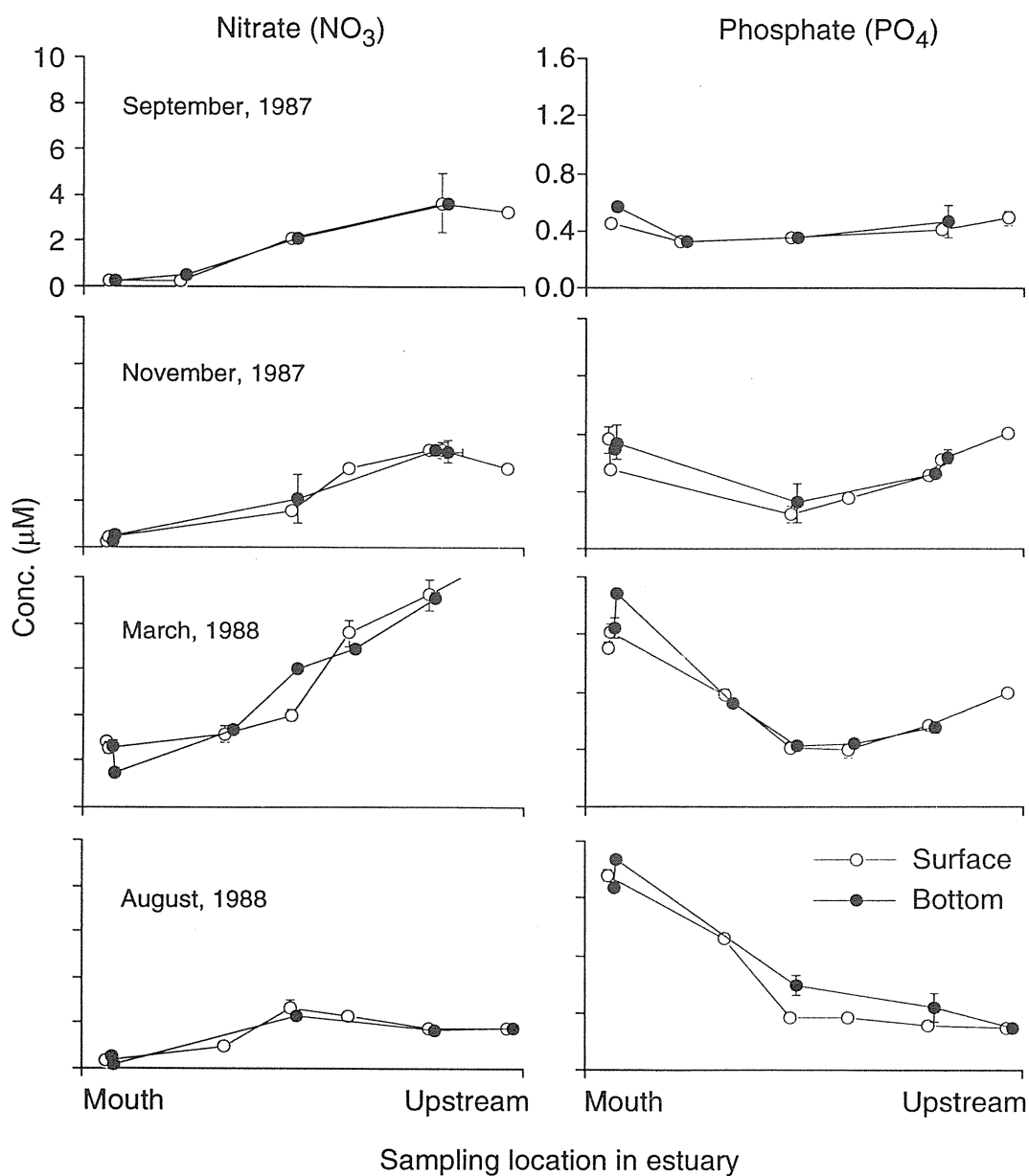


Figure 51. Longitudinal, cross-axial and vertical variability in nitrate and phosphate concentrations in the estuarine section of the Murray River. The error bars shown represent 1 standard deviation about the mean for samples collected at three cross-axial stations for a particular depth.

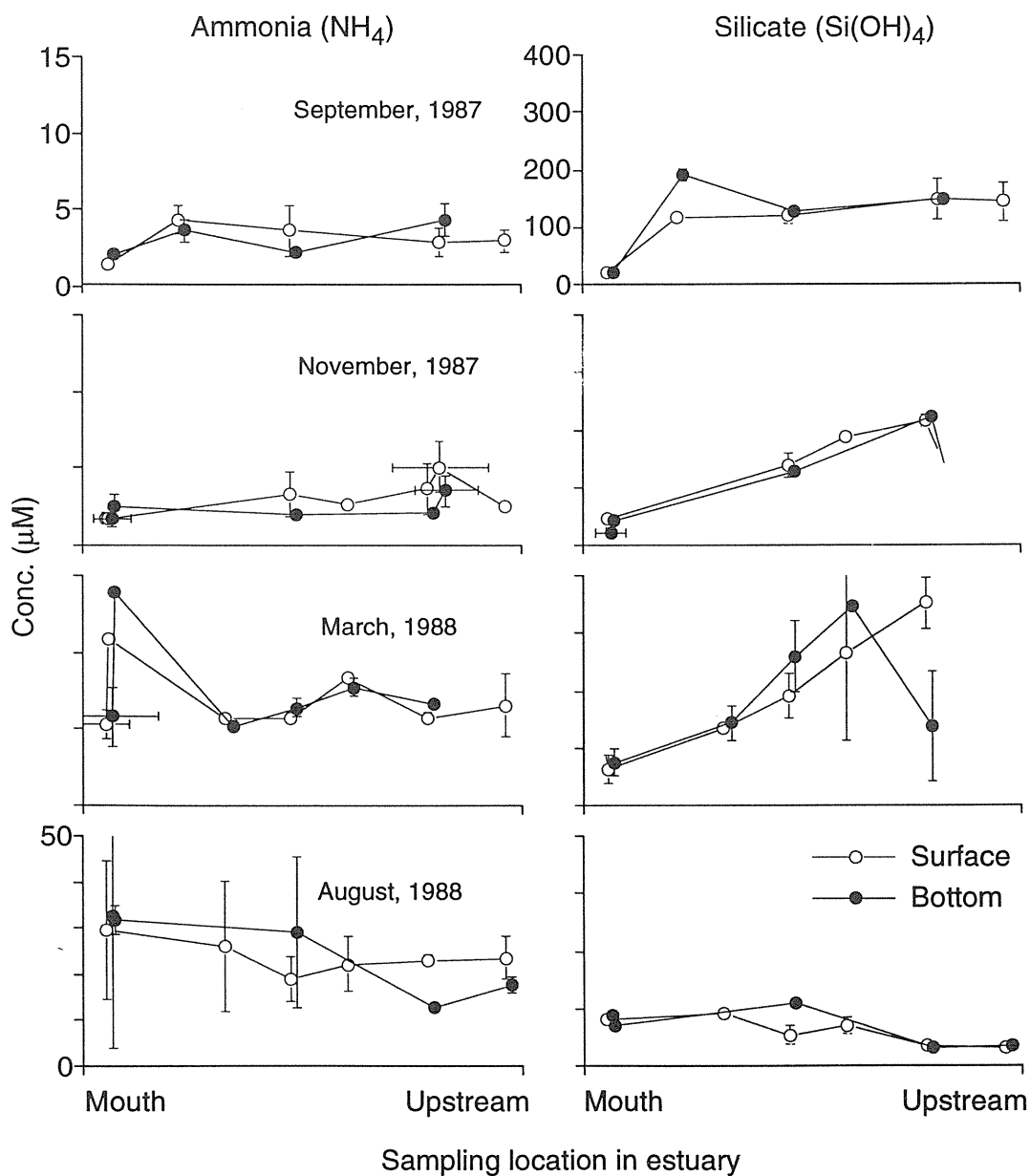


Figure 52. Longitudinal, cross-axial and vertical variability in ammonium and silicate concentrations in the estuarine section of the Murray River. The error bars shown represent 1 standard deviation about the mean for samples collected at three cross-axial stations for a particular depth.

The estuarine survey data, while limited, clearly illustrates that deliveries of inorganic phosphorus to coastal waters are greater than would be apparent from measurements of riverine PO_4 concentrations multiplied by the instantaneous discharge rates. While total dissolved phosphorus concentrations tend to increase steadily downstream in the estuary, phosphate concentrations, *per se*, declined or remained nearly constant within the upper estuary, then increased dramatically in the lower estuary. Phosphorus sorption-desorption processes in estuaries are dynamic (Fox et al., 1986) and are related to both the nature of the particles involved and the concentrations of dissolved PO_4 (Froelich, 1988). At present, too little is known about the dynamics of sorption-desorption processes in north Queensland estuaries to predict the incremental proportion of riverine phosphorus which becomes dispersed as soluble phosphate over short to medium (< 1 year) time scales in estuarine and adjoining coastal systems. The potential for significant levels of PO_4 solubilization during flood events is illustrated by data collected during the 1991 Fitzroy River flood (Brodie and Mitchell, 1992) where PO_4 constituted between one third and one half of the total phosphorus in plume water.

For the most part, lateral (cross-stream) variations in measured nutrient concentrations were small relative to vertical concentration differences at particular stations.

8.4 Riverine Nitrogen and Phosphorus Exports to Coastal Waters

It is clear from the results of the intensive sampling program carried out in the So. Johnstone River that an accurate quantification of annual nutrient exports from any of the north Queensland rivers requires resolution of nutrient concentrations during a small number of short-term, high flow events. The timing, magnitude and contribution of these events to annual fluxes varies from year to year and between watersheds.

At present, the So. Johnstone River is the only one for which an accurate estimate of annual nitrogen and phosphorus fluxes can be integrated from the available data. For the two years in question, total water discharge was 0.80 and $0.87 \times 10^9 \text{ m}^3$, respectively (QWRC). Cyclones Ivor and Joy dominated the two annual hydrographs. These annual discharges can be compared to the long-term average discharge of $0.81 \times 10^9 \text{ m}^3$ (Table 3), which suggests either that cyclone related rainfall does not make a significant addition to annual discharge (unlikely) or that rainfall resulting from cyclones and monsoonal depressions is a regular feature in this region. The latter is more likely the case. Integrated nitrogen and phosphorus exports from the So. Johnstone River for the two years were quite similar (23,100 and 22,400 kmol N 997 and 1,045 kmol P). These give integrated annual N/P discharge ratios of 23.2 and 21.4 (atoms), respectively. These integrated discharge estimates can be used to make first-order calculations of the discharge-weighted mean concentrations of nitrogen and phosphorus in the So. Johnstone River (27.3 and 1.22 mmol m^{-3} for N and P, respectively). The overall N/P ratio in the material exported from the So. Johnstone River is similar to or lower than total N/P ratios (ca. 21-30) in shelf waters (Tables 9, 11).

In the absence of detailed time series of nutrient data from any of the other rivers, the discharge-weighted mean concentrations of nitrogen and phosphorus calculated for the So. Johnstone River were multiplied by the average discharge figures for each river to make first order estimates of exports from all of the rivers discharging into or affecting the two boxes (Table 23). Given the wide disparity in catchment areas, average catchment rainfall (Hausler, 1991) and land use within the catchments, these estimates must be regarded as being provisional, pending the collection of more detailed nutrient data sets from the individual rivers. Overall, we calculate that approximately 139,000 and 314,000 kmol of nitrogen (1,946 and 4,390 metric tonnes) are transported annually by rivers into the Cairns and Tully boxes, respectively. Corresponding estimates of phosphorus export fluxes are 6,209 and 14,000 kmol

(192 and 433 metric tonnes), respectively. For reasons to be discussed later, these are likely high estimates.

Table 23. Estimated nitrogen and phosphorus inputs from gauged rivers discharging into the Cairns and Tully boxes. Estimates are based on volume-weighted nutrient exports from the South Johnstone River (1989-1991).

River	Average Annual Discharge Mm	Weighted Mean Nitrogen concentration mmol m ⁻³	Weighted Mean Phosphorus concentration mmol m ⁻³	kmol N p.a.	kmol P p.a.	m.t. N p.a.	m.t. P p.a.
Cairns box							
Daintree	4250			116025	5185	1626	161
Barron	839			22905	1024	321	32
Total	5089			138930	6209	1946	192
Tully box							
Russell	1036			28283	1264	396	39
Mulgrave	766			20912	935	293	29
North Johnstone	1880			51324	2294	719	71
South Johnstone	811	27.3	1.2	24995	1100	350	34
Tully	3119			85149	3805	1193	118
Murray	170			4641	207	65	6
Herbert	3582			97789	4370	1370	135
Total	11364			313092	13975	4386	433

These estimated inputs are on the order of 16 and 20 percent of the existing summer total water column nitrogen stocks within the Cairns and Tully boxes during summer, and 15 and 27 percent of total summer water column phosphorus stocks. Perhaps more important, the estimated river nitrogen and phosphorus inputs are on the order of 100-500 percent of pre-existing total nitrogen and phosphorus stocks contained in the water inshore of the 20 m isobaths in the two boxes.

9. RAINFALL INPUTS OF NUTRIENTS

Somewhat in excess of 2 metres of rain falls annually onto the central GBR (16-18°S) shelf. The mountain ranges and coastal catchments adjacent to the Tully box are the wettest in Australia, with precipitation in some places exceeding 11 metres per annum (Hausler, 1991). High rainfall is also recorded in and north of the Daintree River catchment, at the northern edge of the Cairns box. Long-term rainfall records over the shelf are available from three local sites: Low Isles (annual mean 1894-1990 = 2.1 m), Green Island (annual mean 1949-1990 = 2.06 m) and Fitzroy Island (annual mean 1962-1990 = 2.70 m). Most of this rainfall comes between January and March (Figure 53), with monthly mean falls increasing from November and declining through July. It is not clear how far the pattern of rainfall measured along the coast extends to sea.

Distributions of inorganic nutrient concentrations measured in rain samples are highly skewed toward low concentrations (Figures 54-56). Concentrations of silicate and phosphate in rainwater are usually very low, suggesting low levels of continental dust in the rainwater or seawater/seasalt contamination of samples. Ammonium and nitrate were the principal species of inorganic nitrogen measured in rain samples. It is unclear what factors were responsible for the very high ammonium and nitrate concentrations in a small number of samples. Considerable effort was made to minimize contamination of the samples and sampler. Organic nitrogen (=DON+PN) concentrations measured in a subset of the rainwater samples averaged approximately $4.5 \mu\text{mol N l}^{-1}$.

Such high concentrations are not unprecedented (Williams, 1967; Knap et al., 1986), and would lead to, if generally occurring in all samples, an appreciable nitrogen flux into the water column. Because of the small number of samples analyzed, the precision of the estimate of organic nitrogen fluxes via rainfall must be viewed with caution until verified. No estimates have been attempted for dry deposition of nitrogen species in the central GBR region (e.g. Duce, 1986).

The median total phosphorus concentration measured in rainwater samples ($0.18 \mu\text{M}$) was similar to that measured in bulk precipitation samples collected at an isolated oceanic site in the central Pacific ($0.18 \mu\text{M}$; Graham and Duce, 1981). Graham and Duce (1981 and sources quoted therein) reported that non-reactive phosphorus in rainwater was present at concentrations equal to or greater than molybdate reactive phosphorus (PO_4). They found that dry phosphorus deposition was on the order of 20-40 percent of the phosphorus flux in rain. At sites near land, local atmospheric recycling of phosphorus could therefore contribute materially to total atmospheric phosphorus fluxes (Graham and Duce, 1981).

DIN/DIP ratios calculated for rainfall samples span a considerable range (Figure 57). Only seven of 48 calculated DIN/DIP ratios fell on or below the Redfield N/P ratio (16), with fifteen samples having DIN/DIP ratios between 50 and 100 (atoms).

Summary statistics for dissolved nutrient concentrations measured in rain samples are given in Table 24. Estimates of nutrient fluxes in rainfall are calculated from the median concentrations to minimize weighting by the few, very high concentrations measured. The Green Island rainfall estimate is used to compute the overall precipitation flux as most of the area considered is away from the coast and would not have any exaggerated topographic bias, such as might influence rainfall at Fitzroy Island which is located closer to the coast and the mountains of Cape Grafton. The input estimates are likely conservative, but not extremely so.

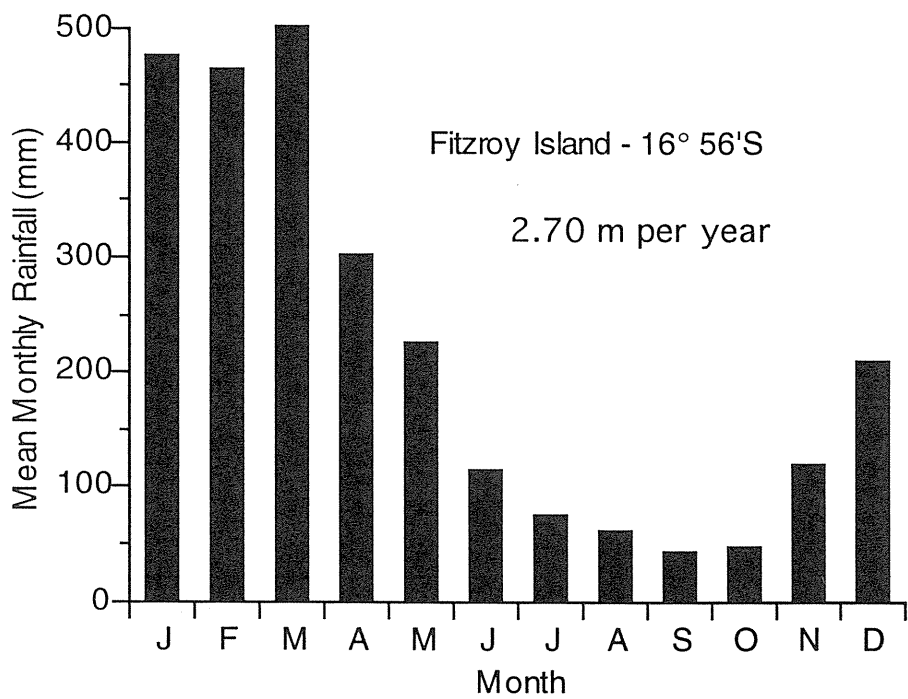
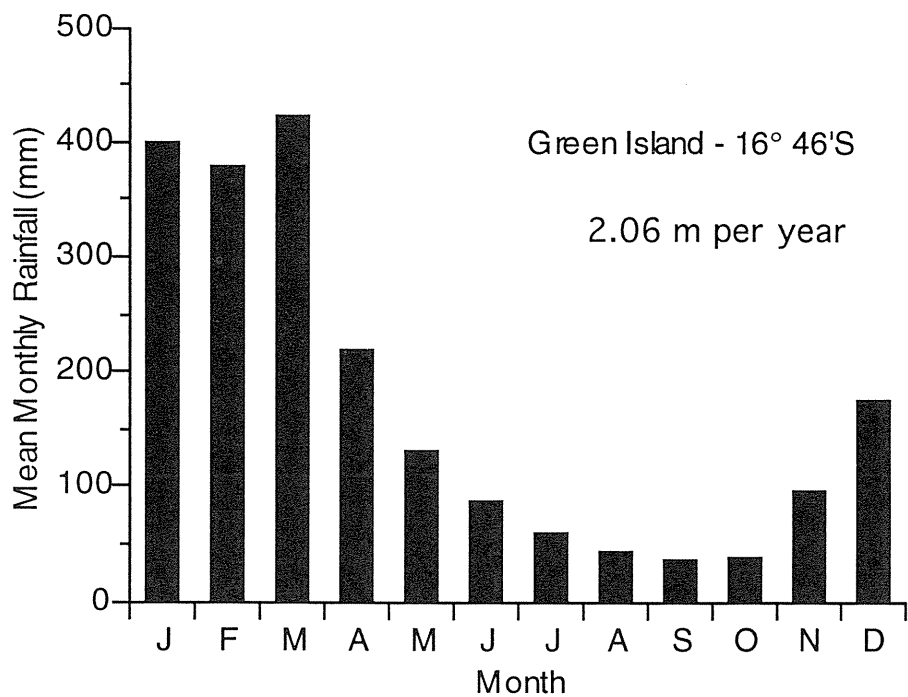


Figure 53. Mean monthly rainfall measured at Green Island (1949-1990) and Fitzroy Island (1962-1990).

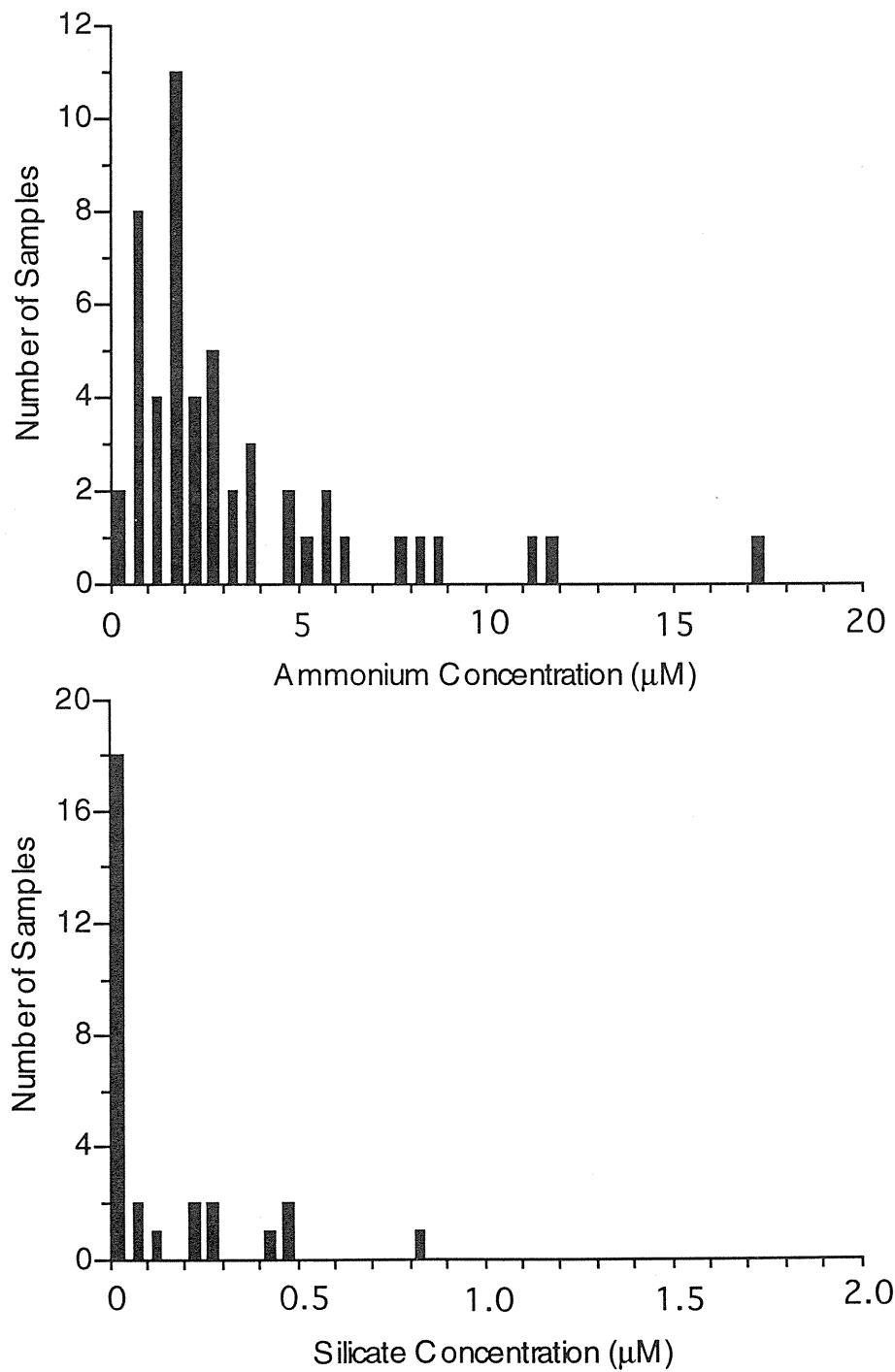


Figure 54. Frequency distributions of measured ammonium and silicate concentrations in rainwater collected at AIMS and in the western Coral Sea (GBR included). Bin widths for ammonium and silicate distributions are 2.5 and 0.5 μM respectively. Silicate concentrations in rain samples exceeded 2 μM on two occasions.

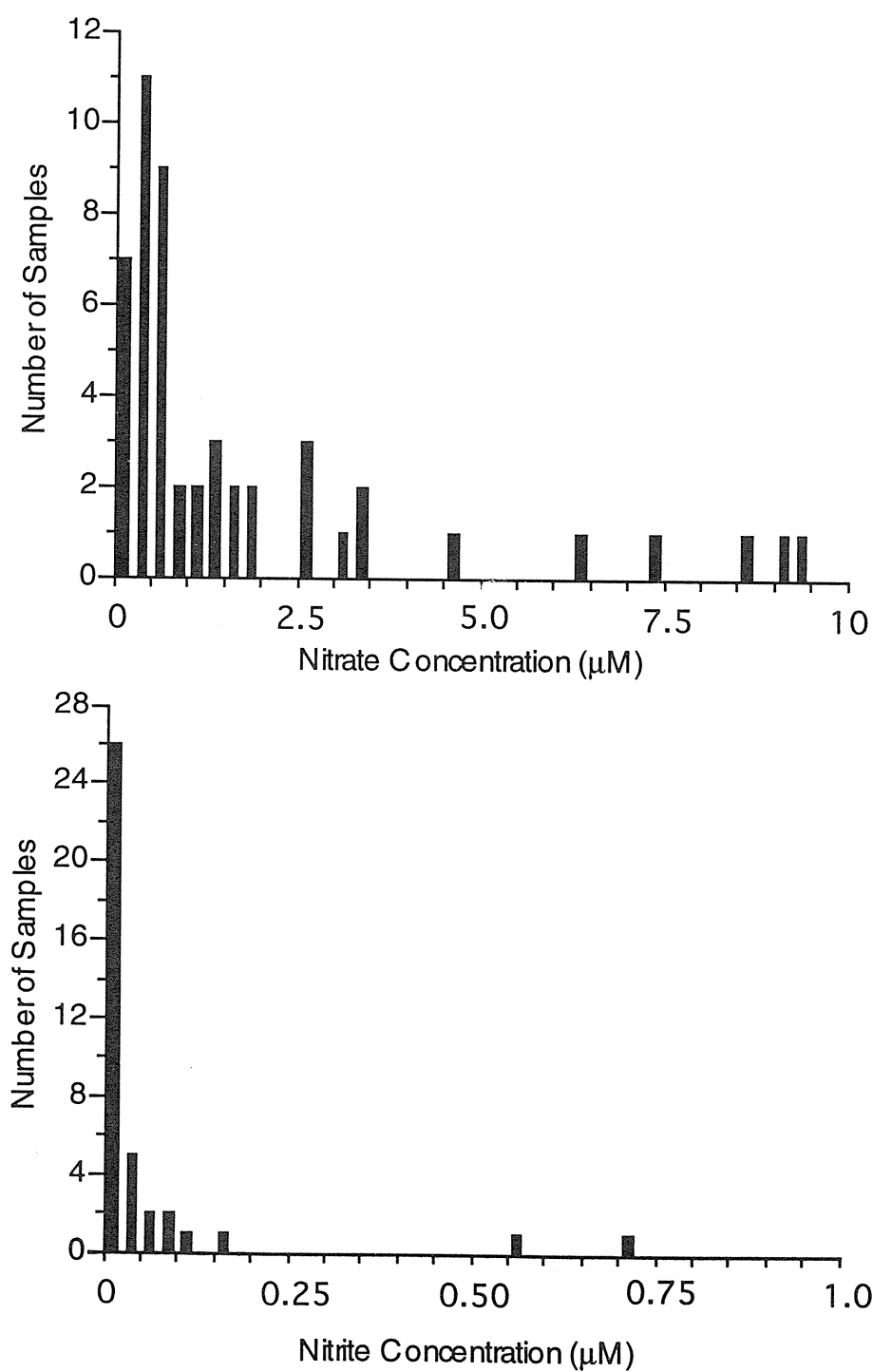


Figure 55. Frequency distributions of measured nitrate and nitrite concentrations in rainwater collected at AIMS and in the western Coral Sea (GBR included). Bin widths for nitrate and nitrite distributions are 0.125 and 0.025 μM , respectively.

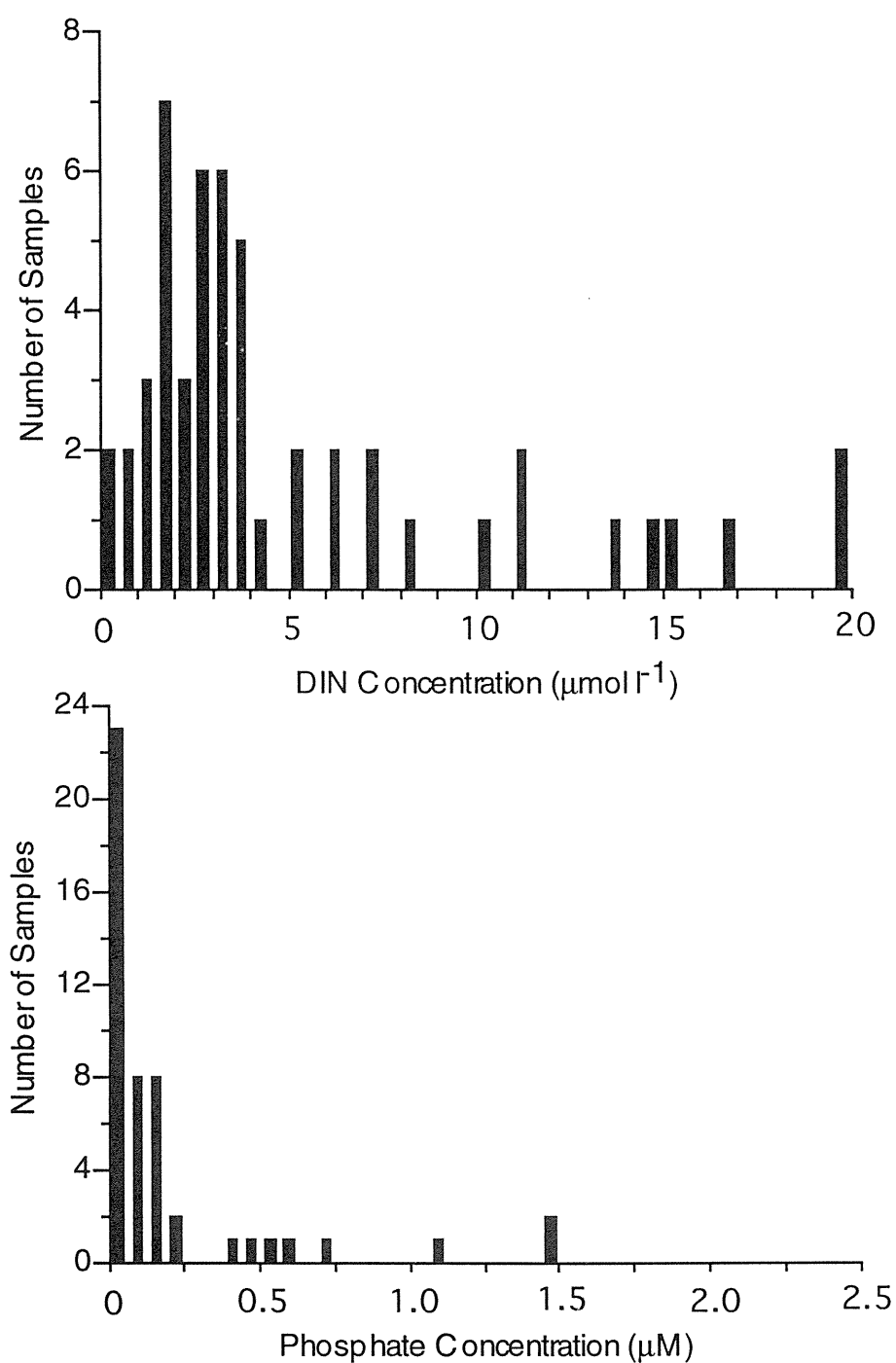


Figure 56. Frequency distributions of dissolved inorganic nitrogen ($\text{DIN}=\text{NH}_4+\text{NO}_2+\text{NO}_3$) and phosphate concentrations in rainwater collected at AIMS and in the western Coral Sea (GBR included). Bin widths for DIN and phosphate distributions are 0.5 and 0.05 μM , respectively.

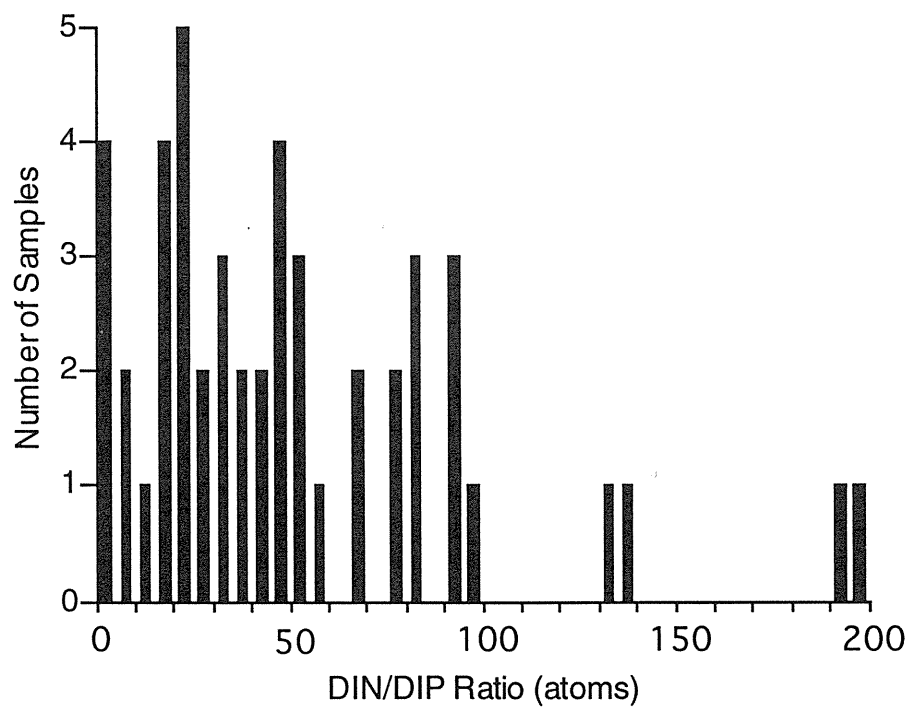


Figure 57. Frequency distribution of DIN/DIP ratios in rainwater collected at AIMS and in the western Coral Sea (GBR included). Bin widths for ratio frequencies are 5.

Table 24. Dissolved nutrients in rainfall collected at sites throughout the GBR and western Coral Sea. Fluxes are estimated from the median concentration to devalue the importance of extreme values. Annual rainfall for the shelf is taken as the long-term (1949-90) average recorded at Green Island.

	NH ₄	NO ₂	NO ₃	Tot N	PO ₄	Tot P	Silicate
Mean (µM)	3.31	0.67	1.31	6.47	0.28	0.24	0.35
Std. Dev.	3.33	1.81	2.31	3.62	0.48	0.16	0.99
no. samples	51	51	51	9	51	12	45
Median (µM)	2.01	0.01	0.36	6.85	0.09	0.18	0.01
Annual rainfall (m)	2.06	2.06	2.06	2.06	2.06	2.06	2.06
Rain Inputs (mmol m ⁻² year ⁻¹)	4.14	0.02	0.73	14.11	0.18	0.37	0.02
Inputs (kmol)							
Cairns box	24583	122	4342	83777	1070	2212	122
Tully box	32404	161	5723	110433	1411	2915	161
Inputs (m.t.)							
Cairns box	344	2	61	1174	33	69	3
Tully box	454	2	80	1547	44	90	5

Ammonium is the principal inorganic nitrogen species deposited in rainfall. We calculate that atmospheric precipitation deposits approximately 29,000 and 38,000 kmol of inorganic nitrogen (NH₄+NO₂+NO₃) per year in the Cairns and Tully boxes, respectively. Estimated organic nitrogen (=DON + PN) inputs of 55,000 and 72,000 kmol from rainfall into the Cairns and Tully boxes are larger than the estimated inorganic nitrogen inputs, but should be viewed with caution until more measurements of DON and PN in rain are made.

Duce (1986) estimated annual atmospheric nitrogen inputs to the subtropical North Pacific Ocean fall between 8 and 26 µmol m⁻². Extrapolated to the areas of the Cairns and Tully boxes, this range of fluxes would translate to annual nitrogen inputs of 48-150 and 63-200 x 10³ kmol, respectively, which bracket the estimated fluxes to these areas based on local measurements.

Inorganic phosphorus inputs from rainfall slightly exceed 1,000 kmol per year for both the Cairns and Tully boxes. Estimated fluxes of inorganic and organic phosphorus (=DOP and PP) are approximately equal. Duce (1986) estimated that atmospheric phosphorus fluxes to the central North Pacific Ocean fall between 0.005 and 0.012 µmol m⁻² day⁻¹. Over an annual time period, these atmospheric fluxes would be equivalent to total atmospheric inputs of 11-26 kmol and 14-34 kmol of phosphorus into the Cairns and Tully boxes, respectively. Duce’s estimated total fluxes are approximately 1-2 percent of the atmospheric input fluxes to the GBR calculated from rainfall collections. Reasons for the discrepancy are unresolved at present. Most of Duce’s sampling sites were located on small islands in the middle of the Pacific Ocean where terrestrial contamination could be expected to be small. Collateral geochemical measurements to establish levels of dust contamination of the rain have yet to be made, but need to be done.

10. INTRUSIONS FROM THE CORAL SEA

Near-bottom intrusions of cool, sub-thermocline waters occur episodically along the shelfbreak of the GBR (Andrews and Furnas, 1986). These events occur predominantly during the summer months (October - April) and the available data suggests that intrusion events can be temporally coherent along hundreds of kilometres of the shelfbreak (Andrews and Furnas, 1986).

The temperature-salinity (T/S) characteristics of the water masses immediately seaward of the GBR in the East Australian Current (EAC) are relatively well defined (Figure 14). In the western Coral Sea, a layer of warm, low-density Coral Sea Surface Water (CSSW) overlies a discrete layer of cooler, high-salinity water known as Subtropical Lower Water (SLW), which in turn, sits atop a broad layer of Antarctic Intermediate Water (AIW; Pickard et al., 1977). The salinity and temperature characteristics of CSSW change seasonally in response to solar heating, evaporation and precipitation. Subtropical Lower Water is formed in the oceanic regions to the east of the Coral Sea and is advected westward until reaching the Australian continent. In contrast to CSSW, the T/S characteristics of SLW in the region adjacent to the GBR are relatively stable. The core of the SLW layer is characterized by temperatures within the range 20.0-22.5°C and salinities between 35.6 and 35.7 ‰. The depth of the salinity maximum which identifies the core of the SLW layer normally falls between 100 m and 150 m immediately seaward of the reef, moving vertically in response to dynamic factors such as the strength of the poleward flowing EAC, transport in the South Equatorial Current and internal tides. At any one time, the transition zone between the CSSW and SLW is characterized by a gradient of mixtures between CSSW and SLW. Accordingly, parcels of water within the transition zone can be partitioned on the basis of their T/S characteristics into constituent proportions of CSSW and SLW. Water and nutrients intruded onto the shelf largely comes from this transition layer between surface waters and SLW.

Surface waters within the GBR also exhibit a cross-shelf gradient of temperatures and salinities (Figure 13). T/S characteristics of inshore water and water within the GBR lagoon are affected by seasonal changes in solar heating, mixing, evaporation, coastal runoff and precipitation (Pickard et al., 1977; Wolanski and Jones, 1981). For the purposes of budget calculations, a seasonally varying water type, Lagoon Water (LW; Andrews, 1983) is operationally defined. As with vertical profiles, the T/S characteristics of surface water parcels within the reef matrix can be partitioned into their relative proportions of LW and CSSW.

Calculated volumes of intruded SLW within a 1-metre wide cross shelf section in both the Cairns and Tully boxes exhibit a general linear relation to both shelfbreak bottom water temperature and the difference between the bulk mixed layer and minimum shelfbreak water temperatures observed in a given section (Figure 58). Variations in near-bottom shelfbreak temperature or the vertical temperature range account for 48-64 percent of the variability in calculated SLW water volume on the shelf (Table 25). For the mean cross-shelf bathymetries of the Cairns and Tully boxes, the largest of the Palm Passage intrusions would have injected slightly less than $5 \times 10^5 \text{ m}^3$ of SLW per metre of coastline onto the shelf, a volume on the order of 22 percent of the volume of the Cairns box and 16 percent of the Tully box (Figure 59). Volumes of SLW imported by most intrusion events, however, were considerably smaller. The total volume of water transported onto the shelf by an intrusion event, however, would be considerably greater as the SLW proper would be diluted by CSSW within the intruded transition layer.

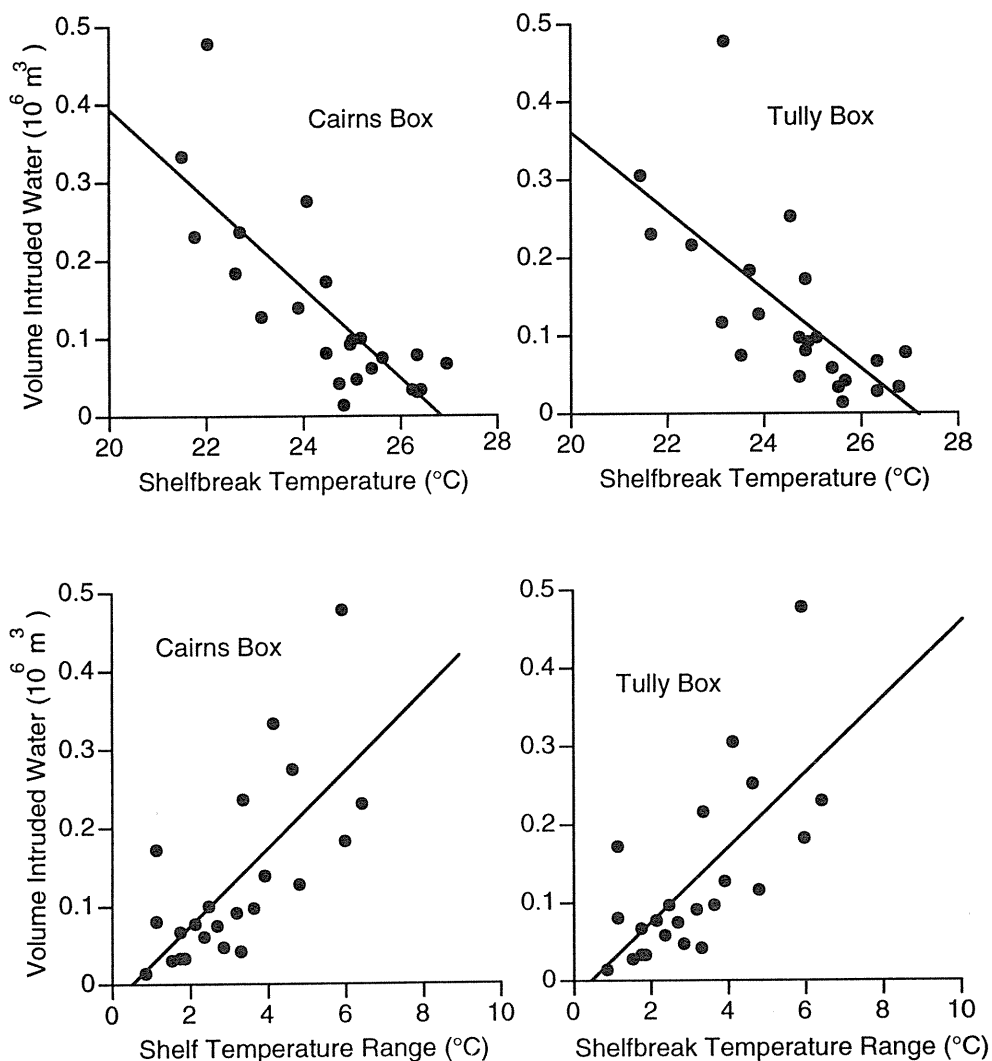


Figure 58. Calculated volumes of undiluted Subtropical Lower Water (SLW) per linear metre of shelf in the Cairns and Tully boxes in relation to (Top) calculated bottom water temperature at 58 m near Euston Reef and (Bottom) the calculated near-surface to bottom temperature difference at the shelfbreak near Euston Reef. Near-bottom temperatures and SLW volumes were calculated from masked Palm Passage sections.

Table 25. Empirical relationships derived for estimating volumes of Subtropical Lower Water and stocks of nitrate and phosphate intruded onto the shelf in the Cairns and Tully boxes from measured near-bottom shelfbreak water temperatures.

Cairns box		
Volume intruded (10 ⁶ m ³)	= 1.55 - 0.058 (Temp)	r ² = 0.64
Volume % SLW	= 69.7 - 2.6 (Temp)	"
Volume intruded (10 ⁶ m ³)	= 0.0494 (delta Temp) - 0.0233	r ² = 0.49
Volume % SLW	= 2.22 (delta Temp) - 1.05	"
Percent change in N per m of shelf	= 87.9 - 3.28 (Temp)	r ² = 0.64
Percent change in P per m of shelf	= 233-8.7(Temp)	r ² = 0.64
Tully box		
Volume intruded (10 ⁶ m ³)	= 1.38 - 0.059 (Temp)	r ² = 0.48
Volume % SLW	= 46.2 - 1.71 (Temp)	"
Volume intruded (10 ⁶ m ³)	= 0.0480 (delta Temp) - 0.0230	r ² = 0.49
Volume % SLW	= 1.61 (delta Temp) - 0.77	"
Percent change in N per m of shelf	= 38.4 - 1.43 (Temp)	r ² = 0.63
Percent change in P per m of shelf	= 53.9 - 2.01 (Temp)	r ² = 0.63

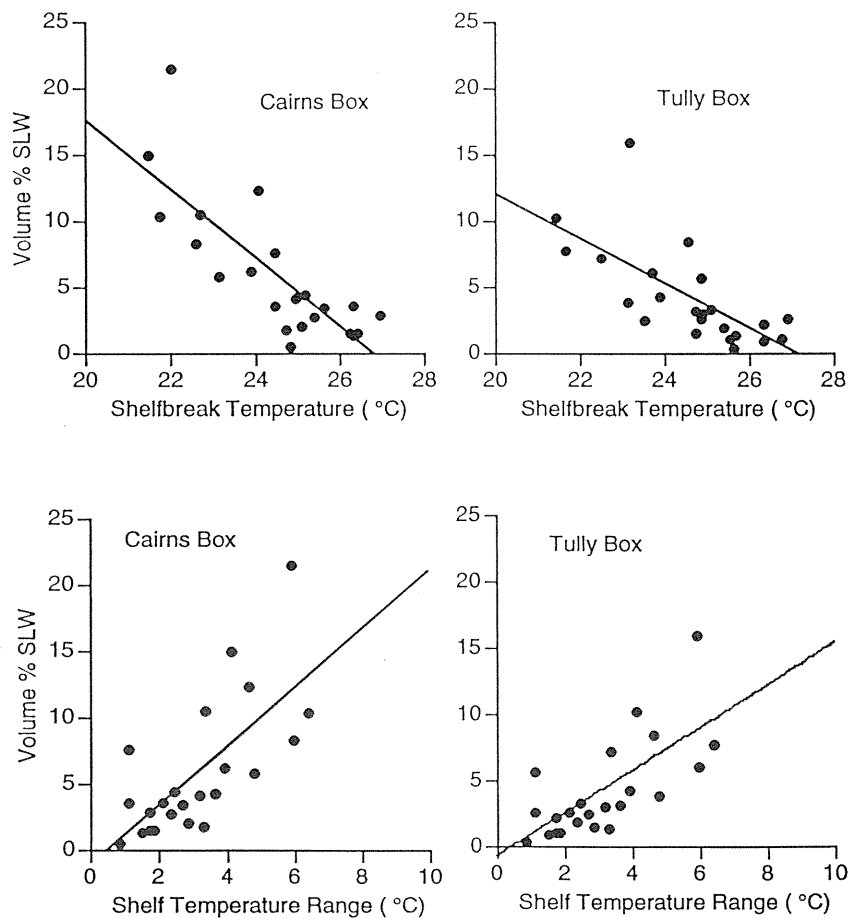


Figure 59. Calculated volume percentages of undiluted Subtropical Lower Water (SLW) per linear metre of shelf in the Cairns and Tully boxes in relation to (Top) calculated bottom water temperature at 58 m near Euston Reef and (Bottom) the calculated near-surface to bottom temperature difference at the shelfbreak near Euston Reef. Near-bottom temperatures and SLW volumes were calculated from masked Palm Passage sections.

Figure 60 illustrates calculated estimates of the net amounts of nitrogen and phosphorus which would be imported per linear metre of shelf into the Cairns and Tully boxes by the intrusion events sampled in Palm Passage and their relation to minimum water temperatures monitored with near-bottom TDR moorings at Euston Reef. Details of nitrogen and phosphorus speciation associated with intrusion events are discussed below. Because the water masses intruded and displaced are presumed to have a constant nutrient composition, the magnitude of nitrogen and phosphorus imports are linearly related to shelfbreak temperature in a manner analogous to the volume of intruded SLW (Figure 58). This is obviously a simplification, but necessary as detailed nutrient (dissolved and particulate) inventories for *in situ* source and outer shelf surface waters are not available for each event.

For very large intrusion events (ca. $5 \times 10^5 \text{ m}^3$ SLW per metre of shelf), net inputs of 2.43[0.28] and 2.49[0.26] kmol of N[P] would be imported into the Cairns and Tully boxes, respectively. Inputs of this order would represent 20[70] and 16[20] percent of existing summer N[P] stocks per linear metre of shelf. The large difference in relative phosphorus imports is due to the large apparent difference between DOP stocks in the two boxes. Reasons for the high DOP concentration in the Tully box are unresolved.

Near-bottom water temperatures were recorded over a two-year period near the shelfbreak at the entrances to Grafton Passage (Euston Reef, Figure 61) and Trinity Opening (Norman Reef, Figure 62). The Grafton Passage record is slightly cooler than the Trinity Opening record, reflecting the slightly deeper location of the temperature recorder (56-58 m vs. 52 m). Near-bottom temperatures varied seasonally in a sinusoidal pattern at both sites. Small spikes aside, the time-averaged maximum water temperature during the summer of 1989-90 was approximately 1°C higher than that recorded during the summer of 1990-91. Reasons for this difference are unresolved at this time. The Euston Reef TDR mooring is being maintained to observe possible interannual fluctuations in shelfbreak water temperatures. The Norman Reef mooring was shifted to the passage between Green Island and Arlington Reef in December 1991. Over the ensuing nine months, two intrusion events (not shown) were recorded in near-bottom waters (41 m depth) adjacent to Green Island.

One large, extended intrusion event was monitored during each of the two summers sampled. A second smaller event was also observed during the summer of 1990-91. Short-lived events occurred during November 1989 and December 1991. Minimum near-bottom temperatures of 26°C and 24.4°C were measured at the Norman Reef site. At Euston Reef, minimum temperatures of 25.1°C (sustained 25.6°C) and 23°C were measured. The onset of the major intrusion during the summer of 1990-91 coincided with the occurrence of Cyclone Joy (25 December 1990). Thereafter, a period of unsettled, monsoonal weather developed which lasted approximately 6 weeks and which likely contributed to much of the observed near-bottom temperature variability over the 1990-91 summer season. A detailed analysis of the temperature record in relation to the local wind dynamics remains to be carried out.

Estimates of **net** nitrate and phosphate inputs to the shelf from intrusions are based upon the assumption that these nutrients are delivered rapidly during the event and that all intruded nutrients are subsequently dispersed within shelf waters. The extent to which intruded water (and nutrients) are returned offshore at the end of an intrusion event by horizontal mixing processes not associated with upwelling or offshore subsidence following the intrusion event is currently unknown. It is highly likely that some intruded water and nutrients are subsequently mixed back off the shelf into the EAC without contributing to shelf productivity in any significant fashion.

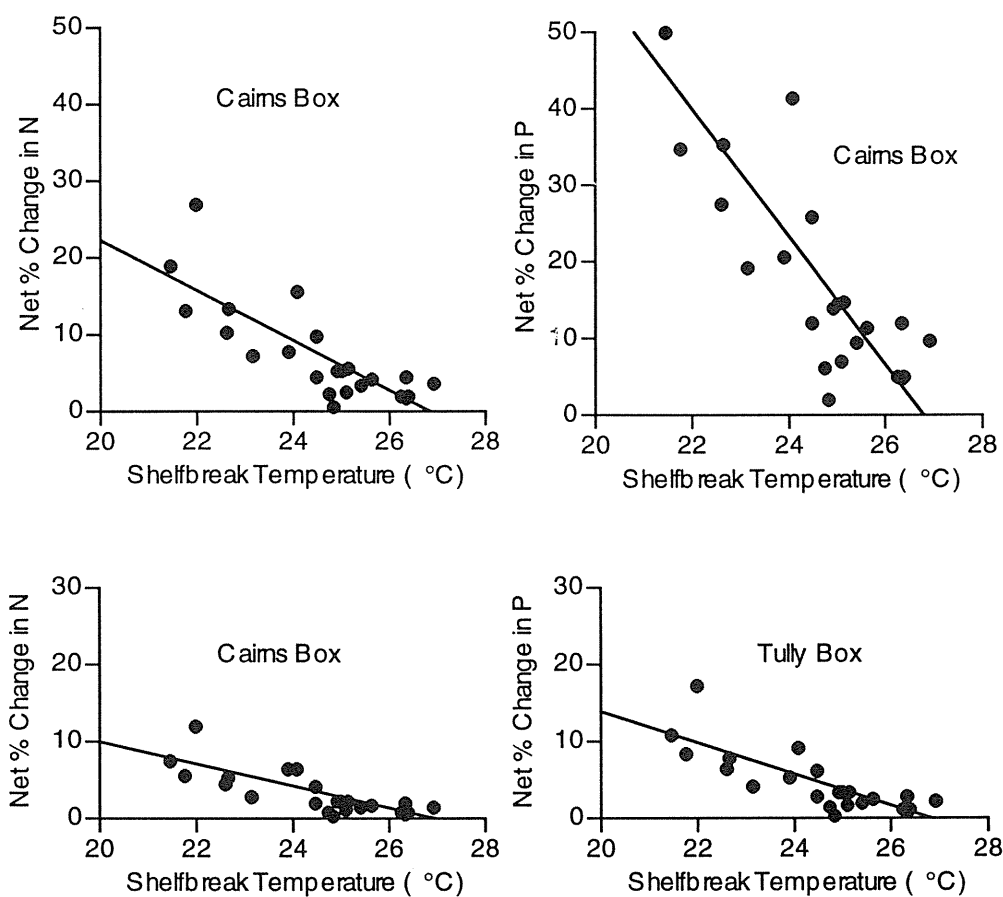


Figure 60. Calculated net changes in nitrogen (Top) and phosphorus (Bottom) stocks per linear metre of shelf in the Cairns and Tully boxes in relation to calculated shelfbreak bottom water temperatures near Euston Reef. Temperatures were taken from masked Palm Passage intrusions.

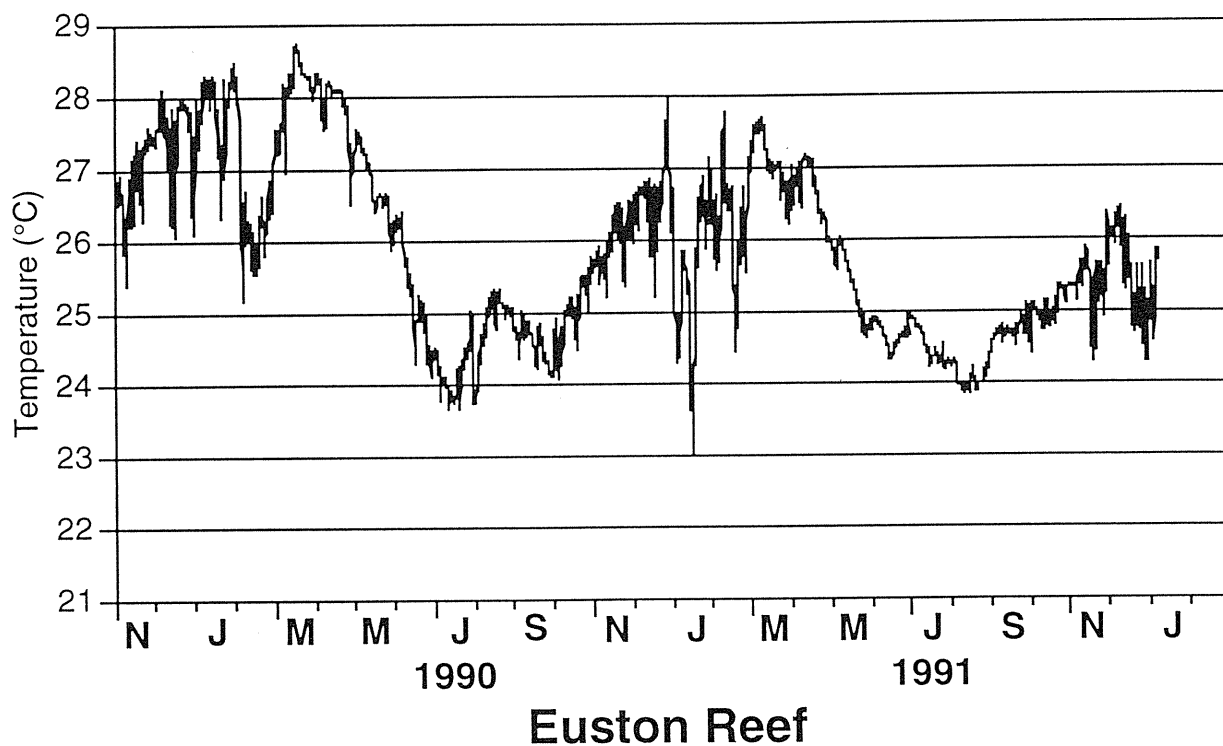


Figure 61. Near-bottom shelfbreak water temperatures recorded near Euston Reef (58 m depth) near the seaward end of Grafton Passage.

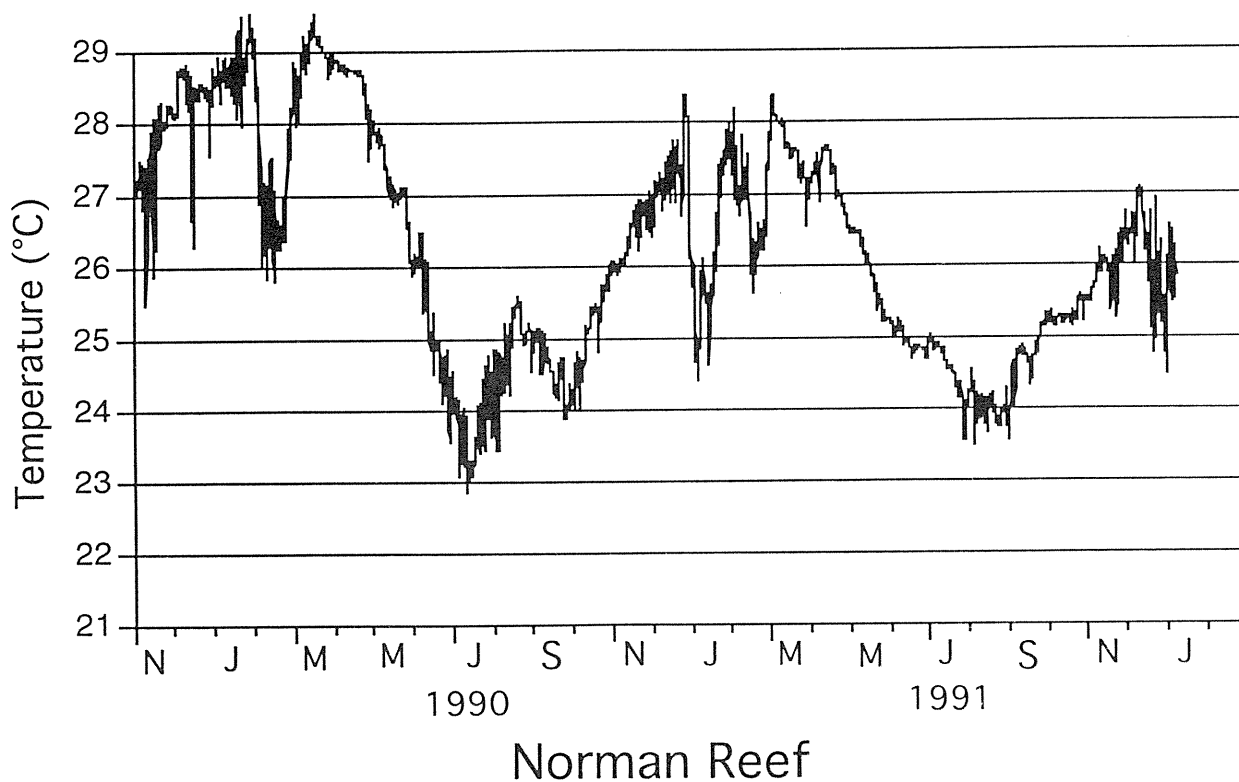


Figure 62. Near-bottom shelfbreak water temperatures recorded near Norman Reef (58 m depth) near the seaward end of Trinity Opening.

Table 26 summarizes calculated estimates of net nitrogen and phosphorus inputs to the Cairns and Tully boxes as a result of individual intrusion events. Most of the nitrogen inputs from intrusions (50 percent) are in the form of nitrate, with the remainder largely as DON (43 percent). Concentrations of DIN ($\text{NH}_4 + \text{NO}_2 + \text{NO}_3$) in intruded SLW are > 20 times the DIN concentrations in outer shelf surface water which is displaced offshore. Net onshore-offshore fluxes of ammonium, however, are close to being in balance. Offshore exports as a result of displacement during intrusion events were overwhelmingly as DON (86 percent), with most of the remainder in the form of PN (11 percent). PN and DON concentrations in displaced outer shelf surface waters are on the order of 1.3-1.5 and 2 times PN and DON concentrations in the intruded SLW. Overall, net nitrogen inputs to the Cairns box from the intrusion of high nitrate SLW are on the order of 1.3 times the size of nitrogen stocks exported in displaced outer shelf waters. The calculation of net nitrogen fluxes associated with intrusion events is therefore highly sensitive to the estimate of the concentration of DON in outer shelf surface waters.

Table 26. Estimates of gross and net nitrogen and phosphorus inputs to outer-shelf waters of the Cairns and Tully boxes from intrusions during the summers of 1989-90, 1990-91 and 1991-92.

		Nitrogen		Phosphorus	
		Mmol	metric tonnes	Mmol	metric tonnes
Cairns box					
	1989-90	53.3	747	6.8	211
	1990-91	85.5	1198	12.9	400
	1991-92*	61.7	864	6.4	198
Tully box					
	1989-90	91.9	1287	9.6	297
	1990-91	197.9	2773	20.7	641
	1991-92*	81.3	1139	8.5	263
Cairns box					
	1989-90	25.1	352	3.6	112
	1990-91	40.3	565	6.4	198
	1991-92*	43.7	612	1.9	59
Tully box					
	1989-90	65.1	912	2.8	87
	1990-91	140.3	1966	6.0	186
	1991-92*	57.6	807	2.4	74
* - partial year					

Virtually all the phosphorus imported onto the shelf by intrusions (Table 26) is in the form of PO_4 (> 97 percent). DOP and PP concentrations in the SLW source water approach the operational detection limits. Exports by displacement during intrusion events are generally balanced between PO_4 , DOP and POP (37, 37 and 26 percent, respectively).

11. NITROGEN FIXATION BY *TRICHODESMIUM*

The nitrogen-fixing pelagic cyanobacterium, *Trichodesmium*, is a seasonally conspicuous element of phytoplankton populations within the GBR (Marshall, 1933; Revelante and Gilmartin, 1982; Furnas, 1992). It can be found at any time of the year throughout the GBR, but is most conspicuous during the summer months (October - April) when large surface slicks are frequently observed, particularly in inshore waters. Despite a large body of anecdotal information on sightings of *Trichodesmium* surface slicks throughout the GBR, there is little, if any, quantitative data on the spatial distribution (vertically, horizontally) of *Trichodesmium* populations or temporal variations in its abundance within regional areas. Two time series of quantitative data are currently available, the pioneering observations of Marshall (1933) near Low Isles (16°S) over an annual cycle and a two year time series published by Revelante and Gilmartin (1982) for inner shelf waters off Townsville (19°S). At present the only data set for which numerical values are available is that of Marshall. *Trichodesmium* population dynamics at both sites are characterized by a series of short-term fluctuations in colony numbers with only a moderate degree of seasonality. Table 27 summarizes seasonal differences in the abundance of *Trichodesmium* populations off Low Isles during 1928-29. All data are presented as depth weighted mean water column concentrations of *Trichodesmium* colonies. Most colonies observed tend to be of the fusiform or (tuft) type, with the remainder of the radial or puff morphology. No quantitative estimates are available for either the number of filaments (trichomes) per colony in GBR waters or number of cells per trichome. By visual inspection, most fusiform colonies consist of only a small number of trichomes, but puffs appear to have a much larger number of trichomes. Individual trichomes are also frequently observed on filters. Cook (quoted in Beaglehole, 1955) first described the presence of *Trichodesmium* in the GBR and noted that colonies consisted of 30-40 filaments, a number consistent with the generally slender morphology of most bundle colonies.

Very broad, first-order estimates of the contribution of atmospheric nitrogen fixed by *Trichodesmium* in the central GBR can be made from the available quantitative data (Table 27) and published measurements of *Trichodesmium* nitrogen fixation rates. Estimates of pelagic N₂ fixation by *Trichodesmium* are directly dependent upon both the nominal N₂ fixation rate per trichome and the number of trichomes per colony. Both estimates are variable over more than one order of magnitude. As N₂ fixation is an energy intensive process, fixation rates are known to be strongly dependent upon ambient light intensity (Gallon and Stal, 1992). Not surprisingly, most colonies of *Trichodesmium* occur in the upper 10 m of the water column (Furnas, unpubl. data), though they are found throughout the water column under normal conditions. Pronounced surface slicks of *Trichodesmium* readily form under calm conditions, visually exaggerating the apparent abundance of local populations.

Recently published measurements of N₂ fixation rates by *Trichodesmium* fall within a 30-fold range (0.53 to 18 pmol N trichome⁻¹ hr⁻¹; Carpenter et al., 1987; Carpenter and Capone, 1992). Based on the seasonal mean and median colony concentrations calculated from Marshall's data (Table 27), a 10-hour period of active fixation per day and a nominal estimate of 40 trichomes per colony (Cook's estimate), the above range of trichome specific N₂ fixation rates translate to annual fixation estimates of 191-6,493 x 10³ and 256-8,692 x 10³ kmol of nitrogen for the Cairns and Tully boxes, respectively, based on the seasonal mean colony concentrations and 140-4,764 x 10³ and 188-6,382 x 10³ kmol of nitrogen based on the seasonal median estimates. The calculation assumes significant N₂ fixation is largely restricted to the top 10 m of the water column and that cellular abundances and fixation rates are uniform over the entire area of each box, a highly doubtful assumption. Accordingly, the estimates given should be considered as covering the extreme maximal range. A sampling program was recently instituted by the Biological Oceanography group to quantify the spatial and temporal variability of *Trichodesmium* populations throughout the GBR; however, given the observed variability in

Trichodesmium abundance off Cairns and Townsville, it should be a number of years before sufficient data is available to derive population estimates with some statistical estimation of variability at the regional scale. Initial indications suggest that *Trichodesmium* concentrations in outer-shelf waters are considerably lower than inshore, which would affect areal weighting of the estimates calculated above.

Table 27. Preliminary estimates of nitrogen fixation by *Trichodesmium* in the Cairns and Tully boxes. Calculations are based on the seasonal depth-weighted mean and median abundances of colonies as counted by Marshall (1933) near Low Isles and the range of published fixation rates in the literature. Fixation is assumed to extend to the bottom or 10 m, whichever is shallower. Volumes are in litres.

Box	Season		colonies	trichomes	kmol	hours	days	Inshore	Offshore	kmol
			litre	colony	trichome-hr	day		volume	volume	
Cairns	Winter	Mean	22.7	40	5.30E-16	10	153	1.90E+12	5.56E+13	42337
		Median	5.1	40	5.30E-16	10	153	1.90E+12	5.56E+13	9512
	Summer	Mean	57.6	40	5.30E-16	10	212	1.90E+12	5.56E+13	148855
		Median	50.6	40	5.30E-16	10	212	1.90E+12	5.56E+13	130765
	Mean Total									191192
	Median Total									140276
Tully	Winter	Mean	22.7	40	5.30E-16	10	153	1.50E+12	7.52E+13	56445
		Median	5.1	40	5.30E-16	10	153	1.50E+12	7.52E+13	12681
	Summer	Mean	57.6	40	5.30E-16	10	212	1.90E+12	7.52E+13	199491
		Median	50.6	40	5.30E-16	10	212	1.90E+12	7.52E+13	175247
	Mean Total									255935
	Median Total									187929
Cairns	Winter	Mean	22.7	40	1.80E-14	10	153	1.90E+12	5.56E+13	1437863
		Median	5.1	40	1.80E-14	10	153	1.90E+12	5.56E+13	323044
	Summer	Mean	57.6	40	1.80E-14	10	212	1.90E+12	5.56E+13	5055437
		Median	50.6	40	1.80E-14	10	212	1.90E+12	5.56E+13	4441061
	Mean Total									6493300
	Median Total									4764105
Tully	Winter	Mean	22.7	40	1.80E-14	10	153	1.50E+12	7.52E+13	1916984
		Median	5.1	40	1.80E-14	10	153	1.50E+12	7.52E+13	430688
	Summer	Mean	57.6	40	1.80E-14	10	212	1.90E+12	7.52E+13	6775165
		Median	50.6	40	1.80E-14	10	212	1.90E+12	7.52E+13	5951794
	Mean Total									8692149
	Median Total									6382482

12. ATMOSPHERIC NITROGEN FIXATION BY REEF COMMUNITIES

Coral reefs within the Cairns and Tully boxes act as both sources and sinks of nitrogen and phosphorus. While a wide range of nutrient related processes occurring on coral reefs have been investigated over the years (summarized by D'Elia, 1988), few of these types of investigations have been carried out on reefs within the study area. The most comprehensive summary of nutrient fluxes onto or off a reef biologically comparable to those in the study area comes from the work of Crossland and Barnes (1983) at Lizard Island, with the proviso that the hydrodynamics of the Lizard Island reef may be significantly different from those on platform reefs in open shelf waters. In contrast to earlier studies (Wiebe et al., 1975), the work of Crossland and Barnes suggested that the reef flat and small lagoonal habitats of this system were not major sources of nitrogen and phosphorus to surrounding waters. More recently, Capone et al. (1992) have reported measurements of a variety of nitrogen transformations in unconsolidated coral reef sediments on central GBR (19°S) reefs. Estimates of potential fluxes associated with specific nutrient processes must therefore be extrapolated from a small number of experimental studies done elsewhere in the GBR.

The spatial extent and distribution of habitat (substratum) types on individual reefs is highly heterogeneous. The calculation of substrate-weighted nutrient processes for entire reefs is therefore dependent upon reliable estimates of area-averaged rate processes within different habitat types and the relative contributions of different substratum types to total reef area. A detailed census of substratum types for all reefs within the study area is beyond the scope of the present study. The analysis of spatial information in the satellite imagery of a large sample of reefs throughout the GBR (Figures 2 and 3) suggests that shallow (< 2 m) substrate, largely reef flat and reef flat sand patches, comprises approximately 18 percent of total reef area, with considerable variations between individual reefs. Sandy substrate similar to that found in reef lagoons at depths < 5 m comprised an additional 33 percent of area of the reefs classified.

Fixation of atmospheric nitrogen (Wiebe et al., 1975) has been identified as one of the major nutrient processes occurring on coral reefs. A variety of measurements of nitrogen fixation by reef communities have been carried out in the GBR (e.g. Burris, 1976; Wilkinson and Sammarco, 1983; Wilkinson et al., 1984; Larkum et al., 1988; Capone et al., 1992), but only the data of Wilkinson et al. (1984), Larkum et al. (1988) and Capone et al. (1992) can be extrapolated to larger scales. Wilkinson et al. (1984) demonstrated that community nitrogen fixation rates are highest on outer shelf reefs where the reef substratum is dominated by actively grazed turfs of cyanobacteria. Analytical considerations dictate that direct measurements of nitrogen fixation must be made with small pieces of reef substratum. The difficulty with using data derived from such experiments revolves around extrapolating measurements made at a very small scale to larger substratum-based habitat structural units. The most detailed study, incorporating estimation of nitrogen fixation rates for a variety of reef substratum types and seasonal fluctuations is that of Larkum et al. (1988). They derived roughness-corrected annual fixation rates of 366 and 9.6 kmol N km⁻² year⁻¹ for hard substrate reef flat and shallow lagoonal sand habitats, respectively. Fixation rates were derived for other structural/substratum types, but the classification of those habitat types in the satellite imagery is less well resolved and will not be included herein. More recently, Capone et al. (1992) estimated average annual nitrogen fixation rates on unconsolidated sediment to be 69.2 kmol N km⁻². On an areal and rate-specific basis, the shallow hard substrate rate measurements are the most important.

Using the imagery derived estimates of reef flat and shallow sand areas (Table 2), annual atmospheric nitrogen fixation by reef associated cyanobacteria in the Cairns and Tully boxes is estimated to be 89 x 10³ and 90 x 10³ kmol, respectively. Despite the lower area-specific rate of fixation in unconsolidated sand substrates, fixation in this habitat appears to account for half of the total fixation. The data available do not allow us to reliably estimate the proportion of this

newly fixed nitrogen which is either rapidly or ultimately exported from reefs to surrounding waters, nor the contribution of this newly fixed nitrogen to the net nitrogen balance of the reefs.

Coral reefs are active centers of nutrient transformation with dissolved nutrients being actively taken up and released by coral reef animals, plants and microbial communities associated with different substratum types. Apart from the results of Crossland and Barnes (1983), there is no information on reef-scale annual fluxes of nitrogen and phosphorus from reef flat systems in the central GBR from which regional scale estimates can be made. Results from measurements made at Lizard Island, which has a geometry considerably different from most shelf reefs, suggest that net exchanges with surrounding waters may be small at times. By area, lagoonal sands, both shallow and deeper, constitute the largest substratum type by area. Measurements by Hansen et al. (1987) indicated that dissolved nutrient fluxes into or out of reef lagoon sands of reefs were small and given the relatively small contribution of reefs to total shelf area (< 15 percent), was therefore unlikely to be significant on the shelf scale. More recent measurements by Capone et al. (1992) indicate that a range of active microbially mediated nitrogen transformations occur in reef sediments. Measurements made on mid- and outer-shelf reefs in the central GBR indicated relatively high rates of NO_3^- reduction ($34 \pm 23 \mu\text{mol N m}^{-2} \text{hr}^{-1}$) and NH_4^+ utilization ($38 \pm 18 \mu\text{mol N m}^{-2} \text{hr}^{-1}$). Nitrogen fixation rates in outer-shelf reef sediments averaged $7.9 \pm 3.7 \mu\text{mol N m}^{-2} \text{hr}^{-1}$. Rates of NH_4^+ efflux from reef sediments ($0.51 \pm 0.64 \mu\text{mol N m}^{-2} \text{hr}^{-1}$) and denitrification ($1.56 \pm 1.28 \mu\text{mol N m}^{-2} \text{hr}^{-1}$) were considerably slower. Overall, a considerable proportion of the nitrogen fixed in reefal sand substrates is taken up by microbial populations in the sand and transformed further.

The major unknown benthic flux associated with coral reefs is the extent of denitrification occurring within reef sediments and the reef matrix following the deposition of particulate organic matter. While mineralization, nitrification and denitrification are known to occur in reef sediments, the magnitude of these processes at the shelfscale in the Great Barrier Reef is unknown.

13. SEDIMENTATION OF PARTICULATE MATERIALS AND NUTRIENTS

Some proportion of the stock of water column particulate nutrients (e.g. PC, PN, PP) are continuously lost from the water column, at least temporarily, through sedimentation to the benthos. On a shelf scale, this sedimentation flux of organic matter provides most of the energy supporting benthic food chains. Particulate matter in the water column is comprised of a number of types of particles with a range of different chemical compositions, sources and sinking characteristics. These particles include phytoplankton and bacteria growing *in situ*, detritus formed from dead plankton, fecal pellets and other organic matter produced by zooplankton feeding on phytoplankton (e.g. Small et al., 1983), organic and inorganic particles washed off coral reefs (Johannes, 1967; Gerber and Marshall, 1974; Barnes, 1989), terrigenous materials washed down rivers (Ittekkot et al., 1983; Ittekkot, 1988) and particulate material resuspended from the benthos (e.g. Oviatt and Nixon, 1975; Roman and Tenore, 1978). The magnitude of the net sedimentation flux varies in response to a number of factors, including: the standing stock of particulate matter; its depth distribution, size structure, density and chemical makeup; rates of particle formation through phytoplankton growth and particle aggregation; rates of zooplankton feeding and fecal pellet formation (Small et al., 1983); local benthic resuspension processes (Roman and Tenore, 1978); and water column mixing rates. All of these processes are variable in time and space.

13.1 Moored Traps

Seasonal, day-to-day and cross-shelf variations in nutrient sedimentation rates at the southern boundary of the Tully box were first measured along a cross-shelf transect extending seaward from the Family Islands (Figure 7). The elemental fluxes presented have been corrected relative to the Lagrangian drifting traps (Figure 19), assuming that the elemental fluxes per unit area derived using Lagrangian drifter traps are twice those concurrently collected by the moored trap arrays. The most inshore trap array was lost on first deployment of the final (August) cruise.

Measured fluxes of sediment mass (Figure 63), organic carbon (Figure 64), particulate nitrogen (Figure 65) and particulate phosphorus (Figure 66) varied significantly between seasonal cruises ($p < 0.005$). Significant cross-shelf differences in deposition fluxes were also observed for sediment mass, carbon and nitrogen, but not phosphorus. Day-to-day differences were not statistically significant. Statistical comparisons were made using a nested ANOVA design (Super ANOVA, Abacus Software). The highest sedimentation fluxes were measured during the February 1989 and May 1989 cruises. Particularly high deposition rates were measured at the inshore site on the May cruise. Sediment collected at the inshore station on all deployments was characterized by fine brownish muds and clays of terrigenous origin, while material collected at the three sites further offshore contained a grayish mixture of amorphous organic matter and fine carbonate mud.

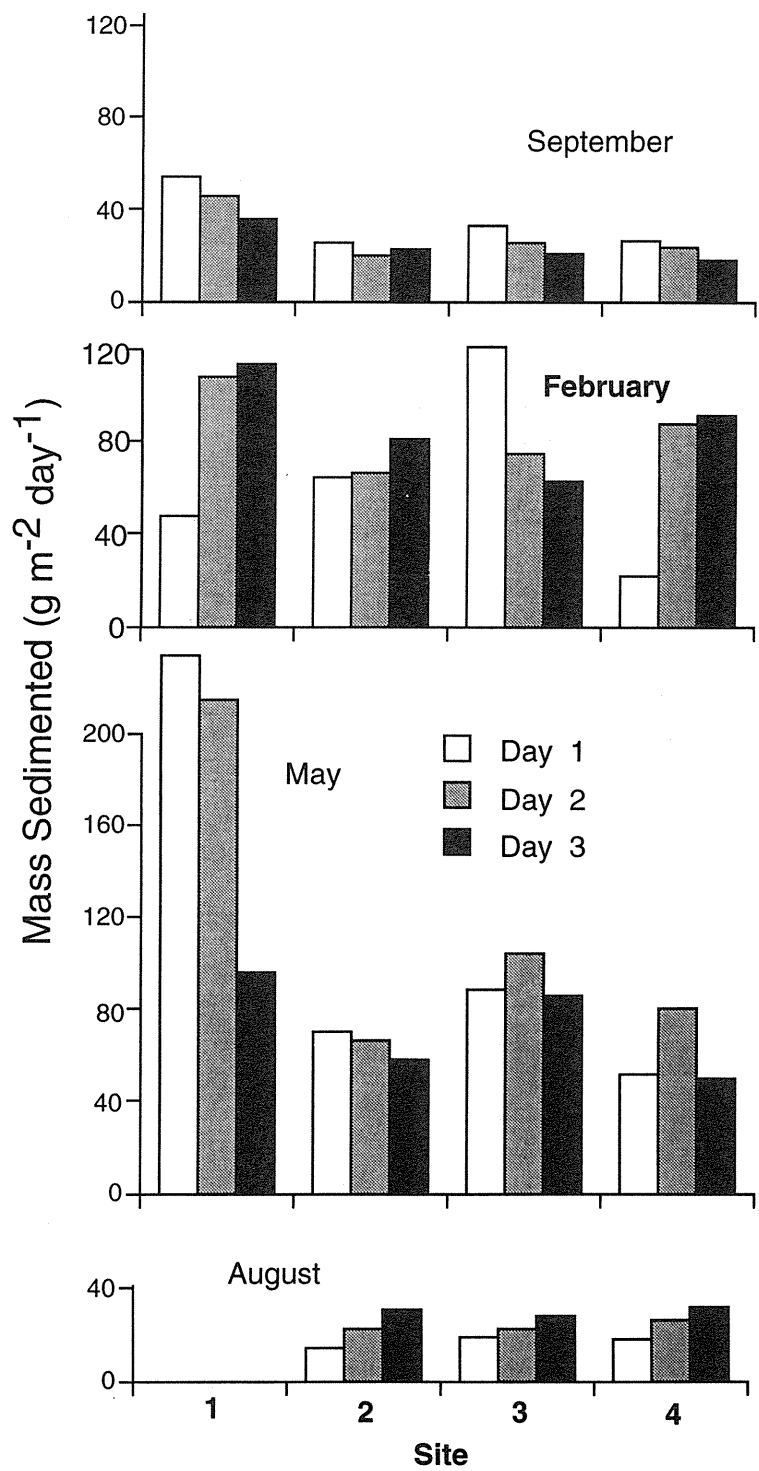


Figure 63. Seasonal and day-to-day variability in gross sedimentation measured with moored sediment traps on a cross-shelf transect seaward of the Family Islands (18°S). Values shown are the means of rates from paired traps installed on individual moorings.

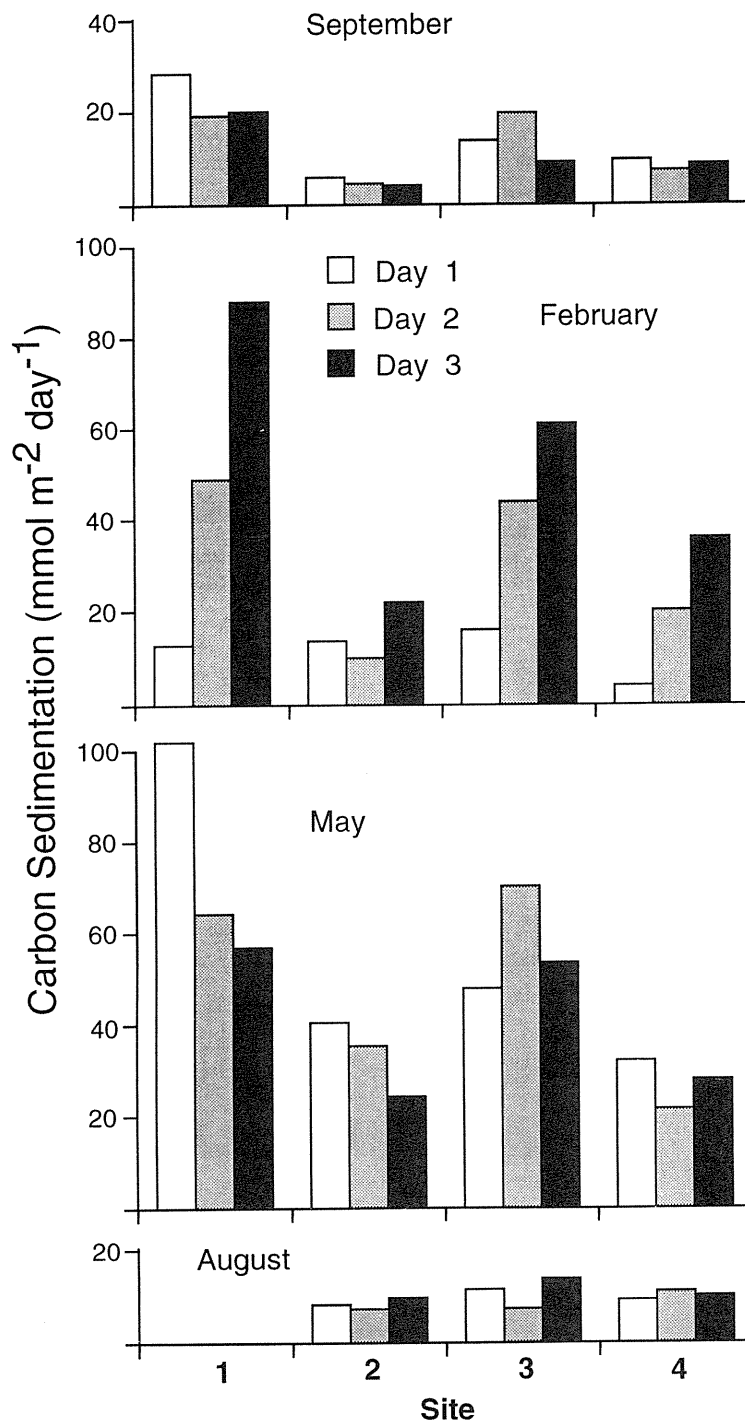


Figure 64. Seasonal and day-to-day variability in gross organic carbon sedimentation measured with moored sediment traps on a cross-shelf transect seaward of the Family Islands (18°S). Values shown are the means of rates from paired traps installed on individual moorings.

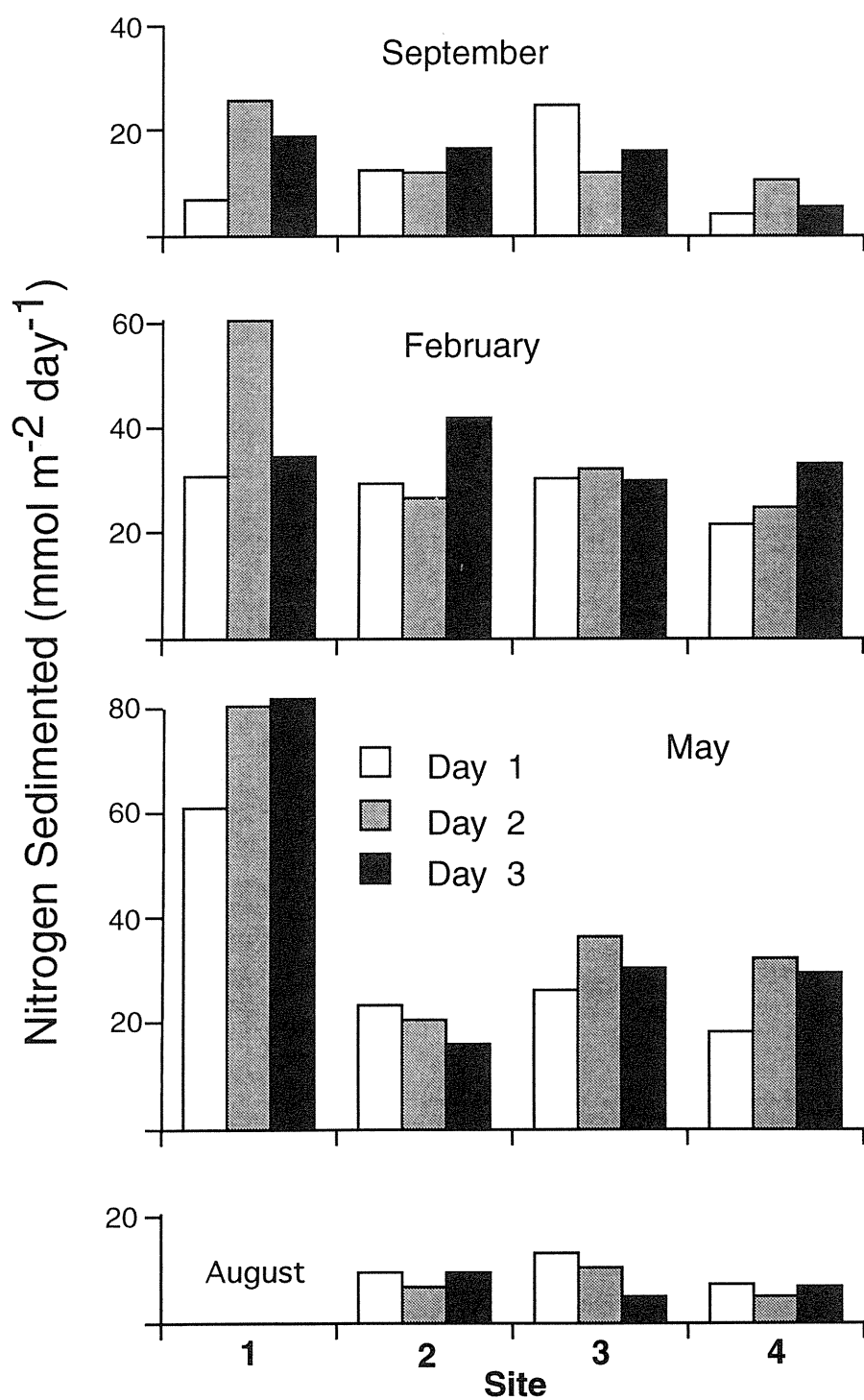


Figure 65. Seasonal and day-to-day variability in gross organic nitrogen sedimentation measured with moored sediment traps on a cross-shelf transect seaward of the Family Islands (18°S). Values shown are the means of rates from paired traps installed on individual moorings.

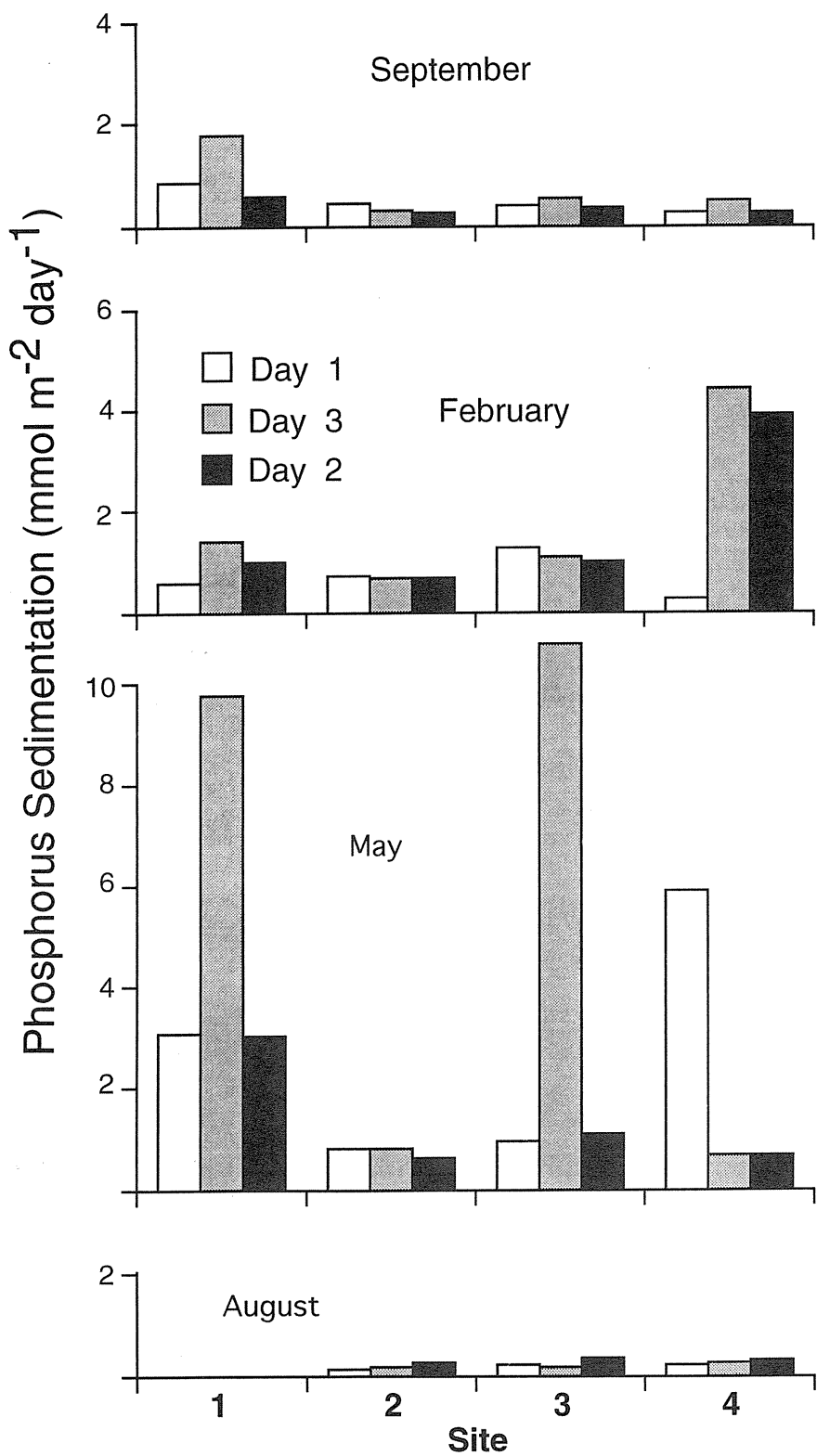


Figure 66. Seasonal and day-to-day variability in gross particulate phosphorus sedimentation measured with moored sediment traps on a cross-shelf transect seaward of the Family Islands (18°S). Values shown are the means of rates from paired traps installed on individual moorings.

Organic carbon deposition rates ranged between 83 and 1785 mg C m⁻² day⁻¹ (6.9-148.8 mmol C m⁻² day⁻¹). Extreme values aside, deposition rates during the three cruises averaged (\pm 1 S.D.): September 1988 14.6 \pm 8.7 mmol C m⁻² day⁻¹; February 1989 - 45.1 \pm 25.5 mmol C m⁻² day⁻¹; May 1989 - 43.8 \pm 26.9 mmol C m⁻² day⁻¹ and August 1989 - 11.9 \pm 3.7 mmol C m⁻² day⁻¹. No measurements were made of the standing stock of water column particulate carbon, precluding an estimation of water column PC turnover times. Mean daily water column primary production on the outer shelf in the central GBR is approximately 400 mg C m⁻² day⁻¹ (32.8 mmol C m⁻² day⁻¹), ranging between 130 and 675 mg C m⁻² day⁻¹ (10.8-56.3 mmol C m⁻² day⁻¹)(Furnas and Mitchell, 1987). The mean sedimentation rates measured, therefore, range between 36 and 133 percent of the mean daily production value, with individual daily sedimentation rates potentially being as much as 50 times the mean production rate. A functional regression (Ricker, 1973) of the relationship between the organic carbon content of the trapped material and sediment mass in the traps yielded a slope of 1.53 mmol carbon per gram dry weight ($r^2 = 0.67$), or 1.8 percent, by weight.

Based on visual inspection of the sedimented material, living or newly dead phytoplankton did not comprise a significant fraction of the sedimented material. Therefore, it is unlikely that there is a close (day-to-day) coupling between water column primary production and organic carbon sedimentation. The observed temporal variations in carbon sedimentation (seasonal and daily) more likely reflect medium term (weekly or longer) changes in water column phytoplankton biomass and event-scale (daily) changes stocks of resuspended benthic material. The extent to which daily resuspension is coupled to variations in wind strength remains to be examined in detail.

Table 28. Mean daily deposition rates of carbon, nitrogen and phosphorus (mmol m⁻²) on a cross-shelf transect seaward of the Family Islands. Values in brackets are 1 standard deviation.

Station	1	2	3	4
Depth	22	31	35	56
Deployments	9	12	12	12
C	105.4 [73.3]	45.2 [24.3]	57.0 [36.7]	44.0 [27.9]
N	44.5 [27.2]	18.7 [10.3]	22.2 [10.4]	16.5 [11.3]
P	2.5 [2.9]	0.5 [0.3]	1.5 [2.9]	1.5 [2.0]

Temporal patterns of nitrogen fluxes (Figure 65) measured with the moored traps were similar to those observed for carbon. Daily deposition rates ranged between 20 and 80 mmol N m⁻² day⁻¹. Mean (\pm 1 S.D.) nitrogen sedimentation (collection) rates for individual cruises were 6.9 \pm 3.8, 17.6 \pm 7.0, 17.9 \pm 15.9 and 4.1 \pm 2.0 mmol N m⁻² day⁻¹. With only one exception, cross-shelf and day-to-day fluctuations in nitrogen sedimentation rates varied less than 2-fold. Based on functional (GM) regression analysis, the sedimented material had a composition of 0.55 mmol N per gram dry weight ($r^2 = 0.373$), or 0.8 percent by weight.

The proportion of the water column stock of particulate nitrogen (PN) collected daily by the sediment traps varied across shelf and between cruises (Figure 67). On three of the four seasonal cruises, the percentage of the water column stock collected decreased progressively

with distance offshore. The higher relative collection rates inshore reflect the more active dynamics of sediment deposition and resuspension in shallow waters. Daily PN sedimentation fluxes at the inshore station (22 m) frequently approached or exceeded 100 percent of the water column stock of PN. At the offshore stations, daily deposition fluxes were on the order of 25 to 50 percent of the water column PN stock. The lowest apparent deposition rates were observed during the August 1989 cruise.

Cross-shelf patterns of phosphorus sedimentation (Figure 66) did not show a consistent pattern between cruises. Mean daily deposition fluxes for the four cruises were 0.28 ± 0.23 , 0.78 ± 0.69 , 1.59 ± 2.89 and 0.11 ± 0.04 mmol P m⁻² day⁻¹. In most cases, PP sedimentation fluxes were similar at mid-shelf and offshore stations. The proportion of water column PP deposited each day on the first three cruises were generally between 25 and 50 percent of the measured water column stock of PP (Figure 68). A functional (GM) regression of phosphorus in sedimented material on mass sedimented yielded a slope of 0.021 mmol P per gram dry weight ($r^2 = 0.42$), or 0.07 percent of dry weight.

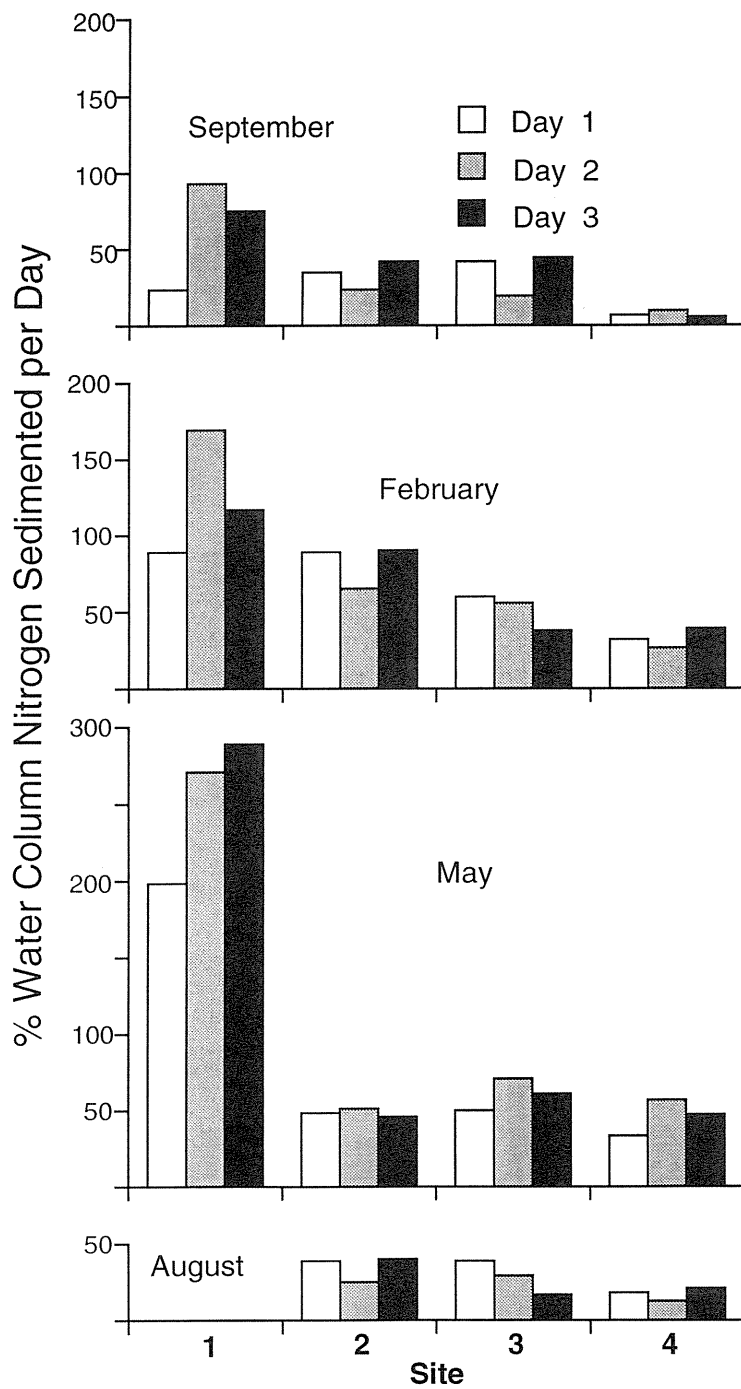


Figure 67. Seasonal and day-to-day variability in the percentage of the integrated water column stock of particulate nitrogen collected by moored sediment traps deployed on a cross-shelf transect seaward of the Family Islands (18°S).

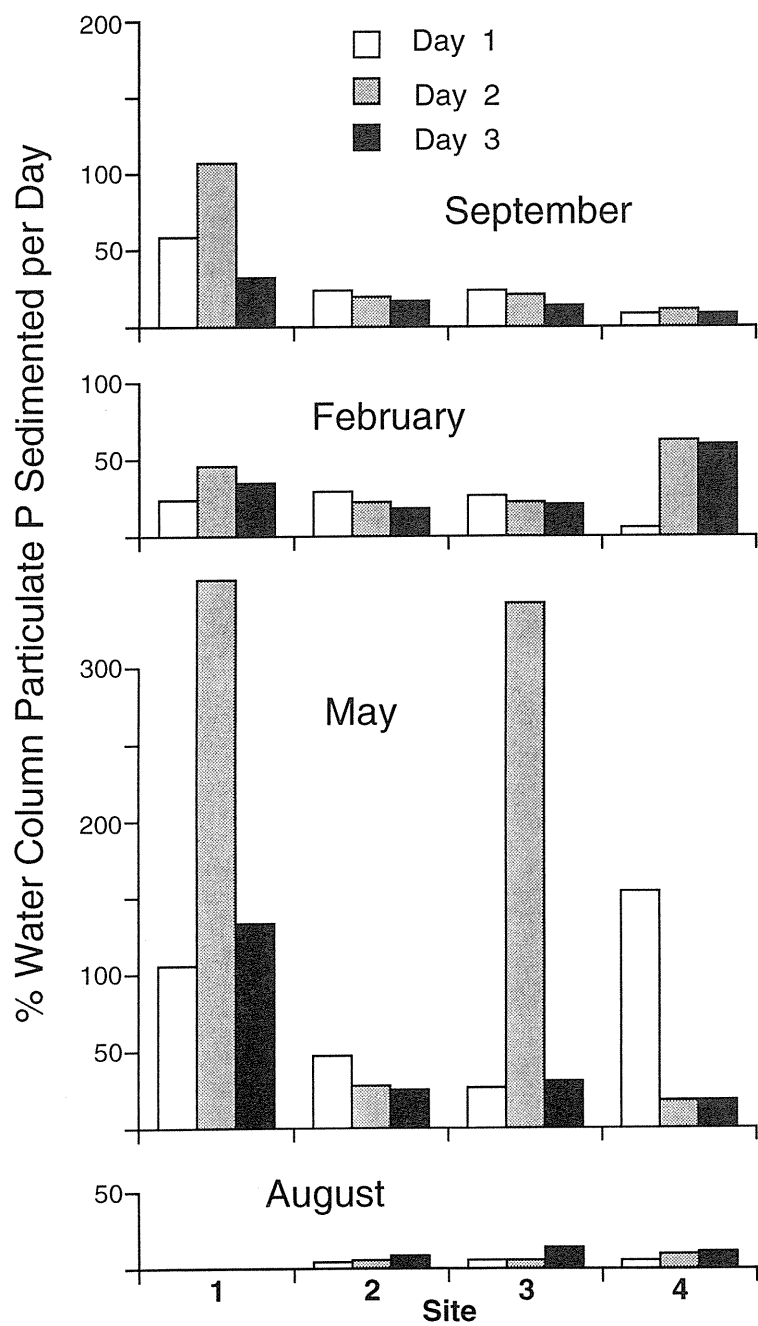


Figure 68. Seasonal and day-to-day variability in the percentage of the integrated water column stock of particulate phosphorus collected by moored sediment traps deployed on a cross-shelf transect seaward of the Family Islands (18°S).

Stoichiometric ratios between carbon, nitrogen and phosphorus in sedimented material were highly variable on a seasonal, cross-shelf and day-to-day basis (Figures 69 and 70). Statistical relationships between elements were distorted by high concentrations of particular elements, usually phosphorus, in a small number of samples. The source of the material contributing to the aberrant ratios was not resolved. If these small numbers of samples are excluded, stoichiometric ratios between carbon, nitrogen and phosphorus were reasonably consistent (Figure 71). Functional regressions between carbon, nitrogen and phosphorus yielded slope values of 88.0 ($r^2 = 0.84$), 3.9 ($r^2 = 0.67$) and 36.6 ($r^2 = 0.61$) for C/P, C/N and N/P ratios in the sedimented material. The carbon-based ratios are low relative to the Redfield ratios for phytoplankton (C/P = 106; C/N = 6.6), while the N/P ratio is high relative to phytoplankton (Redfield N/P = 16) and riverine particulate matter (7.5). The nitrogen content of the trapped material appears to be elevated. It is unclear to what extent the acid decarbonation stage in the processing might have lead to carbon loss from samples, or some degree of nitrogen contamination. The C/N ratio, in particular, is at the lower end expected from proteinaceous materials. The measured C/N ratio in trapped material falls within the range measured in surficial sediments across the GBR shelf (range 1.9-15; Alongi, 1989), but is considerably lower than found in temperate estuaries (7-10; Oviatt and Nixon, 1975). Given the capacity of carbonate sediments to bind phosphorus, the low C/P ratio is not surprising, though the high N/P was unexpected.

13.2 Lagrangian Drifting Traps

Six deployments of the free-drifting sediment trap array were carried out in nearshore waters (depths 20-24 m) of the Cairns box. Sediment collection (particle interception) rates (Figure 72) ranged between 19 and 71 g m⁻² day⁻¹, with distinct daily variations and a mean value of 42 ± 18 g m⁻² day⁻¹ (1 s.d.: median = 43 g m⁻² day⁻¹). As with the nearshore moored traps in the Tully box, the gross inshore sedimentation fluxes in all cases exceeded 100 percent of the measured water column standing stock of suspended solids (median = 161 percent).

Particulate organic carbon deposition fluxes in nearshore trap deployments (Figure 73) averaged 76 ± 19 mmol m⁻² day⁻¹ (median = 70). Again, water column PC was not measured, precluding an estimation of water column particulate carbon turnover rates. The slope of the GM functional regression (Ricker, 1973) yielded a PC/sediment mass ratio of 1.04 mmol organic C/g sediment (1.25 percent organic carbon by weight).

Particulate nitrogen deposition fluxes (Figure 74 Top) in nearshore deployments averaged 8.4 ± 7.2 mmol m⁻² day⁻¹ (median = 4.5). Relative to the standing stock of PN in the water column, the mean (median N) sedimentation flux averaged 34 (25) percent of the water column stock per day (Figure 74 Bottom). No clear relationship was observed between PN deposition and the mass of sediment collected, suggesting substantial changes in the composition of sedimenting material may occur.

Particulate phosphorus deposition rates (Figure 75 Top) at the nearshore sites averaged 1.2 ± 0.8 mmol m⁻² day⁻¹ (median = 1.1). The observed fluxes averaged 76 percent of the measured water column particulate phosphorus stock (median = 49 percent: Figure 75 Bottom). The slope of the GM functional PP/sedimentation ratio was 0.019 mmol/g, comparable to the value measured in moored trap samples (0.021 mmol/g).

Stoichiometric ratios (C/P, N/P, C/N) in sedimented materials varied considerably between cruises (Figure 76). The number of inshore trap deployments, however, is too small to draw definitive conclusions as to mean ratios or seasonal fluctuations.

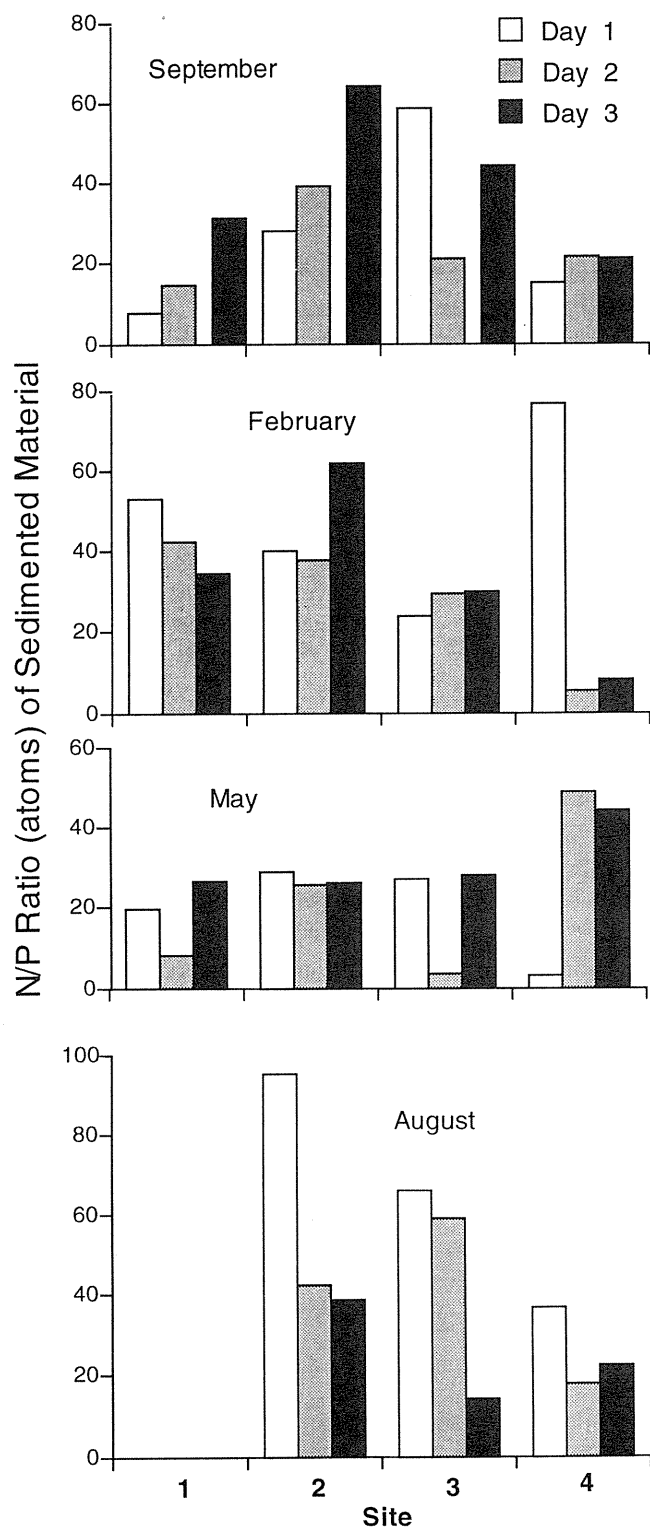


Figure 69. N/P ratios (atoms) of particulate material collected by moored sediment traps on a cross-shelf transect seaward of the Family Islands (18°S).

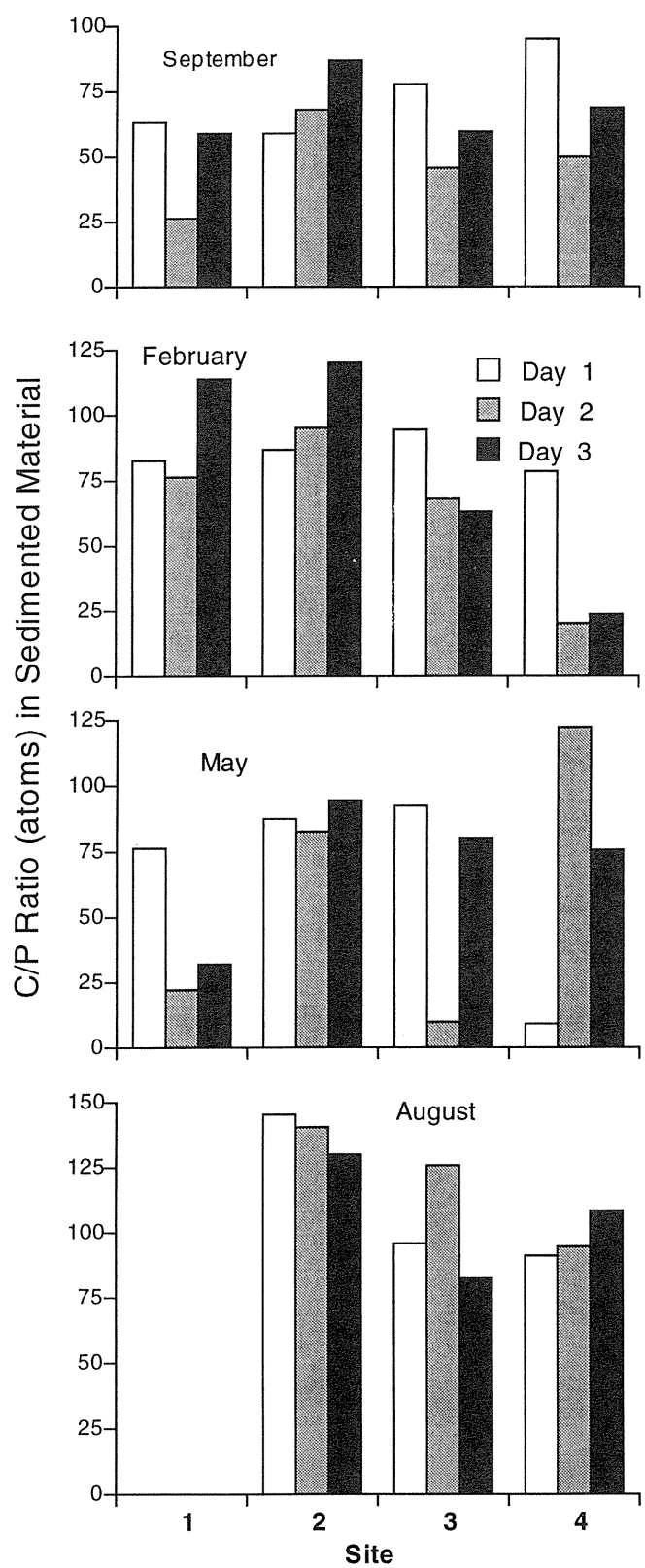


Figure 70. C/P ratios (atoms) of particulate material collected by moored sediment traps on a cross-shelf transect seaward of the Family Islands (18°S).

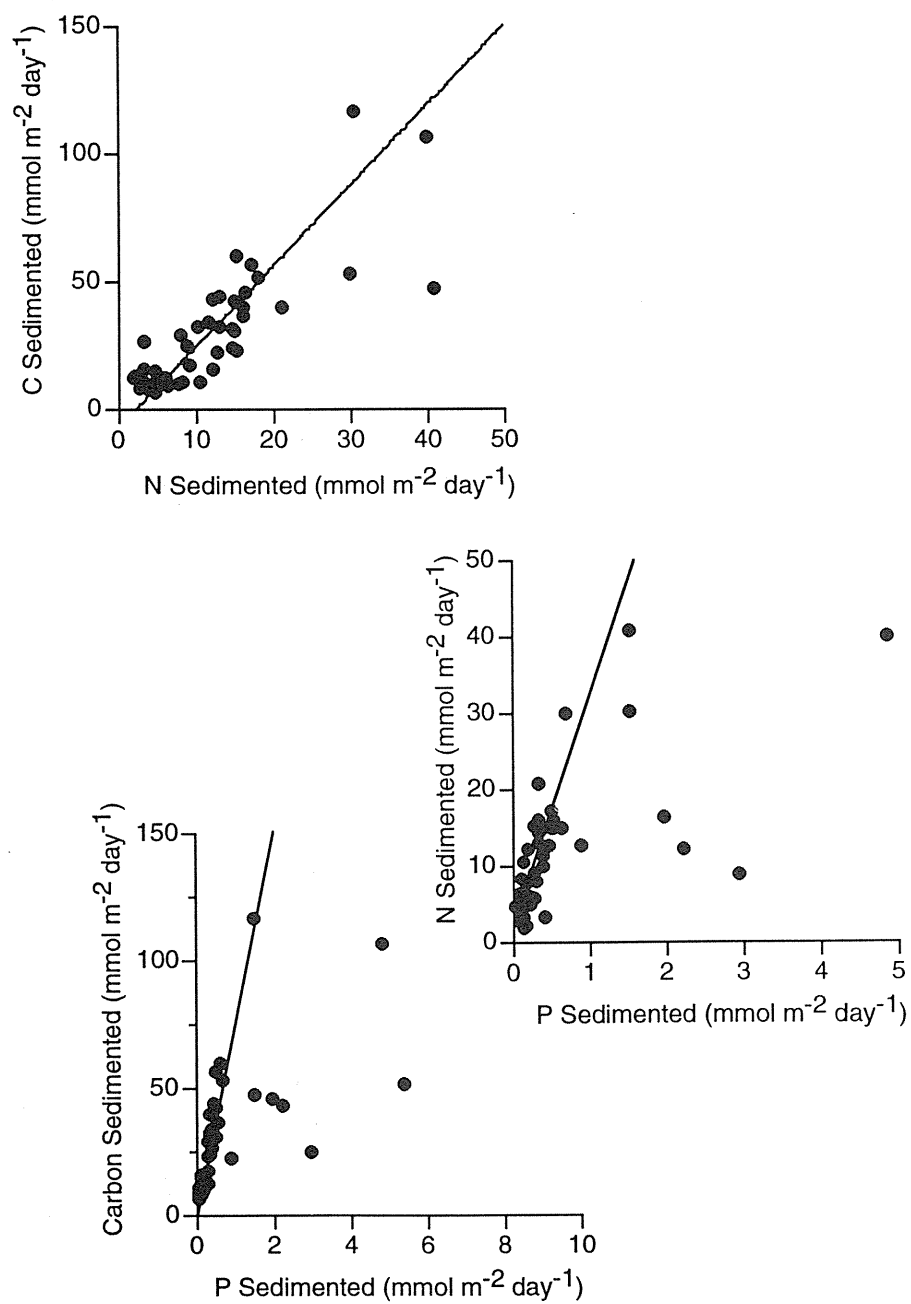


Figure 71. Scatter plots showing relationships between carbon, nitrogen and phosphorus in material collected by moored sediment traps off the Family Islands (18°S). The lines fitted to the data are GM functional regressions with outliers disregarded.

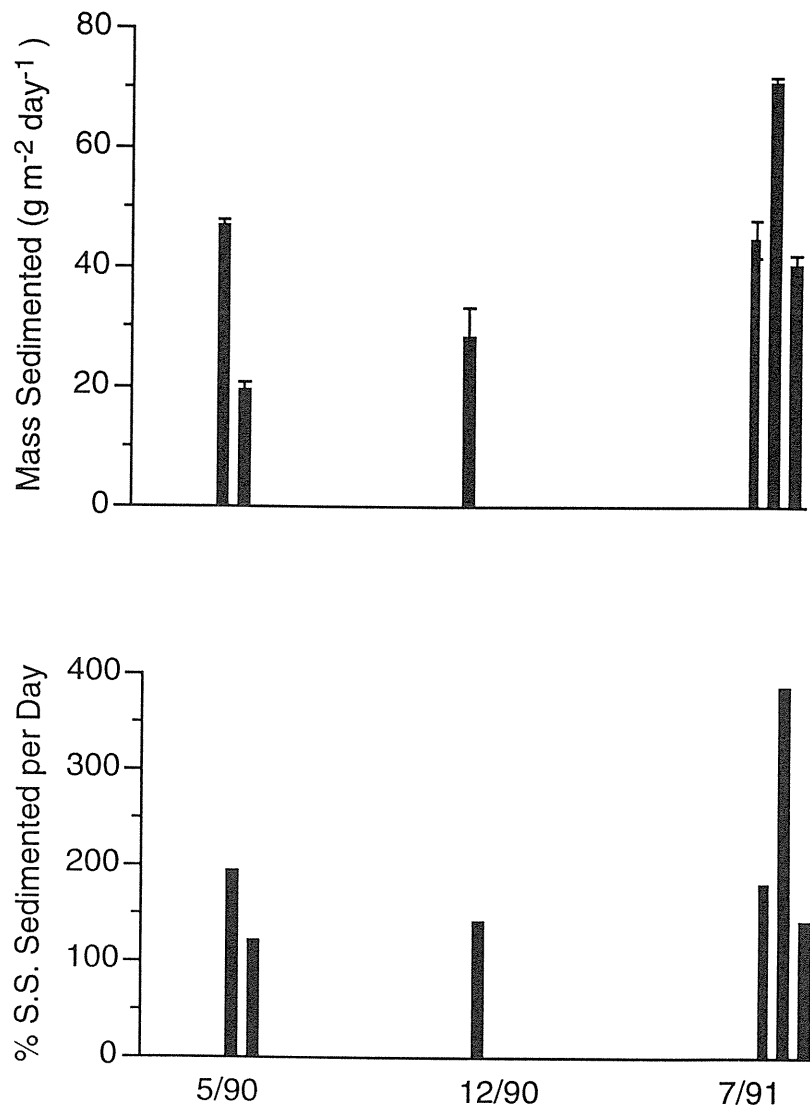


Figure 72. Top: Gross sedimentation fluxes (g m^{-2}) measured in nearshore waters (depth < 22 m) of the Cairns box with free drifting sediment traps. Error bars = 1 standard deviation about the mean for 6-12 sub-traps sampled from the trap array. Adjacent bars in groups show measured fluxes on successive days. Bottom: Calculated percentages of the water column stock of suspended particulates sedimenting daily.

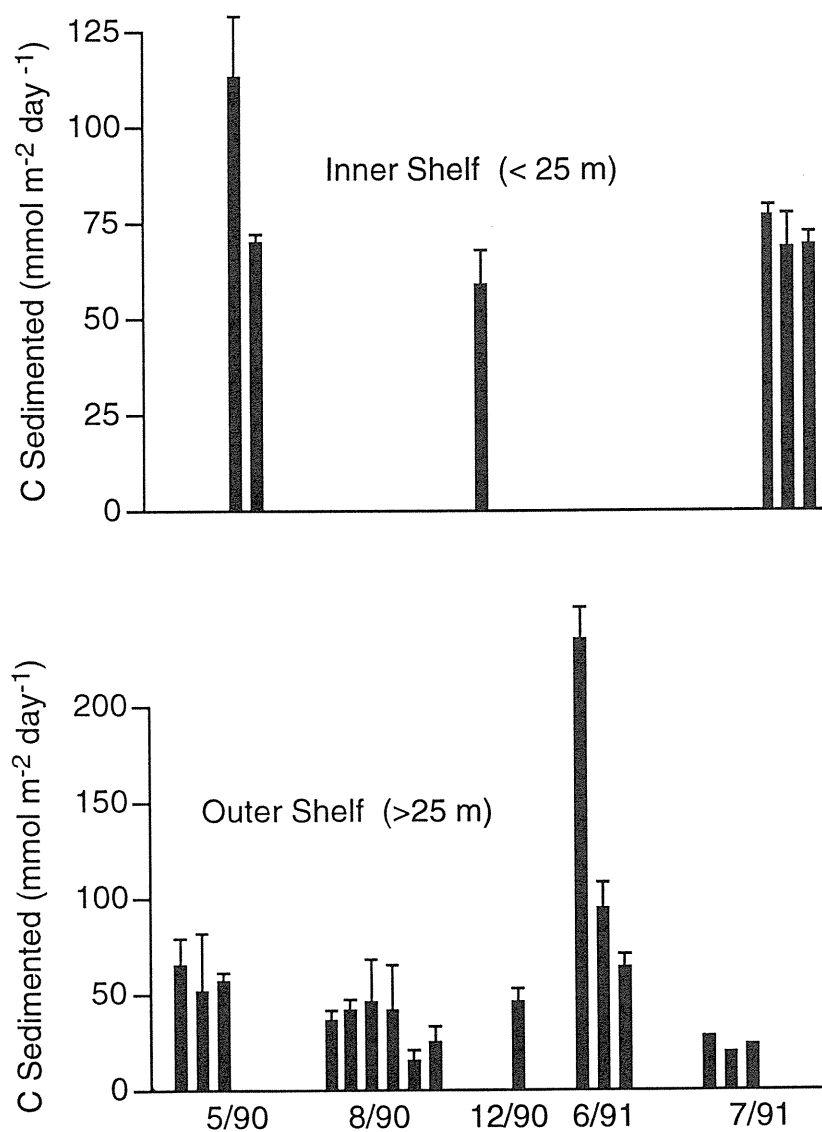


Figure 73. Top: Gross sedimentation fluxes of particulate organic carbon in nearshore waters of the Cairns box with free drifting sediment traps. Bottom: Gross sedimentation fluxes of particulate organic carbon in mid- and outer-shelf waters of the Cairns box. Error bars = 1 standard deviation about the mean for 6-12 sub-traps sampled from the trap array. Adjacent bars in groups show measured fluxes on successive days.

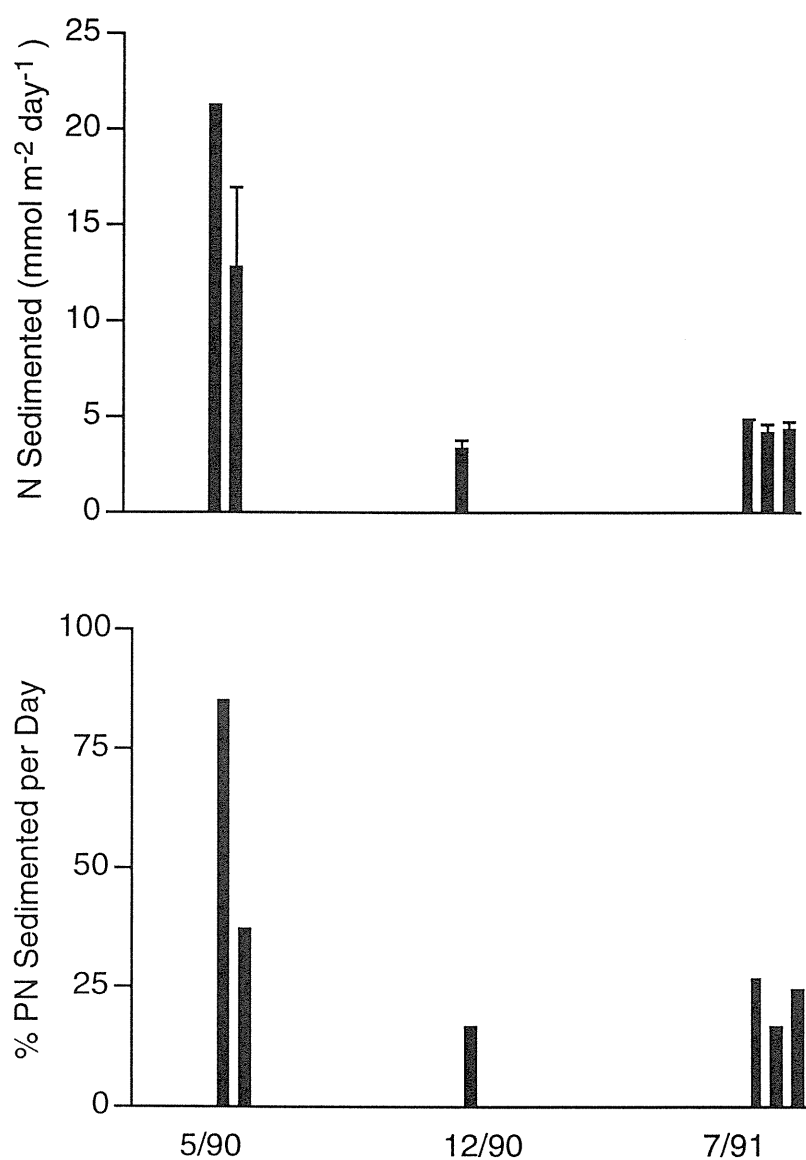


Figure 74. Top: Particulate nitrogen sedimentation fluxes (mmol m⁻²) measured in nearshore waters (depth < 22 m) of the Cairns box with free drifting sediment traps. Error bars = 1 standard deviation about the mean for 6-12 sub-traps sampled from the trap array. Adjacent bars in groups show measured fluxes on successive days. Bottom: Calculated percentages of the water column stock of particulate nitrogen sedimenting daily.

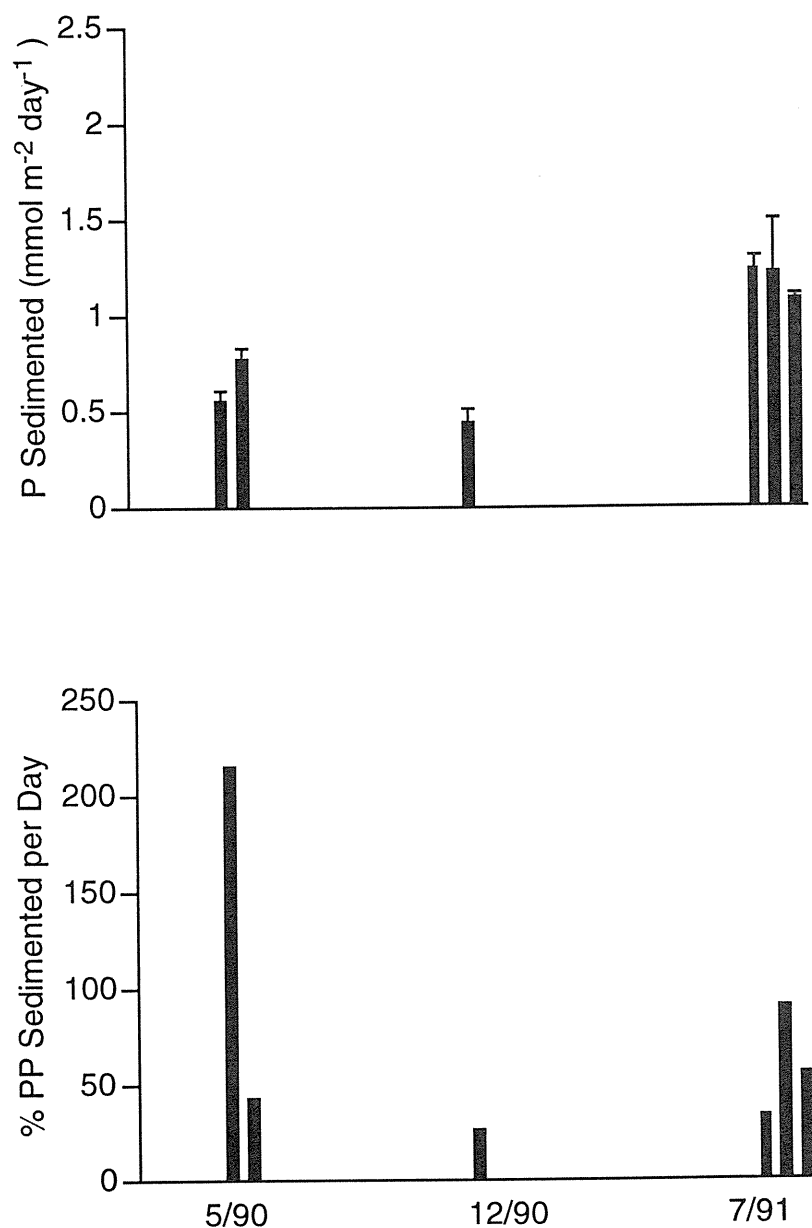


Figure 75. Top: Particulate phosphorus sedimentation fluxes (mmol m⁻²) measured in nearshore waters (depth < 22 m) of the Cairns box with free drifting sediment traps. Error bars = 1 standard deviation about the mean for 6-12 sub-traps sampled from the trap array. Adjacent bars in groups show measured fluxes on successive days. Bottom: Calculated percentages of the water column stock of particulate phosphorus sedimenting daily.

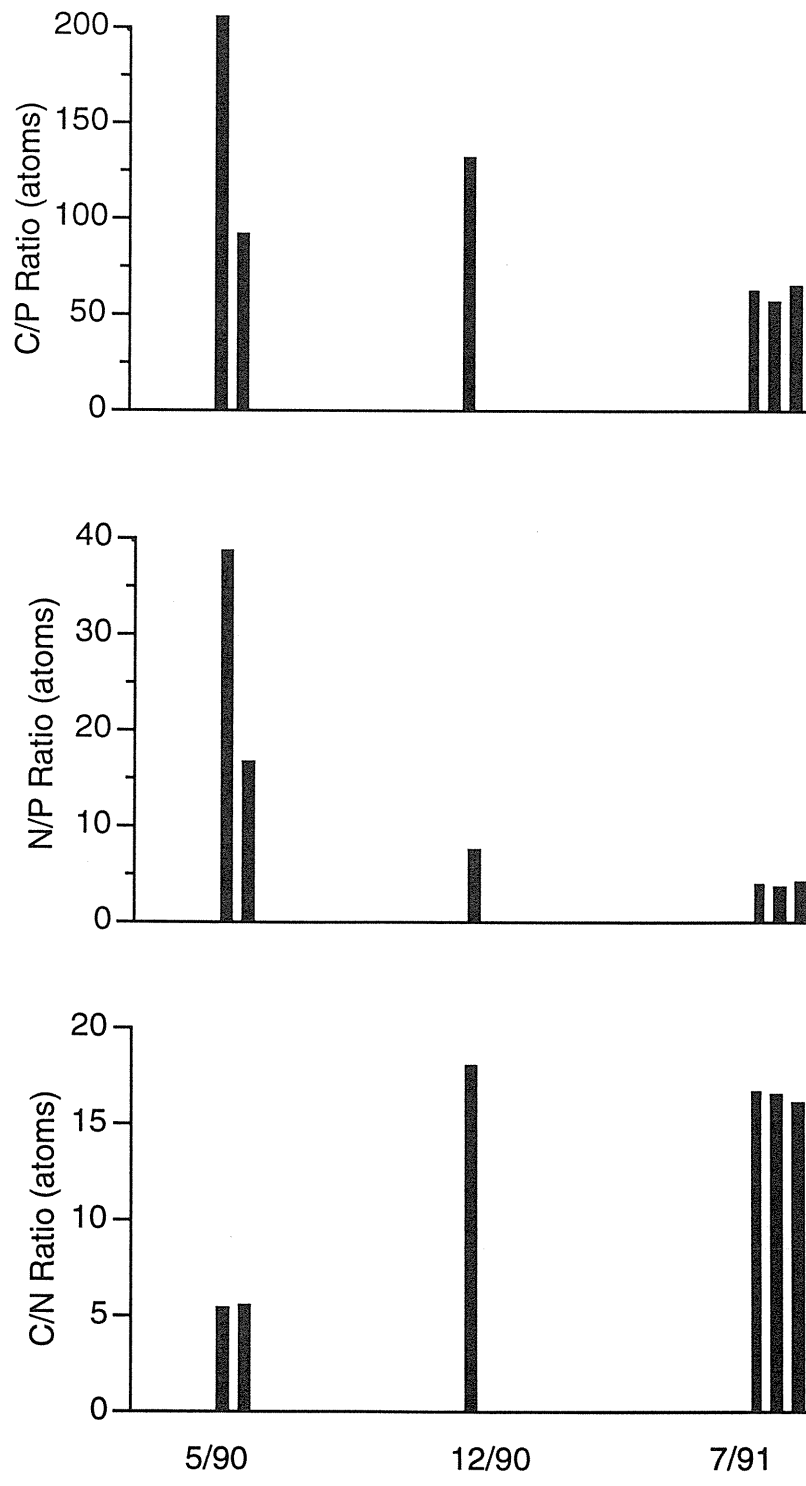


Figure 76. Day-to-day and between-cruise variability in atomic ratios between carbon, nitrogen and phosphorus in material collected by free-drifting sediment traps in nearshore waters (depth < 22 m) of the Cairns box.

With two clear exceptions (Figure 77 Top), gross sedimentation fluxes on the outer half of the shelf in the Cairns box (depth > 25 m, n=16 deployments) were considerably lower than measured inshore. Taking the two extreme fluxes measured in July 1991 aside, gross sedimentation averaged $9.4 \pm 9.0 \text{ g m}^{-2} \text{ day}^{-1}$ (median = 9.7). The relative proportion of the water column suspended solids load sedimenting was highly variable, with a median estimate of 59 percent daily (range 6.4 - 595 percent). Despite the difference in gross particle sedimentation, organic carbon fluxes (Figure 73 Bottom) on the outer half of the shelf (mean $54 \pm 52 \text{ mmol m}^{-2} \text{ day}^{-1}$, median = 45) were only on the order of 30-35 percent lower than flux rates on the inner shelf.

Particulate nitrogen sedimentation fluxes (Figure 78 Top) on the outer half of the shelf (mean $6.9 \pm 4.3 \text{ mmol m}^{-2} \text{ day}^{-1}$, median = 6.5) were very similar to those measured inshore (mean $8.4 \pm 7.2 \text{ mmol m}^{-2} \text{ day}^{-1}$, median = 4.5). The median percentage of the water column stock sedimented daily (Figure 78 Bottom) on the outer half of the shelf (21.5) was very similar to that measured in inshore deployments (25.4) despite the difference in depths.

Outer shelf phosphorus deposition fluxes (Figure 79 Top: mean $0.37 \pm 0.33 \text{ mmol P m}^{-2} \text{ day}^{-1}$, median = $0.23 \text{ mmol P m}^{-2} \text{ day}^{-1}$) were approximately one-third of the mean (and median) deposition fluxes measured during the inshore deployments. The measured deposition rates accounted for less than 15 percent of the measured water column phosphorus stocks (Figure 79 Bottom).

With a few exceptions, atomic ratios between carbon, nitrogen and phosphorus in sedimented material from outer shelf deployments (Figure 80) tended to be consistent between consecutive deployments on a given cruise, but varied considerably between cruises on a pairwise basis. When all drifter trap deployments are considered, GM functional regressions of organic C on phosphorus and nitrogen yielded C/P and C/N ratios (slopes) of 68.9 and 8.9 (by atoms), respectively. These slope values are 22 percent lower and 2.3 times greater, respectively, than determined for the Tully box moored trap samples. Reasons for the differences are unresolved at this time.

Table 29 summarizes estimates of gross (uncorrected for resuspension) nutrient (C, N, P) sedimentation fluxes to the benthos in the Cairns and Tully boxes. The rates are stratified by depth bands but not by season, as there are too few measurements to make such a distinction at this time. The mean daily deposition fluxes estimated from trap catches were extrapolated to annual box-scale fluxes. These sedimentation flux estimates, on the order of 10^5 Mmoles per year, are very, very large in comparison to the other annual box-scale input fluxes of nitrogen and phosphorus estimated to date.

On an area-specific basis, outer-shelf carbon, nitrogen and phosphorus sedimentation fluxes in the Cairns and Tully boxes were of similar order (ca. within 50 percent). Apparent outer-shelf carbon and nitrogen sedimentation fluxes on the Tully box transect tended higher than measured in the Cairns box, while the Cairns box, outer shelf phosphorus fluxes were higher. Within the shallower depth bands, estimated sedimentation fluxes of carbon and phosphorus in the Cairns and Tully boxes were also within 2-fold of each other. For unknown reasons, measured nitrogen deposition fluxes in the Tully box were nearly 3 times greater than measured in the Cairns box. Given the observed variability in fluxes at both inshore and offshore sites on short time scales and the small number of measurements, both sets of estimates can be considered to be of similar order.

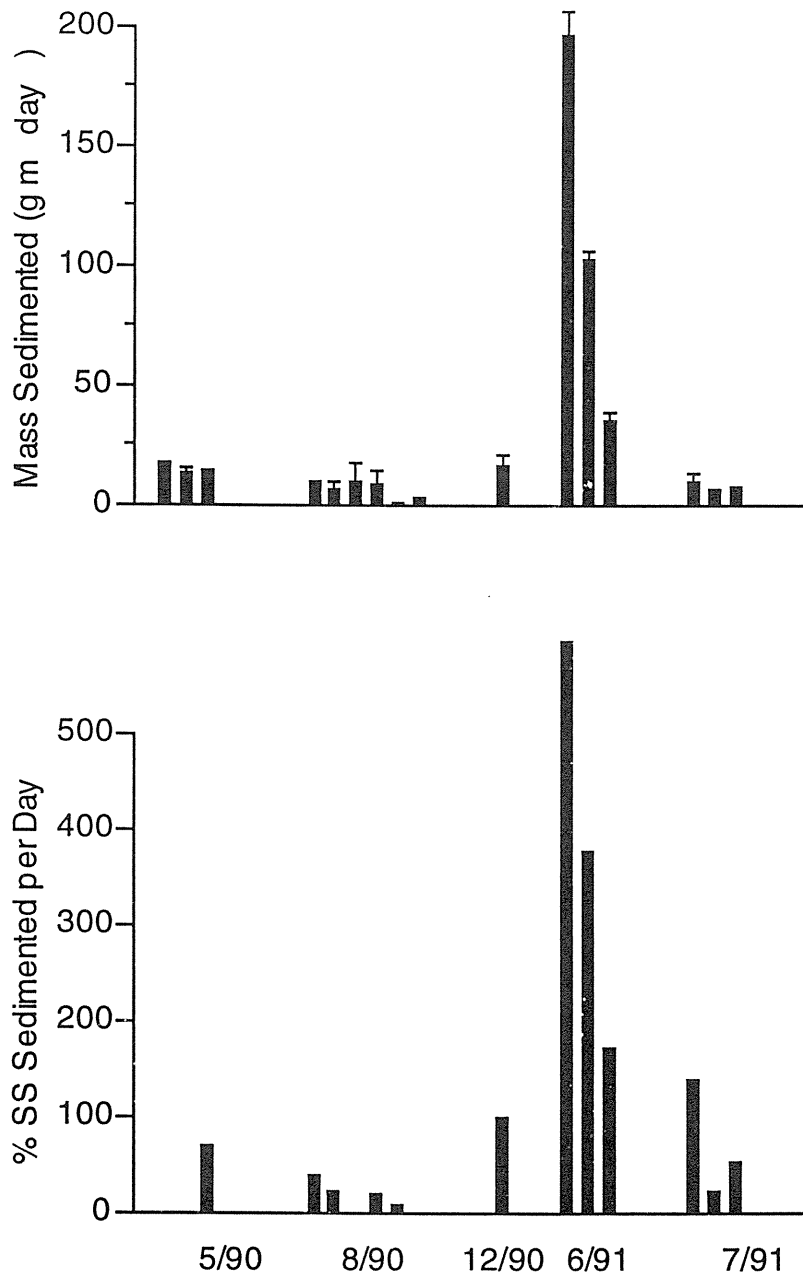


Figure 77. Top: Gross sedimentation fluxes (g m^{-2}) measured in mid- and outer-shelf waters (depth > 30 m) of the Cairns box with free drifting sediment traps. Error bars = 1 standard deviation about the mean for 6-12 sub-traps sampled from the trap array. Adjacent bars in groups show measured sedimentation on successive days. Bottom: Calculated percentages of the water column stock of suspended particulates sedimenting daily.

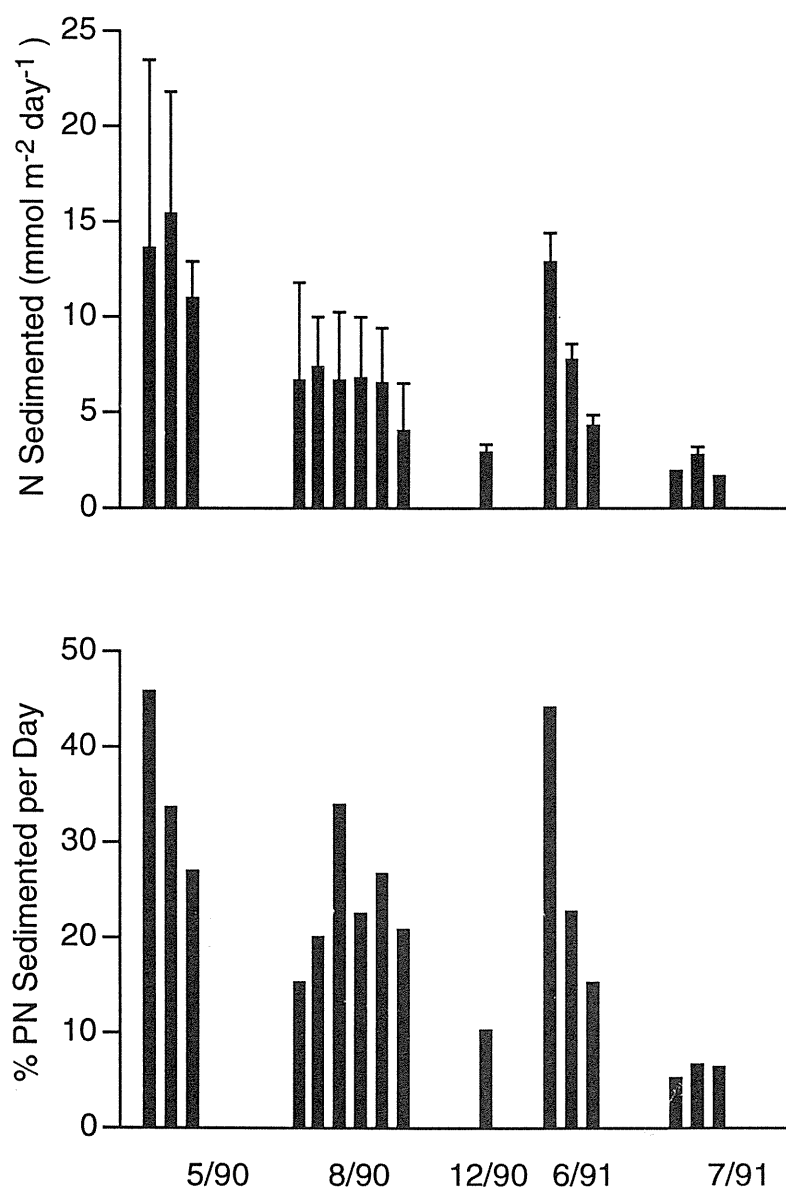


Figure 78. Top: Particulate nitrogen sedimentation fluxes (mmol m⁻²) measured in mid- and outer-shelf waters (depth > 30 m) of the Cairns box with free drifting sediment traps. Error bars = 1 standard deviation about the mean for 6-12 sub-traps sampled from the trap array. Adjacent bars in groups show measured sedimentation fluxes on successive days. Bottom: Calculated percentages of the water column stock of particulate nitrogen sedimenting daily.

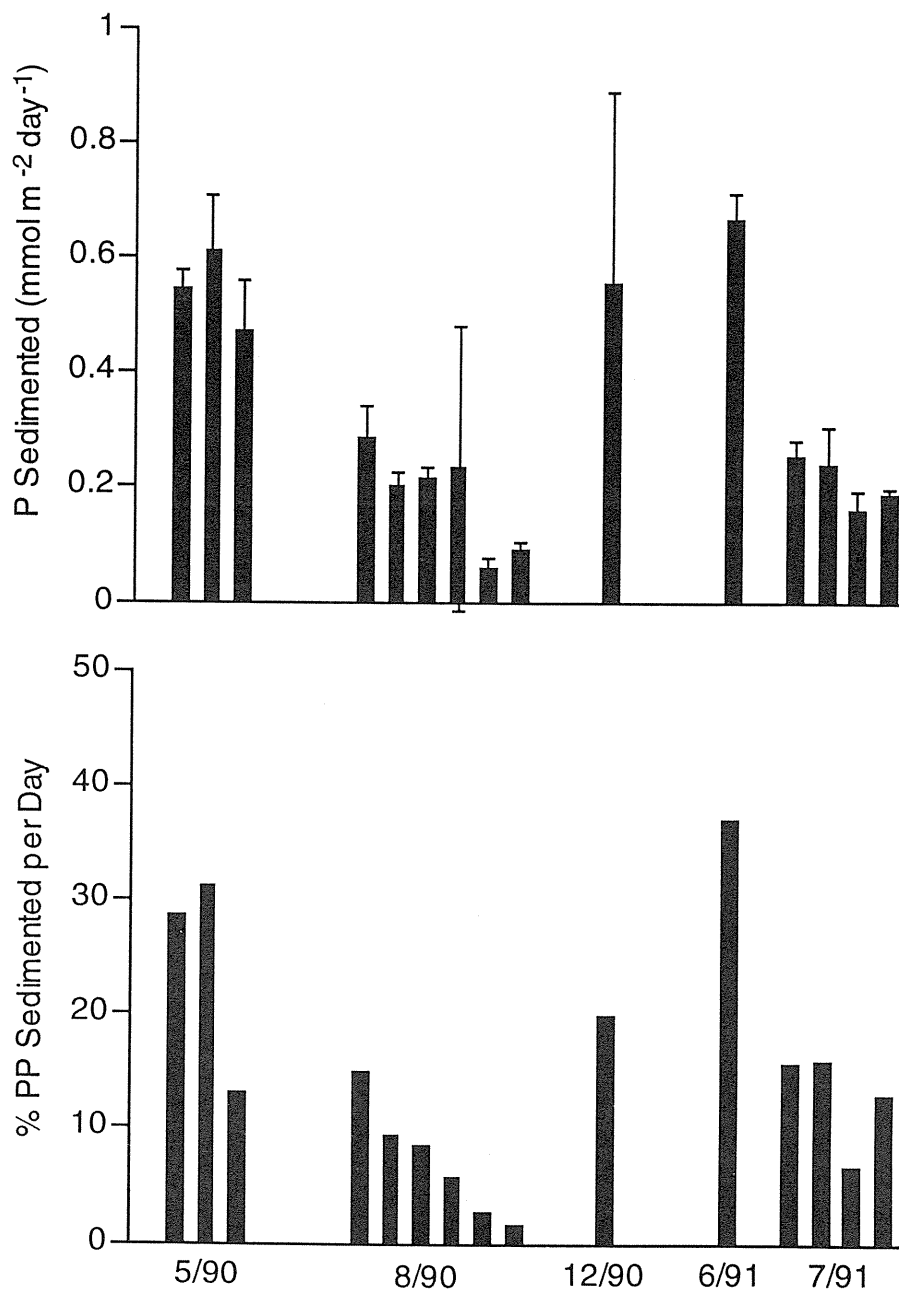


Figure 79. Top: Particulate phosphorus sedimentation fluxes (mmol m⁻²) measured in mid- and outer-shelf waters (depth > 30 m) of the Cairns box with free drifting sediment traps. Error bars = 1 standard deviation about the mean for 6-12 sub-traps sampled from the trap array. Adjacent bars in groups show measured sedimentation fluxes on successive days. Bottom: Calculated percentages of the water column stock of particulate phosphorus sedimenting daily.

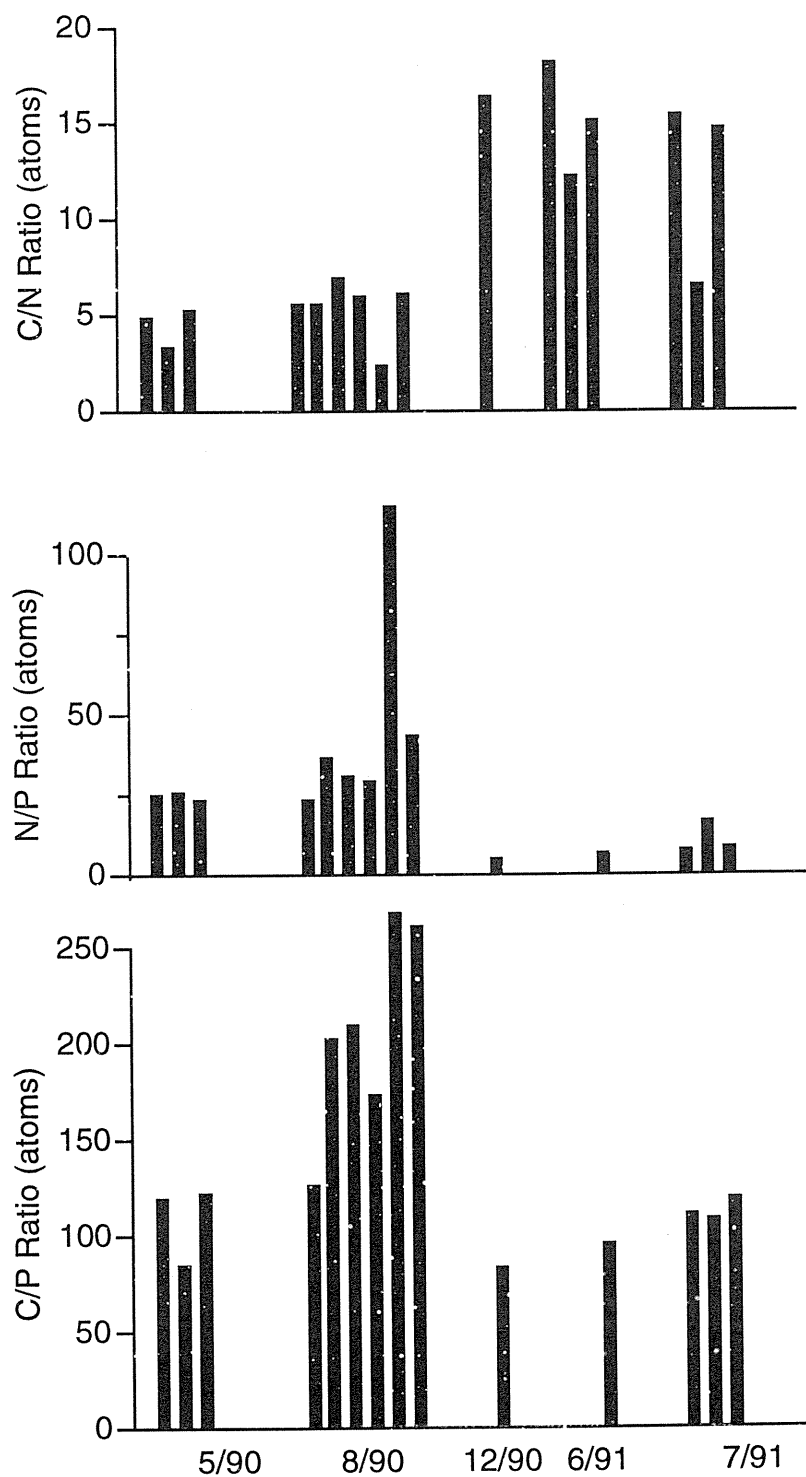


Figure 80. Day-to-day and between-cruise variability in atomic ratios between carbon, nitrogen and phosphorus in material collected by free-drifting sediment traps in mid- and outer-shelf waters (depth > 30 m) of the Cairns box.

Table 29. Estimated annual organic nutrient sedimentation rates (mmol m⁻² per day) in the Cairns and Tully boxes.

	Depth Band	Flux mmol m ⁻² day ⁻¹	Area km ²	Mmoles p.a.
Cairns				
C	0-10 m	76	377	10458
	10-20 m	76	636	17643
	20-30 m	54	856	16872
	30+ m	54	4068	80180
				125153
N	0-10 m	8.4	377	1156
	10-20 m	8.4	636	1950
	20-30 m	6.9	856	2156
	30+ m	6.9	4068	10245
				15507
P	0-10 m	1.2	377	165
	10-20 m	1.2	636	279
	20-30 m	0.37	856	116
	30+ m	0.37	4068	549
				1109
Tully				
C	0-10 m	105.4	310	11926
	10-20 m	105.4	535	20582
	20-30 m	45.2	1306	21546
	30+ m	50.5	5675	104604
				158659
N	0-10 m	22.24	310	2516
	10-20 m	22.24	535	4343
	20-30 m	9.37	1306	4467
	30+ m	9.68	5675	20051
				31377
P	0-10 m	0.77	310	87
	10-20 m	0.77	535	150
	20-30 m	0.24	1306	114
	30+ m	0.27	5675	559
				911

14. BENTHIC NUTRIENT FLUXES

Fluxes of dissolved inorganic nutrients (NH₄, NO₂+NO₃, PO₄) from the benthos to the water column were estimated from the benthic nutrient release rates reported by Alongi (1989, 1990) and Capone et al. (1992). Given that relatively few measurements of benthic metabolism and nutrient release have been measured in GBR shelf waters, the available measurements, none of which were made within the defined boxes, have been extrapolated carefully. Alongi measured inorganic nutrient release rates from sediments collected at a number of sites along a cross-shelf line just south of the Tully box and within the adjoining Rockingham Bay. For the budget herein, near-shore (0-20 m water depth) nutrient excretion fluxes are calculated from the mean of excretion rates measured at two stations located off the mouth of the Murray River. These sites were deemed to be the most representative of inner shelf environments in the central GBR. Mid-shelf (20-30 m water depth) benthic excretion fluxes are estimated from means of rates measured at two sites located in the GBR lagoon immediately seaward of Hinchinbrook Island. Outer shelf rates are taken from the means of excretion rates measured at two stations located between Otter Reef and Britomart Reef. Where possible, excretion rates are partitioned into time-averaged seasonal rates for the winter (April - September) and summer (October - March) periods (Table 30). No benthic metabolism and benthic nutrient release rates are currently available for sites in the Cairns box. It is unclear to what extent the Capone et al. (1992) measurements of NH₄ fluxes can be applied to inter-reefal sediments. The Alongi (1989) excretion rates are therefore used for both the Cairns and Tully boxes with the proviso that the Cairns box estimates are based upon data which may not be wholly representative of benthic conditions within this box.

Table 30. Daily benthic nutrient excretion rates used to estimate benthic nutrient recycling. Negative rates indicate net uptake by the benthos. Rates are derived from Alongi (1989 and 1990).

Depth Range	Ammonia		Nitrate+Nitrite		Phosphorus		Silicate	
	μmol m ⁻² day ⁻¹		μmol m ⁻² day ⁻¹		μmol m ⁻² day ⁻¹		μmol m ⁻² day ⁻¹	
	W	S	W	S	W	S	W	S
0 to 10 m	775	352	198	19	40	60	3420	3305
10 to 20 m	775	352	198	19	40	60	3420	3305
20 to 30 m	1212	1212	24	24	111	111	3435	3435
30 to 100 m	414	414	-36	-36	71	71	3378	3378

Estimates of annual benthic fluxes of inorganic nutrients to the water column are given in Table 31. No estimates are currently available for dissolved organic nutrient fluxes between the water column and benthos. Concentrations of DON and DOP in GBR shelf sediment porewaters are not greatly elevated (D. Alongi, pers. comm); therefore, it is likely that fluxes of DON and DOP from shelf sediments to the water column are not large. Where seasonal comparisons were possible within depth bands, the means of winter nitrogen excretion fluxes tended to be higher (2- to >10-fold) than summer excretion fluxes. This likely reflects greater denitrification activity in shelf sediments during the summer, though no direct denitrification measurements have been made to confirm this. This is in contrast to the situation in temperate systems where benthic nutrient N (and P) release fluxes generally increase with temperature (e.g. Nixon, 1981). Summer benthic phosphate excretion fluxes were higher in the summer than in the winter. There was little difference, however, between winter and summer silicate (Si) release fluxes.

Table 31. Estimated annual shelf-scale benthic nutrient fluxes for the Cairns and Tully boxes.

Depth Range	Area	Winter		Summer		Total Annual	% Total
	km ²	Release Rate μmol m ⁻² day ⁻¹	days	Release Rate μmol m ⁻² day ⁻¹	days	Flux kmol	
Cairns box							
Ammonium							
0-10	377	775	153	352	212	72836	6.1
11 to 20	636	775	153	352	212	122875	10.3
21 to 30	856	1212	153	1212	212	378677	31.8
31-100	4068	414	153	414	212	614715	51.7
Total						1189103	
Nitrate+Nitrite							
0-10	377	40	153	19	212	3826	-10.7
11 to 20	636	40	153	19	212	6454	-18.1
21 to 30	856	24	153	24	212	7499	-21.0
31-100	4068	-36	153	-36	212	-53454	149.8
Total						-35675	
Phosphate							
0-10	377	40	153	60	212	7103	4.5
11 to 20	636	40	153	60	212	11982	7.5
21 to 30	856	111	153	111	212	34681	21.8
31-100	4068	71	153	71	212	105422	66.2
Total						159188	
Tully box							
Ammonia							
0-10	310	775	153	352	212	59892	3.7
11 to 20	535	775	153	352	212	103361	6.5
21 to 30	1306	1212	153	1212	212	577748	36.1
31-100	5675	414	153	414	212	857549	53.6
Total						1598551	
Nitrate+Nitrite							
0-10	310	40	153	19	212	3146	-5.8
11 to 20	535	40	153	19	212	5429	-10.0
21 to 30	1306	24	153	24	212	11441	-21.0
31-100	5675	-36	153	-36	212	-74570	136.7
Total						-54554	
Phosphate							
0-10	310	40	153	60	212	5840	2.7
11 to 20	535	40	153	60	212	10079	4.7
21 to 30	1306	111	153	111	212	52913	24.5
31-100	5675	71	153	71	212	147068	68.1
Total						215900	

Not surprisingly, when estimated benthic nutrient fluxes are weighed by shelf areas, the bulk of the shelf-scale benthic fluxes again occur on the outer shelf (water depth > 30 m). The highest area-specific rates, however, were measured on the mid-shelf. The relatively scant data available suggests that outer shelf sediments are a net sink for nitrate (negative excretion rates), while inshore sediments are a net source. It should be noted, however, that the net loss of inorganic nitrogen from the water column due to benthic nitrate uptake is less than 5 percent of net ammonium release from the benthos.

Area-specific particulate nitrogen and phosphorus deposition fluxes (Table 29) in the Cairns and Tully boxes consistently exceeded measured benthic release fluxes (Table 31) for these two elements. Seasonally averaged benthic nitrogen release fluxes were on the order of $1 \text{ mmol m}^{-2} \text{ day}^{-1}$, while the majority of nitrogen deposition fluxes fell between 2.5 and $20 \text{ mmol m}^{-2} \text{ day}^{-1}$. Maximal benthic nitrogen release fluxes were $2.5 \text{ mmol m}^{-2} \text{ day}^{-1}$ (Alongi, 1989). A similar discrepancy was also observed between measured phosphorus deposition fluxes and benthic phosphorus release fluxes. Most gross phosphorus deposition rates fell between 0.2 and $1 \text{ mmol m}^{-2} \text{ day}^{-1}$, while time-averaged phosphorus release rates from the benthos ranged between 0.04 and $0.11 \text{ mmol m}^{-2} \text{ day}^{-1}$.

The discrepancies between nitrogen and phosphorus deposition fluxes and measured benthic remineralization rates clearly indicates that the shelf benthos is a sink for carbon, nitrogen and phosphorus. Of these three elements, only phosphorus would likely accumulate over long periods in the sediment. The mean weight percent of carbon, nitrogen and phosphorus in sedimenting material from the Tully box moored traps (1.5, 0.8 and 0.07 % D.W.) are considerably higher than the organic carbon (0.2-0.4 % D.W.), N (0.02-0.12 % D.W.) and phosphorus (0.02 - 0.05 % D.W.) content of bulk shelf sediments collected away from the inshore zone (Alongi, 1989). The phosphorus composition of bulk sediment is closest to that of sedimenting material. Organic carbon and nitrogen can be converted to either gaseous or dissolved organic forms by aerobic and anaerobic metabolic processes (respiration, denitrification). Phosphorus, on the other hand, is readily adsorbed to particulate matter and converted to insoluble mineral phases (e.g. apatites) in carbonate sediments (Entsch, 1983; Froelich, 1988).

At present, there are no independent estimates available for either relative or absolute sediment and organic nutrient resuspension fluxes on the GBR shelf. It is quite clear that resuspension due to wind waves occurs on a regular basis in nearshore waters (< ca. 20 m; e.g. Oviatt and Nixon, 1975; Roman and Tenore, 1978) as almost all traps deployed in depths < 25 m collected significant quantities of terrigenous mud. Varying amounts of fine-grained carbonate muds were collected in traps deployed on the mid- and outer-shelf (depths 30-55 m). It is unclear, however, whether this outer-shelf inorganic material was resuspended from the inter-reefal benthos, or was transported laterally from reefs. Resuspension of mid- and outer-continental shelf sediments and organic matter has been documented in temperate shelf systems (e.g. Falkowski et al., 1983; Fanning et al., 1982). Resuspension is particularly pronounced during storm events (Fanning et al., 1982). The observed discrepancy between measured sedimentation fluxes and benthic nutrient release rates clearly points to the need to quantify rates and variability in resuspension and particle cycling processes in shelf waters.

Annual estimates of shelf-scale benthic nutrient releases estimated from Alongi's measured nutrient fluxes are given in Table 31. Ammonium is the principal form of inorganic nitrogen released from the sediments, with annual inputs to the water column of 1.2 and $1.6 \times 10^3 \text{ Mmol}$ from Cairns and Tully box sediments, respectively. Although the area-specific fluxes are highest on the inner shelf and in the GBR lagoon, over half of the total benthic flux came from the larger area of the outer shelf. Oxidized nitrogen ($\text{NO}_x = \text{NO}_2 + \text{NO}_3$) releases from shelf sediments are relatively small in comparison and restricted to the inner shelf. The outer shelf is a net sink for oxidized forms of nitrogen, with a net NO_x uptake equalling 5 percent of the NH_4 release flux.

The cross-shelf pattern of phosphate release from sediments differed from nitrogen. The highest area-specific release rates were measured on the middle and outer shelf (Alongi, 1989). Accordingly, over two-thirds of the estimated annual PO_4 release from shelf sediments is calculated to come from the calcareous outer lagoon and inter-reefal sediments located at depths greater than 30 m. The total estimated annual benthic PO_4 release fluxes for the Cairns and Tully boxes are estimated to be 1.6 and $2.2 \times 10^5 \text{ kmol}$, respectively. The time- and area-

weighted benthic N/P ratios release for the Cairns and Tully boxes are 7.25 and 7.15 (atoms), considerably lower than the Redfield ratio for healthy phytoplankton. This low ratio would contribute to the apparent nitrogen-limited state of shelf phytoplankton populations by maintenance of water column DIN/DIP ratios conducive to nitrogen limitation.

15. PHYTOPLANKTON NUTRIENT DEMAND

Algal blooms are a regular and particularly noticeable feature of aquatic ecosystems with enhanced nutrient inputs (Anderson, 1989). To date, few direct measurements of phytoplankton demand for nitrogen or phosphorus have been made in waters of the GBR (e.g. Furnas, 1988). Virtually all of the inorganic nitrogen and phosphorus being added to GBR shelf waters will be taken up by phytoplankton before being recycled to other components of the ecosystem by feeding, sedimentation and mineralization processes. In the well-studied Kaneohe Bay system (Smith et al., 1981), the nutrients added were rapidly taken up by phytoplankton. Water column concentrations away from the immediate site of addition were not greatly elevated. The added nutrients produced a well defined plume (Kimmerer et al., 1980) as phytoplankton rapidly grew downstream of the addition site. Once incorporated into phytoplankton, the nutrients sedimented onto both reefs and the flat benthos, producing long-lived pools of carbon, nitrogen and phosphorus which took a number of years to disperse (Smith et al., 1981).

In the absence of direct uptake data, indirect estimates of demand can be made using daily and seasonally averaged estimates of primary production and C:N:P ratios (106:16:1) in natural phytoplankton (Redfield et al., 1963). The interpretation of such estimates must be restrained, however, in that the carbon uptake, nutrient uptake and growth kinetics of phytoplankton can be unbalanced over daily and shorter time periods (e.g. Goldman et al., 1981). Despite their limitations, primary-production based estimates of nutrient demand place first-order constraints on estimates of time averaged nutrient demand.

Furnas and Mitchell (1987) made measurements of water column primary production rates within the reef matrix on the outer half of the shelf in Palm Passage. Mean daily production rates during summer on the mid and outer shelf were $550 \text{ mg C m}^{-2} \text{ day}^{-1}$ ($45.7 \text{ mmol m}^{-2} \text{ day}^{-1}$) and $412 \text{ mg C m}^{-2} \text{ day}^{-1}$ ($34.3 \text{ mmol m}^{-2} \text{ day}^{-1}$). During the winter season primary production rates for the mid and outer shelf averaged $390 \text{ mg C m}^{-2} \text{ day}^{-1}$. Both experimental sites in Palm Passage would fall into the outer shelf depth band of the Cairns and Tully boxes (depth >30 m). It is realistic to expect that the production rates measured in Palm Passage are directly extrapolatable to conditions in the outer-shelf regions of the Cairns and Tully boxes.

Based on the Redfield ratios quoted above, the summer [winter] primary production rates on the outer shelf would translate to demand fluxes of 5.2 [4.9] $\text{mmol N m}^{-2} \text{ day}^{-1}$ and 0.32 [0.31] $\text{mmol P m}^{-2} \text{ day}^{-1}$. For the mid-shelf production measurements, the estimated summer [winter] nitrogen and phosphorus demands are 6.9 [4.9] $\text{mmol N m}^{-2} \text{ day}^{-1}$ and 0.43 [0.31] $\text{mmol P m}^{-2} \text{ day}^{-1}$, respectively. When weighted seasonally, annual outer shelf nitrogen and phosphorus demand fluxes in Palm Passage are calculated to be 1850 and 115 mmol m^{-2} . For the mid-shelf measurements, the estimated annual nitrogen and phosphorus demand fluxes are 2210 and 139 mmol m^{-2} . The average of the outer shelf nitrogen demand estimates, when multiplied by the outer shelf areas (>20 m) of the Cairns and Tully boxes, translate to overall nitrogen demand fluxes of 8.3 and $11.5 \times 10^6 \text{ kmol}$ per year, respectively, into phytoplankton (and pelagic bacterial) biomass. For phosphorus, the corresponding annual demand fluxes for the Cairns and Tully boxes would be 5.2 and $7.2 \times 10^5 \text{ kmol}$.

Seven measurements of water column primary production were made off Cairns during November-December 1990 (Figure 8, Table 32). With areal weighting, these summer primary production rates translate to estimated annual phytoplankton nitrogen and phosphorus demand fluxes of 26.9×10^6 and $1.65 \times 10^6 \text{ kmol}$, which are 3.2 times the rate extrapolated from the outer-shelf production measurements made over an annual cycle in Palm Passage. This is likely a high estimate as it is based upon a single summer series of measurements when production is normally high. Based on the Redfield C/N ratio (6.6 by atoms), the estimated nitrogen demand associated with above production estimates ranges between 58 and 272 mmol

$\text{N m}^{-2} \text{ day}^{-1}$. Phosphorus demand would range between 3.6 and 17 $\text{mmol m}^{-2} \text{ day}^{-1}$ based on the Redfield C/P ratio (106). Calculated depletion times for depth integrated water column DIN stocks ranged from 33 to 163 hours (1.4-6.7 days). With one exception, water column averaged DIP depletion times were longer than DIN depletion times, ranging between 48 and 143 hours (2-6 days). The difference is largely due to the relatively larger size of the water column PO_4 pool. Both DIN and DIP depletion times are long relative to the potential growth rates of phytoplankton populations in GBR waters (Furnas, 1991). Most of the primary production occurs at isolume depths above 20 percent of surface irradiance, while in many cases, particularly at outer-shelf stations, most of the DIN and DIP stocks exist at depths below this time-averaged isolume. Care should therefore be taken about drawing conclusions that turnover times of water column stocks of DIN and DIP are relatively slow in GBR waters. In surface waters where the highest rates of primary production occur, depletion (turnover) times for both DIN and DIP are likely to be on the order of hours, if not less. Under these circumstances, nutrient availability is likely determined by coupling to water column mineralization processes.

That being said, there was no clear differentiation between depletion times calculated for integrated water column DIN and DIP stocks in inshore and offshore experiments. No primary production measurements have been made in the Cairns region during the winter season. If the seasonal difference between mean water column production rates observed in Palm Passage holds for the Cairns region, the seasonal variation in turnover times are also likely to be less than 2-fold.

For comparison, the box-averaged, area-specific annual benthic DIN and DIP fluxes ($194.3 \text{ kmol km}^{-2}$ and $26.8 \text{ kmol km}^{-2}$), as calculated from the data of Alongi (1989), account for only 13 percent of the nitrogen and 29-30 percent of the phosphorus demand derived from primary production estimates for the Cairns and Tully boxes.

Table 32. Water column primary production rates off Cairns during November - December 1990. Daily primary production is estimated as eight times the mid-day (1000-1400) hourly carbon uptake rate.

Station	Location	Depth m	Hourly C uptake mg C m ⁻² hr ⁻¹	Daily Primary Production g C m ⁻²	N Demand (C / 6.6) mmol m ⁻² day ⁻¹	P Demand (C / 106) mmol m ⁻² day ⁻¹	DIN Stock mmol m ⁻²	DIN Depletion Time hrs	DIP Stock mmol m ⁻²	DIP Depletion Time hrs
CNS196	Outer Shelf	45	100.5	0.8	10.2	0.6	31.5	74.4	3.2	121.5
CNS198	Outer Shelf	62	224.5	1.8	22.7	1.4	45.9	48.6	3.1	52.7
CNS201	Inshore	21	63.0	0.5	6.4	0.4	17	64.2	1.5	90.9
CNS204	Inshore	23	48.0	0.4	4.8	0.3	19.3	95.6	1.8	143.1
CNS207	Midshelf	33	61.5	0.5	6.2	0.4	41.9	162.0	2.3	142.8
CNS209	Inshore	23	126.9	1.0	12.8	0.8	17.7	33.2	1.6	48.1
CNS214	Inshore	17	100.0	0.8	10.1	0.6	15.6	37.1	1.2	45.8
				0.83				73.6		92.1

16. WATER COLUMN NUTRIENT MINERALIZATION BY ZOOPLANKTON AND MICROBIAL POPULATIONS

16.1 Macro- and Microzooplankton

Particulate organic nitrogen and phosphorus in the water column are continuously mineralized to dissolved inorganic forms by macrozooplankton (e.g. copepods, chaetognaths, ctenophores), microzooplankton (e.g. copepod nauplii, tintinnids, ciliates) and other heterotrophic microbes (bacteria, flagellates). Bacteria also have the capability to mineralize and recycle significant amounts of nitrogen and phosphorus from dissolved organic matter. Estimates of water column mineralization fluxes in both temperate (e.g. Harrison et al., 1983; Furnas et al., 1986) and subtropical systems (e.g. Caperon et al., 1979) clearly show that in all but the shallowest of water bodies, water column mineralization processes provide most of the nitrogen and phosphorus required by phytoplankton and pelagic bacteria (e.g. Furnas, 1991). No direct measurements of either water column nitrogen or phosphorus mineralization rates were made during the course of the present study. However, a relevant body of experimental results from work carried out earlier in the GBR, Hawaii and elsewhere, used in combination with estimates of macrozooplankton community biomass, permit a first order estimate of the magnitude of water column nitrogen and phosphorus recycling fluxes to be made.

Tables 33 and 34 summarize measurements of zooplankton community biomass (as dry weight - mg m^{-3}) and standing crop (as dry weight - mg m^{-2}) derived from net collections for the Cairns and Tully boxes. To the extent possible, the biomass data are separated by season and cross-shelf depth band. The collections were made with a 73 μm mesh net and are therefore subject to contamination by large phytoplankton (e.g. certain diatoms, *Trichodesmium*) and amorphous (gelatinous) detrital organic matter. There are at present few equivalent measurements (published or otherwise) of either microzooplankton and heterotrophic microbial biomass for waters in the Cairns and Tully boxes *per se*. (Ayukai, 1992; Hopkinson et al., 1987). Using material from water bottle samples collected off Townsville, Ikeda et al. (1982b) calculated that microzooplankton biomass ranged between 4 and 15 percent (mean 7.7 percent) of macrozooplankton biomass collected with a 202 μm net with a mean of 7.7 percent. On a dry weight basis, the 73 μm mesh nets used in the present study collect 186 percent of the material collected by a 200 μm mesh net (Mitchell, unpubl. data).

On a volume basis, zooplankton biomass varied only slightly with increasing depth across the shelf in both the Cairns and Tully boxes. The difference was most pronounced in the winter (May-September) when the median biomass levels in outer shelf waters of the Cairns box were 20 percent of those measured inshore (25 percent for median values). During the summer, the onshore-offshore differences, as shown by the median values, were less than 1.5-fold. Overall, seasonal differences in mean biomass within depth bands were not significant (2-way ANOVA, $p = 0.14$), though considering the offshore depth band (> 40 m depth alone), there was a quite significant 4-fold difference from inshore biomass levels (t-test). There were insufficient zooplankton biomass data available for the Tully box to make a similar statistical comparison. Inspection of the summary data suggests that seaward of the 10 m isobath, the cross-shelf gradients in biomass was weak, and likely non-significant statistically.

When the biomass values are integrated over depth, clear and statistically significant ($p = 0.003$) cross-shelf increases in zooplankton standing crop ($\text{mg dry weight m}^{-2}$) are clearly apparent. The increase in depth over which biomass estimates were integrated more than compensates for the slight declines in volume-specific biomass. The median summer standing crop on the outer shelf was approximately 50 percent greater than that measured during the winter months. Cross shelf trends in zooplankton standing crop in the Tully box were similar to those observed in the Cairns box.

Table 33. Summary statistics for depth-averaged zooplankton biomass (mg dry weight m⁻³) in the Cairns and Tully boxes.

	0-10 m	10-20 m	20-30 m	30+ m
Cairns box				
Summer				
Mean	16.6	14.1	11.0	14.0
Std Dev.	8.6	7.0	8.2	14.5
n	12	25	17	17
Median	15.1	13.0	8.1	10.2
Winter				
Mean	16.0	13.6	12.0	3.4
Std Dev.	0.8	8.9	6.7	1.4
n	6	20	11	8
Median	15.8	12.2	11.5	3.8
Tully box				
Summer				
Mean		7.7	10.2	7.0
Std Dev.		10.5	9.2	6.3
n		4	7	20
Median		2.5	9.5	4.1
Winter				
Mean			6.8	5.0
Std Dev.			1.4	2.0
n			3	8
Median			6.1	4.5

Table 34. Summary statistics for areal zooplankton standing crop (mg dry weight m⁻³) in the Cairns and Tully boxes.

	0-10 m	10-20 m	20-30 m	30+ m
Cairns box				
Summer				
Mean	138.8	172.8	293.2	517.5
Std Dev.	68.1	99.2	237.9	454.7
n	12	12	17	47
Median	127.5	126.8	225.6	395.0
Winter				
Mean	136.2	220.9	297.3	288.4
Std Dev.	4.8	161.7	193.2	134.6
n	6	20	11	28
Median	137.6	199.7	242.5	254.6
Tully Box				
Summer				
Mean		153.4	229.3	381.9
Std Dev.		210.2	182.7	304.8
n		4	7	23
Median		50.4	205.9	228.3
Winter				
Mean			150.0	214.6
Std Dev.			29.7	128.2
n			3	12
Median			134.1	185.9

Chemical analysis of dried zooplankton (Figure 11) showed that the material collected by a 73 µm mesh net had a mean carbon content of 25.3 ± 6.4 (1 S.D., n=85) percent of dry weight and a mean nitrogen composition of 5.7 ± 1.7 (n=85) percent of dry weight. These estimates of zooplankton carbon and nitrogen content fall at the lower end of the composition range normally found for estuarine and oceanic zooplankton (Parsons et al., 1977). It is unclear at this stage whether the low values represent the true organic composition of net zooplankton in the > 73 µm size fraction, or more likely, are due to the dilution of zooplankton carbon and nitrogen content by inorganic salts or carbonate particles trapped in the zooplankton/macro-aggregate matrix of field collections. The material collected by the 73 µm net frequently, if not usually, contained gelatinous organic material. The carbon and nitrogen content of gelatinous zooplankton are well known to be lower than crustacean zooplankton because much of the mass of gelatinous zooplankton is merely seawater with its constituent salts (Kremer, 1975). Zooplankton samples heavily contaminated by phytoplankton, especially diatoms, are also characterized by low percentages of carbon and nitrogen (Furnas, unpubl. data). The phosphorus content of copepod-dominated oceanic zooplankton assemblages usually falls between 0.5 and 1 percent of dry weight (Parsons et al., 1977). Because the carbon and nitrogen contents of GBR zooplankton fall at the low end of the natural range, it is likely that the phosphorus composition of dried zooplankton (not measured to date) would also fall at the low end. For the purpose of this report, we will assume that the phosphorus composition of the zooplankton collected by the 73 µm netting is 0.5 percent of dry weight.

Results from two experimental studies (Smith et al., 1981; Ikeda et al., 1982 a,b) can be applied to the zooplankton community standing crop measurements to estimate macro- and micro-zooplankton nitrogen and phosphorus mineralization fluxes. Ikeda et al. (1982a) quantified mass-dependent nitrogen and phosphorus excretion rates for a wide range of zooplankton

species or groups. Macrozooplankton assemblages throughout the GBR are numerically dominated by copepods (Ikeda et al., 1982b; Liston, 1990), which also dominate estimates of community biomass. The relative homogeneity of zooplankton community structure throughout the GBR (Liston, 1990) allows locally measured zooplankton rate processes to be extrapolated to other, oceanographically similar areas with some confidence.

Tables 35 and 36 present mean seasonal and annual estimates of the volumetric and area-weighted shelf-scale nitrogen and phosphorus excretion rates for macro- and microzooplankton populations using the biomass-specific excretion rate ($1.35 \mu\text{mol N mg DW}^{-1} \text{ day}^{-1}$) calculated by Ikeda et al. (1982b) for macrozooplankton. Microzooplankton standing crop estimates were calculated from the macrozooplankton standing crop estimates as 7.7 percent of macrozooplankton dry weight. Ikeda et al. considered microzooplankton to consist of larger ciliates (e.g. tintinnids) and larval or juvenile stages of macrozooplankters (e.g. copepod nauplii and copepodite stages). The contribution of heterotrophic microflagellates and bacteria are not considered in Ikeda et al.'s estimates of microzooplankton biomass and excretion rates. Their mineralization rates were experimentally measured at 27.5°C , then converted to mean seasonal rates at temperatures of 28° and 22°C using a Q_{10} value of 2.53 (Q_{10} is the relative difference between two metabolic rates for a 10°C change in temperature in the normal temperature range for growth). Biomass-specific nitrogen and phosphorus excretion rates of microzooplankton during the summer are approximately 1.7-fold greater than during the winter months. In the case of macrozooplankton, Ikeda et al., calculated a 1.9-fold seasonal difference in the biomass specific excretion rate for nitrogen and 3.7-fold difference for phosphorus.

Based on the work of Szyper et al. (1976), Smith et al. (1981) calculated biomass-specific nitrogen and phosphorus excretion rates for Kaneohe Bay macrozooplankton of $1.78 \mu\text{mol N mg DW}^{-1} \text{ day}^{-1}$ and $0.11 \mu\text{mol P mg DW}^{-1} \text{ day}^{-1}$. Verity (1985) calculated a biomass weighted population ammonium excretion rate of $1.73 \mu\text{mol NH}_4 \text{ mg DW}^{-1} \text{ day}^{-1}$ for Sargasso Sea crustacean zooplankton. These estimates lie slightly above the seasonal range of excretion rates estimated by Ikeda et al. (1982b) for GBR zooplankton. The measurement or estimation of zooplankton community excretion rates is a difficult process, subject to a number of experimental artefacts and procedural problems (Ikeda, 1977; Takahashi and Ikeda, 1975), so the discrepancy between the estimates is not large or surprising. The general agreement between estimates of dry-weight specific nitrogen and phosphorus rates between studies indicates that the rates taken from Ikeda et al. are reasonable estimators of community excretion rates, particularly as the dry weights used are likely to be affected by some degree of dilution with detrital organic matter and phytoplankton.

Based on the available data for zooplankton standing crop in the Cairns box, annual mineralization fluxes of $\text{NH}_4\text{-N}$ and PO_4 were estimated to be 870×10^3 and $59.9 \times 10^3 \text{ kmol}$, respectively (Table 35). The respective estimates for annual zooplankton N and P mineralization fluxes in the Tully box are 647×10^3 and $37.6 \times 10^3 \text{ kmol}$ (Table 36). Microzooplankton were estimated to have contributed approximately 10 percent of the nitrogen mineralized and 17 percent of the phosphorus. For macrozooplankton, 72 percent of the nitrogen mineralization and 83 percent of the estimated phosphorus mineralization occurs during the summer (October-April) season. In the case of microzooplankton, we calculate that 70 percent of both the nitrogen and phosphorus mineralization occurs during the summer.

Table 35. Estimates of water column nitrogen and phosphorus mineralization by macro- and microzooplankton in the Cairns box.

Depth band	Zooplankton standing crop mg m ⁻³	Volume m ³	Summer		Winter			
			N excretion rate μmol mg ⁻¹ day ⁻¹	Days	Total excretion kmol	N excretion rate μmol mg ⁻¹ day ⁻¹	Days	Total excretion kmol
Nitrogen								
0-10 m	14.9	1.9E+09	1.35	212	8078	0.7	153	3023
10-20 m	12.7	1.09E+10	1.35	212	39720	0.7	153	14864
20-30 m	8.0	2E+10	1.35	212	45550	0.7	153	17046
30 + m	10.1	1.64E+11	1.35	212	473117	0.7	153	177047
Seasonal Totals					566465			211979
					Annual N Mineralized			778445
Microzooplankton								
0-10 m	1.14	1.9E+09	2.00	212	921	1.15	153	382
10-20 m	0.98	1.09E+10	2.00	212	4531	1.15	153	1880
20-30 m	0.61	2E+10	2.00	212	5196	1.15	153	2156
30 + m	0.78	1.64E+11	2.00	212	53970	1.15	153	22396
Seasonal Totals					64619			26815
					Annual N Mineralized			91434
Phosphorus								
0-10 m	14.9	1.9E+09	0.08	212	503	0.023	153	99
10-20 m	12.7	1.09E+10	0.08	212	2471	0.023	153	488
20-30 m	8.0	2E+10	0.08	212	2834	0.023	153	560
30 + m	10.1	1.64E+11	0.08	212	29438	0.023	153	5817
Seasonal Totals					35247			6965
					Annual P Mineralized			42212
Microzooplankton								
0-10 m	1.14	1.9E+09	0.19	212	85	0.108	153	36
10-20 m	0.98	1.09E+10	0.19	212	419	0.108	153	177
20-30 m	0.61	2E+10	0.19	212	481	0.108	153	203
30 + m	0.78	1.64E+11	0.19	212	4992	0.108	153	2103
Seasonal Totals					5977			2518
					Annual P Mineralized			8496

Table 36. Estimates of water column nitrogen and phosphorus mineralization by macro- and microzooplankton in the Tully box.

Depth band	Zooplankton standing crop mg m ⁻³	Volume m ³	Summer		Winter				
			N excretion rate μmol mg ⁻¹ day ⁻¹	Days	Total excretion kmol	N excretion rate μmol mg ⁻¹ day ⁻¹	Days	Total excretion kmol	
Nitrogen									
0-10 m	2.7	1.5E+09	1.35	212	1139	0.7	153	426	
10-20 m	2.7	8.5E+09	1.35	212	6453	0.7	153	2415	
20-30 m	9.5	3.1E+10	1.35	212	84724	0.7	153	31705	
30 + m	4.2	2.71E+11	1.35	212	329178	0.7	153	123183	
Seasonal Totals					421493			157729	
					Annual N Mineralized			579222	
Microzooplankton									
0-10 m	0.20	1.5E+09	2.00	212	130	1.15	153	54	
10-20 m	0.20	8.5E+09	2.00	212	736	1.15	153	305	
20-30 m	0.74	3.1E+10	2.00	212	9665	1.15	153	4011	
30 + m	0.33	2.71E+11	2.00	212	37551	1.15	153	15583	
Seasonal Totals					48081			19953	
					Annual N Mineralized			68034	
Phosphorus									
0-10 m	2.7	1.5E+09	0.08	212	71	0.023	153	14	
10-20 m	2.7	8.5E+09	0.08	212	402	0.023	153	79	
20-30 m	9.5	3.1E+10	0.08	212	5272	0.023	153	1042	
30 + m	4.2	2.71E+11	0.08	212	20482	0.023	153	4047	
Seasonal Totals					26226			5183	
					Annual P Mineralized			31409	
Microzooplankton									
0-10 m	0.20	1.5E+09	0.19	212	12	0.108	153	5	
10-20 m	0.20	8.5E+09	0.19	212	68	0.108	153	29	
20-30 m	0.74	3.1E+10	0.19	212	894	0.108	153	377	
30 + m	0.33	2.71E+11	0.19	212	3473	0.108	153	1463	
Seasonal Totals					4448			1874	
					Annual P Mineralized			6321	

17. MICROBIAL MINERALIZATION

Hopkinson et al. (1987) made a small number of direct measurements of NH₄-N mineralization rates in GBR reef waters using ¹⁵N isotope dilution techniques. The lowest microbial NH₄ mineralization rate (0.0013 μmol N l⁻¹ hr⁻¹ = 0.031 μmol N l⁻¹ day⁻¹) was measured in mid-shelf waters collected well to windward of the study reef (Davies Reef, ca. 19°S). Higher rates (to 0.0112 μmol N l⁻¹ hr⁻¹ = 0.27 μmol N l⁻¹ day⁻¹) were measured within cave systems along the backside of the reef, and particularly within narrow crevices with lower flushing rates and higher microbial population levels. These measurements were made during low-biomass winter conditions (August 1984). An extrapolation of these few measured mineralization rates to summer conditions is difficult as mineralization rates are dependent upon temperature, food or substrate levels and nanoplankton standing crop, all of which are highly variable and essentially unquantified. If the Q₁₀ value (above) estimated by Ikeda et al. (1982b) also holds for micro-organisms, the measured open water mineralization rates would translate to 0.0023 μmol N l⁻¹ hr⁻¹ (= 0.054 μmol N l⁻¹ day⁻¹). Using the same multiplier, the highest within-reef ammonium mineralization rates would similarly translate to 0.0196 μmol N l⁻¹ hr⁻¹ (= 0.47 μmol N l⁻¹ day⁻¹).

Based on the conditions prevailing at the time, the nitrogen mineralization rate measured by Hopkinson et al., 1987 in shelf waters outside the reef system would be most applicable to low-nutrient, outer shelf waters. The higher nitrogen mineralization rates measured within reef caves, though not verified as such, would more likely typify conditions prevailing in inshore waters characterized by higher phytoplankton and bacteria standing crops, dissolved organic nutrient concentrations and particulate matter loads. Taking Hopkinson et al.’s high and low measured rates as cross-shelf end members, Table 37 presents an annual estimate of microbial nitrogen mineralization within the Cairns and Tully boxes.

Table 37. Estimates of water column nitrogen mineralization by heterotrophic microbes in the Cairns and Tully boxes.

Cairns box		Summer			Winter		
Depth band	Volume	N excretion rate	Days	Total excretion	N excretion rate	Days	Total excretion
	m ³	μmol m ⁻¹ day ⁻¹		kmol	μmol m ⁻¹ day ⁻¹		kmol
0-10 m	1.9E+09	470.00	212	189316	270	153	78489
10-20 m	1.09E+10	330.00	212	762564	190	153	316863
20-30 m	2E+10	190.00	212	805600	110	153	336600
30 + m	1.64E+11	54.00	212	1877472	31	153	777852
Seasonal Totals				3634952			1509804
				Annual N Mineralized			5144756

Tully box		Summer			Winter		
Depth band	Volume	N excretion rate	Days	Total Excretion	N excretion rate	Days	Total Excretion
	m	μmol m day		kmoles	μmol m day	d	kmoles
0-10 m	1.5E+09	470.00	212	149460	270	153	61965
10-20 m	8.5E+09	330.00	212	594660	190	153	247095
20-30 m	3.1E+10	190.00	212	1248680	110	153	521730
30 + m	2.71E+11	54.00	212	3102408	31	153	1285353
Seasonal Totals				5095208			2116143
				Annual N Mineralized			7211351

These calculations, though of a first-order nature, clearly suggest that microbial nitrogen mineralization processes in shelf waters ($5.1\text{--}7.2 \times 10^6$ kmol per year) are likely to be of far greater magnitude than macrozooplankton and benthic mineralization processes and are of similar order to nitrogen demand by phytoplankton. As with macrozooplankton, much of this mineralization is likely to occur during the warmer and more productive summer months. Because of the rather limited nature of the data from which this estimate was derived, the accuracy and precision of this mineralization estimate is unknown.

Table 38 presents estimates of water column ammonium (NH_4), DIN ($\text{NH}_4 + \text{NO}_2 + \text{NO}_3$), DON and PON replacement (turnover) times (Furnas et al., 1986) within the two study boxes. Replacement times for the aggregate inorganic nitrogen (DIN) pool are largely determined by the estimated replacement times for ammonium (NH_4), the predominant constituent.

Ammonium pool replacement times within the two boxes range between 5 hours and 1.5 weeks. The calculated replacement times are largely constrained by the magnitude of the estimated mineralization rates rather than the sizes of the ammonium or DIN pools. The fastest replacement times for ammonium (and DIN) occur in the shallow inshore depth bands where the volume specific mineralization rates are the highest. The estimates suggest that in the Cairns box, ammonium pools in nearshore waters are turning over at least once per day, regardless of season. In the Tully box, estimated inshore turnover times range from < 1 day during summer to 3 days in winter. Offshore turnover times in both boxes are of similar order (≥ 1 week) during the winter.

Not surprisingly, estimated replacement times for DON stocks in both boxes are quite long, ranging from ca. 1.5 weeks at inshore stations during summer to 2-5 months in the offshore (>30 m depth) band during winter. These times do not reflect the likely turnover times of some biologically active constituents of the DON pool, such as dissolved amino acids, which are only present at low (nM) concentrations and are known to have turnover times on the order of hours in some systems (Fuhrman and Ferguson, 1986). Calculated PN pool replacement times on the basis of microbial mineralization ranged from ca. 3 days to four weeks, depending on the season and depth band.

No measurements of microbial phosphorus mineralization have been made to date in open shelf waters of the GBR. Dunlap (1985) measured potential enzymatic mineralization rates of DOP in waters flowing over shallow reef flat habitats in the central GBR, but it is difficult to extrapolate these results to the wider shelf environment. Nonetheless, his results indicated that on reef flats at least, enzymatic mineralization of DOP could be a major source of inorganic phosphorus to benthic algal communities. Laboratory studies of phosphorus remineralization by pelagic microflagellates and bacteria have yielded conflicting results. Both nitrogen and phosphorus mineralization rates are strongly dependent upon the physiological state of microbial populations involved and the C:N:P composition ratios of their food source (e.g. Goldman et al., 1987). As a result, microbial populations can either act as sources or sinks for nitrogen and phosphorus. The data most useful for deriving insights about microbial phosphorus cycling rates in GBR waters comes from field studies which were largely carried out near Hawaii (Smith et al., 1985; Harrison and Harris, 1986; Orrett and Karl, 1987). While measured mineralization rates were shown to vary with time over the course of a day, for time periods on the order of 24 hours, water column phosphorus uptake and mineralization rates appear to be balanced. As a result, the estimates of phosphorus demand derived from primary production rates and the Redfield ratio can supply a first-order estimate of water column phosphorus mineralization.

Table 38. Estimates of mean seasonal replacement times (days) for water column stocks of ammonium, DIN, DON, and PON in the Cairns and Tully boxes based on *in situ* mineralization rates of Hopkinson et al. (1987). Summer mineralization rates are estimated to be 1.75 times winter rates and are not adjusted for seasonal differences in biomass.

Depth Range (m)	Concentration (μM)				Replacement Time (days)			
	0-10 m	10-20 m	20-30 m	30 m +	0-10 m	10-20 m	20-30 m	30 m +
Cairns box								
Summer								
Mineralization Rate ($\mu\text{M day}^{-1}$)	0.47	0.33	0.193	0.054				
NH ₄	0.21	0.29	0.17	0.18	0.4	0.9	0.9	3.3
DIN	0.25	0.33	0.20	0.21	0.5	1.0	1.0	3.9
DON	5.45	4.68	6.14	6.17	11.6	14.2	31.8	114.3
PON	1.60	1.10	0.99	0.80	3.4	3.3	5.1	14.8
Winter								
Mineralization Rate ($\mu\text{M day}^{-1}$)	0.27	0.19	0.110	0.031				
NH ₄	0.26	0.33	0.33	0.23	1.0	1.7	3.0	7.4
DIN	0.30	0.36	0.39	0.27	1.1	1.9	3.5	8.7
DON	5.00	5.21	4.99	4.97	18.5	27.4	45.4	160.3
PON	1.63	1.12	1.06	0.72	6.0	5.9	9.6	23.2
Tully box								
Summer								
Mineralization Rate ($\mu\text{M day}^{-1}$)	0.47	0.33	0.193	0.054				
NH ₄	0.17	0.10	0.05	0.09	0.4	0.3	0.3	1.7
DIN	0.27	0.10	0.05	0.09	0.6	0.3	0.3	1.7
DON		4.21	3.68	4.65		12.8	19.1	86.1
PON		1.37	1.16	1.20		4.2	6.0	22.2
Winter								
Mineralization Rate ($\mu\text{M day}^{-1}$)	0.27	0.19	0.110	0.031				
NH ₄	0.89	0.56	0.30	0.32	3.3	2.9	2.7	10.3
DIN	1.14	0.91	0.40	0.42	4.2	4.8	3.6	13.5
DON								
PON	2.19	2.69	1.27	0.91	8.1	14.2	11.5	29.4

18. BUDGET SYNTHESIS AND DISCUSSION

Figures 81 and 82 present estimates of annual nitrogen and phosphorus inputs to shelf waters of the Cairns and Tully boxes based on direct measurements made in the central GBR or calculations from relevant literature sources. Table 39 summarizes these estimates numerically in relation to mean stocks of dissolved and particulate nitrogen and phosphorus waters in the two boxes. Relationships between the magnitude of estimated water column stocks in the Cairns and Tully boxes and calculated inputs are shown graphically in Figures 83 and 84.

Water column concentrations of dissolved nutrient species (Tables 5-8) are of similar order to those reported earlier for mid- and outer-shelf stations in the central GBR (Andrews, 1983; Furnas et al., 1990b). Unfortunately, no comparable measurements of particulate and dissolved organic nutrient species from the central GBR are available at this time. Median water column concentrations of NH_4 within depth bands in the Cairns box (0.17-0.33 μM) and summer concentrations in the Tully box (0.05-0.17 μM) were between 1-2 times the concentrations measured in surface waters (0-15 m) south of the Tully box (ca. 0.17 μM ; Furnas et al., 1990b). Winter NH_4 concentrations in the Tully box were considerably higher (0.30-0.89 μM) though the reasons are unclear. Median NO_2 (non-detectable - 0.05 μM) and NO_3 concentrations (0.03-0.10 μM) were similar. In contrast, median PO_4 concentrations in both the Cairns and Tully boxes were consistently less (0.5-1 times) than the mean values reported by Andrews (1983) and Furnas et al. (1990b). In the case of silicate, mean (and median) concentrations within inshore and mid-shelf (< 30 m) depth bands were considerably higher than reported by the above previous studies. Outer-shelf concentrations, however, were virtually identical. Mean and median depth-weighted chlorophyll concentrations in both the Cairns and Tully boxes were very similar to results reported in the earlier studies. Because dissolved nutrient and chlorophyll concentrations tend to fall into log-normal distributions, mean values are often, though not always higher than median values. Overall, dissolved nutrient concentrations do not appear to be enriched within either the Cairns box or at the southern end of the Tully box compared to the more open waters of the central GBR. A more detailed comparison will require comparison of the distributions of depth-weighted mean concentrations from the various boxes.

It is difficult to apply verifiable error estimates to the input, export and recycling fluxes discussed herein. Most of the estimates are based upon relatively small numbers of flux measurements (< 20) made within a short time span (ca. 2.5 years), or are extrapolations based upon arbitrary, though hopefully reasonable and conservative assumptions. Obviously, the small numbers of measurements limit generalizations regarding spatial and event-scale temporal variability in fluxes. The short duration over which most measurements were made is barely long enough to resolve even gross inter-annual fluctuations in pool sizes, rate processes or fluxes. For example, the ranges of nitrogen and phosphorus inputs from shelfbreak upwelling (Table 26) illustrate the magnitude of potential inter-annual variability in inputs from one source due to variability in the number and size of intrusion events. The overall nutrient input fluxes associated with upwelling include both primary nutrients intruded onto the shelf by individual events and the displacement of existing outer-shelf nutrient stocks. The seasonal mean concentrations of dissolved and particulate nutrients in the exchanged water masses are, in turn, subject to statistical uncertainty.

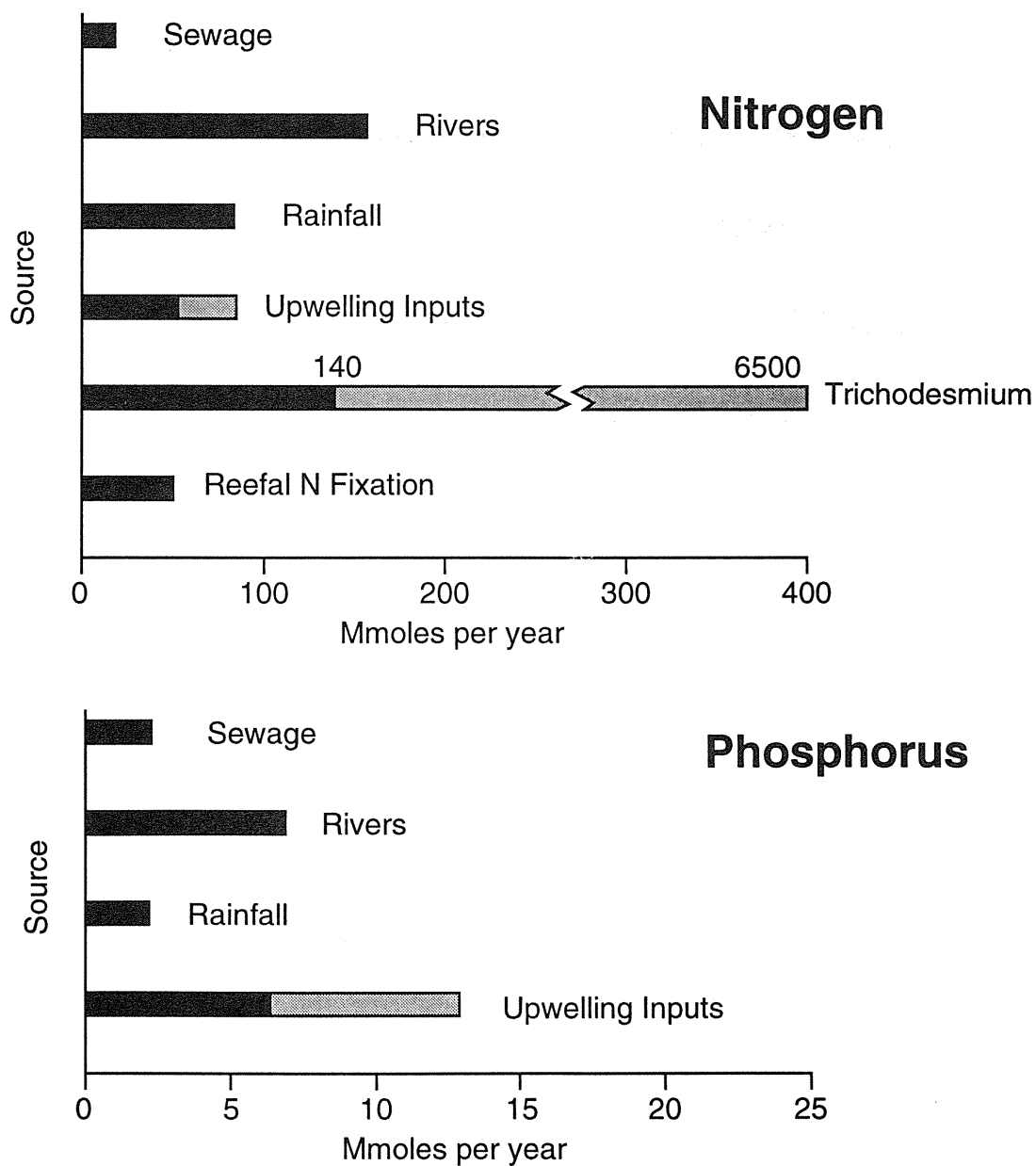


Figure 81. Calculated annual inputs of nitrogen and phosphorus to the Cairns box. Shaded portions of bars indicate the difference between the upper and lower end of a range where it could be estimated or was observed.

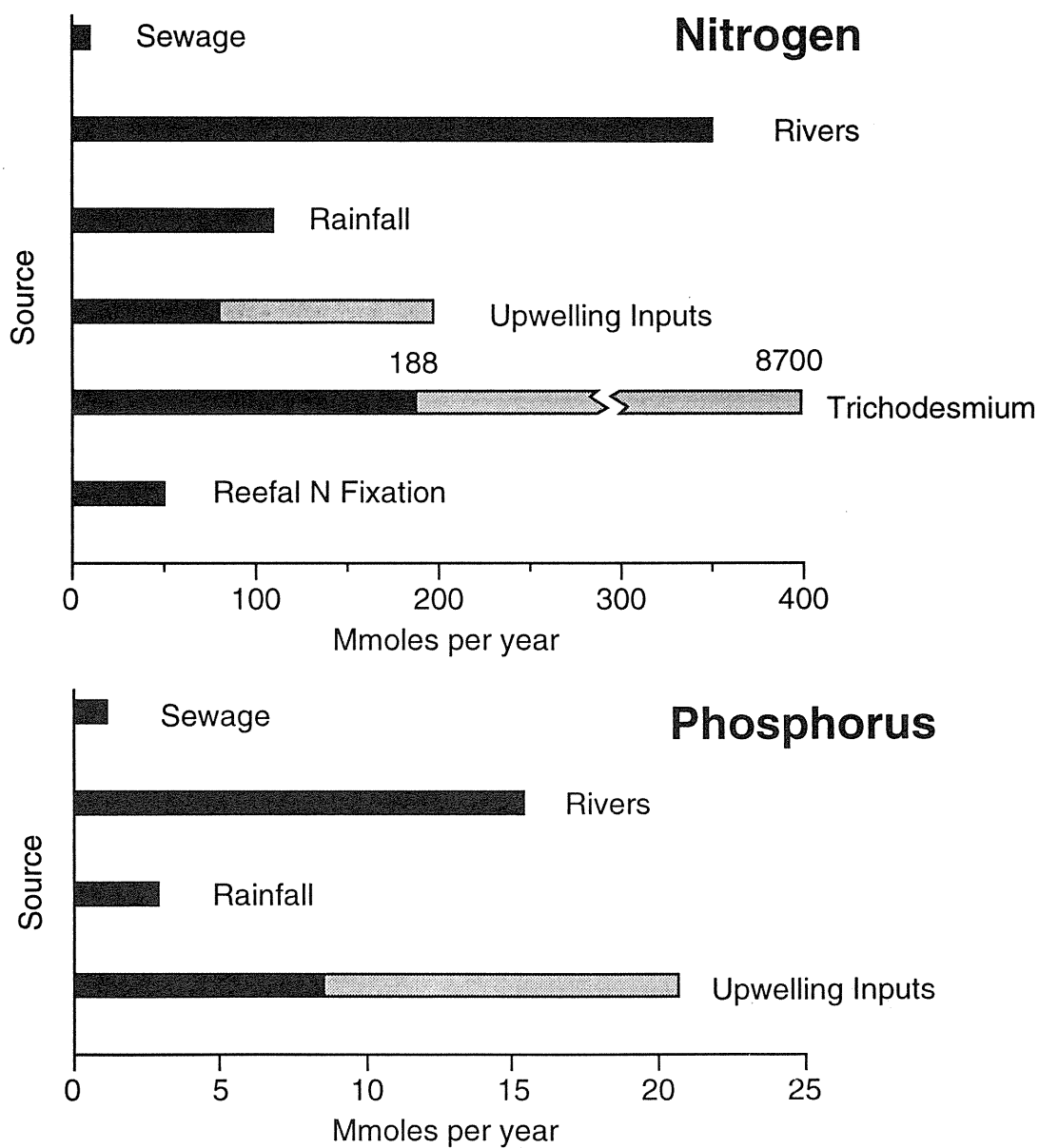


Figure 82. Calculated annual inputs of nitrogen and phosphorus to the Tully box. Shaded portions of bars indicate the difference between the upper and lower end of a range where it could be estimated or was observed.

Table 39. Calculated water column stocks of biogeochemically active nitrogen and phosphorus in the Cairns and Tully boxes and estimated annual fluxes of nitrogen and phosphorus through major sources and sinks and within major water column recycling pools.

Stocks	Cairns box				Tully box			
	Nitrogen		Phosphorus		Nitrogen		Phosphorus	
	Mmol	metric tonnes	Mmol	metric tonnes	Mmol	metric tonnes	Mmol	metric tonnes
Dissolved Inorganic	154	2153	29	886	159	2221	42	1298
Dissolved Organic	1806	25302	25	768	1773	24833	136	4201
Particulate	291	4080	22	678	445	6234	31	957
Total	2251	31535	75	2333	2376	33288	208	6456
Inputs								
	Mmol p.a.	metric tonnes	Mmol p.a.	metric tonnes	Mmol p.a.	metric tonnes	Mmol p.a.	metric tonnes
Sewage	19	265	2.3	70	10	142	1.2	38
Rivers	157	2197	6.9	214	350	4906	15.4	477
Rainfall	84	1174	2.2	68	110	1547	2.9	90
Upwelling	53-85	746-1198	6.4-12.9	124-400	81-198	1138-2773	8.5-20.7	263-641
<i>Trichodesmium</i>	140-6500	1960-91000			188-8700	2634-121900		
Reefal N Fixation	50	698			51	709		
Sinks								
	Mmol p.a.	metric tonnes	Mmol p.a.	metric tonnes	Mmol p.a.	metric tonnes	Mmol p.a.	metric tonnes
Upwelling Displacement	18-45	251-633	3-6.5	96-201	24-58	332-807	6-15	186-455
Shelfbreak Exchanges	?	?	?	?	?	?	?	?
Advection	?	?	?	?	?	?	?	?
Shelf Denitrification	1200-2600	16800-36400			1600-3430	22430-48000		
Reefal Denitrification	0.3	4			0.3	4		
Burial	58	813	11.9	369	67	939	13.7	424
Recycling Fluxes								
	Mmol p.a.	metric tonnes	Mmol p.a.	metric tonnes	Mmol p.a.	metric tonnes	Mmol p.a.	metric tonnes
Sedimentation/Resuspension	15500	217155	1109	34357	31400	439914	911	28223
Benthic Mineralization	1189	16658	159	4926	1599	22402	216	6692
Phytoplankton Demand	8260	115723	517	16017	11500	161115	721	22337
Zooplankton	870	12189	51	1580	647	9064	38	1177
Mineralization								
Microbial Mineralization	5145	72081	?	?	7211	101026	?	?

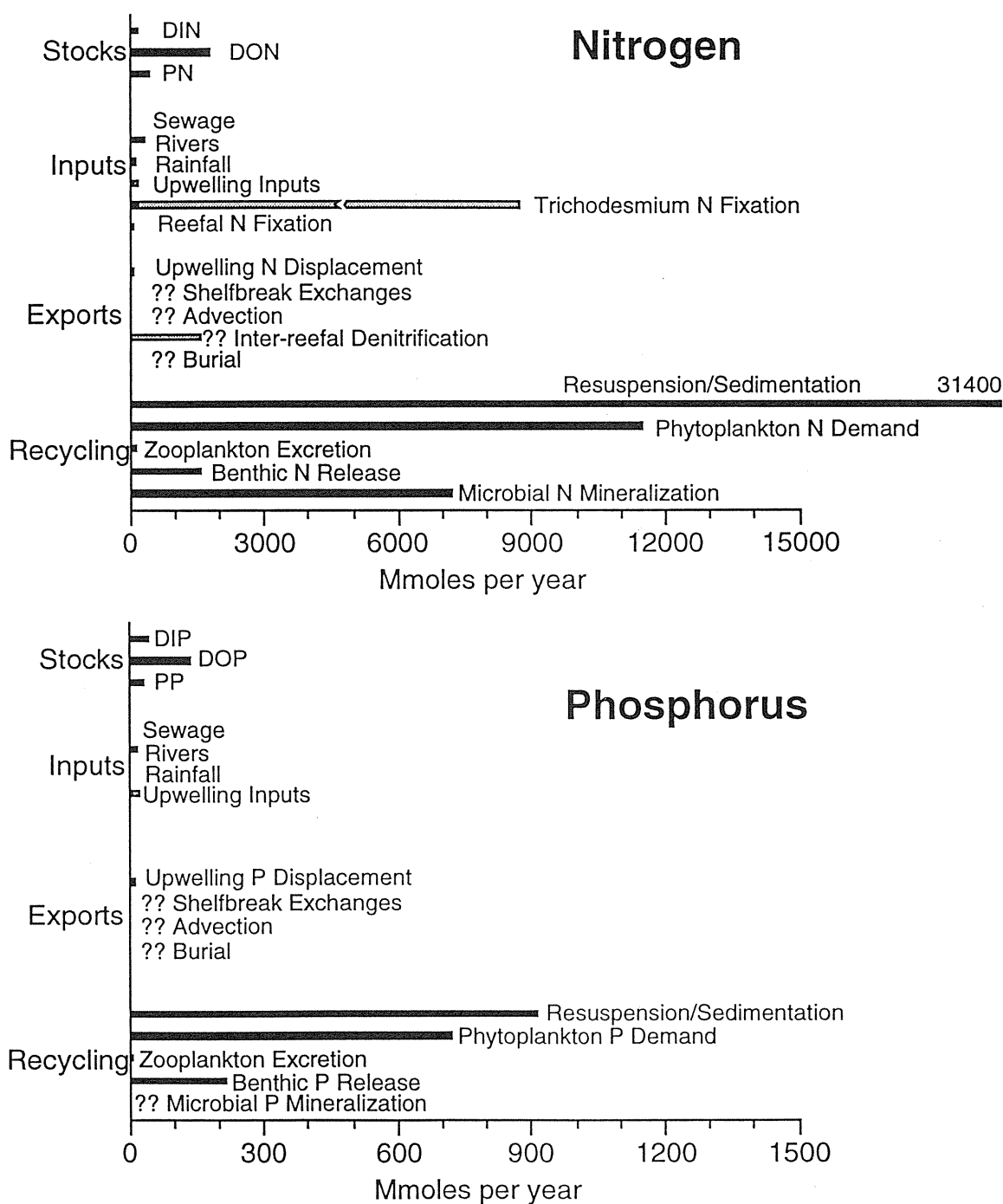


Figure 83. Calculated stocks of nitrogen and phosphorus in the Cairns box in relation to system-scale input, export and recycling fluxes where they could be measured or estimated. All fluxes are for annual periods and are integrated over the area of the box. Question marks indicate significant fluxes for which no estimates have been made.

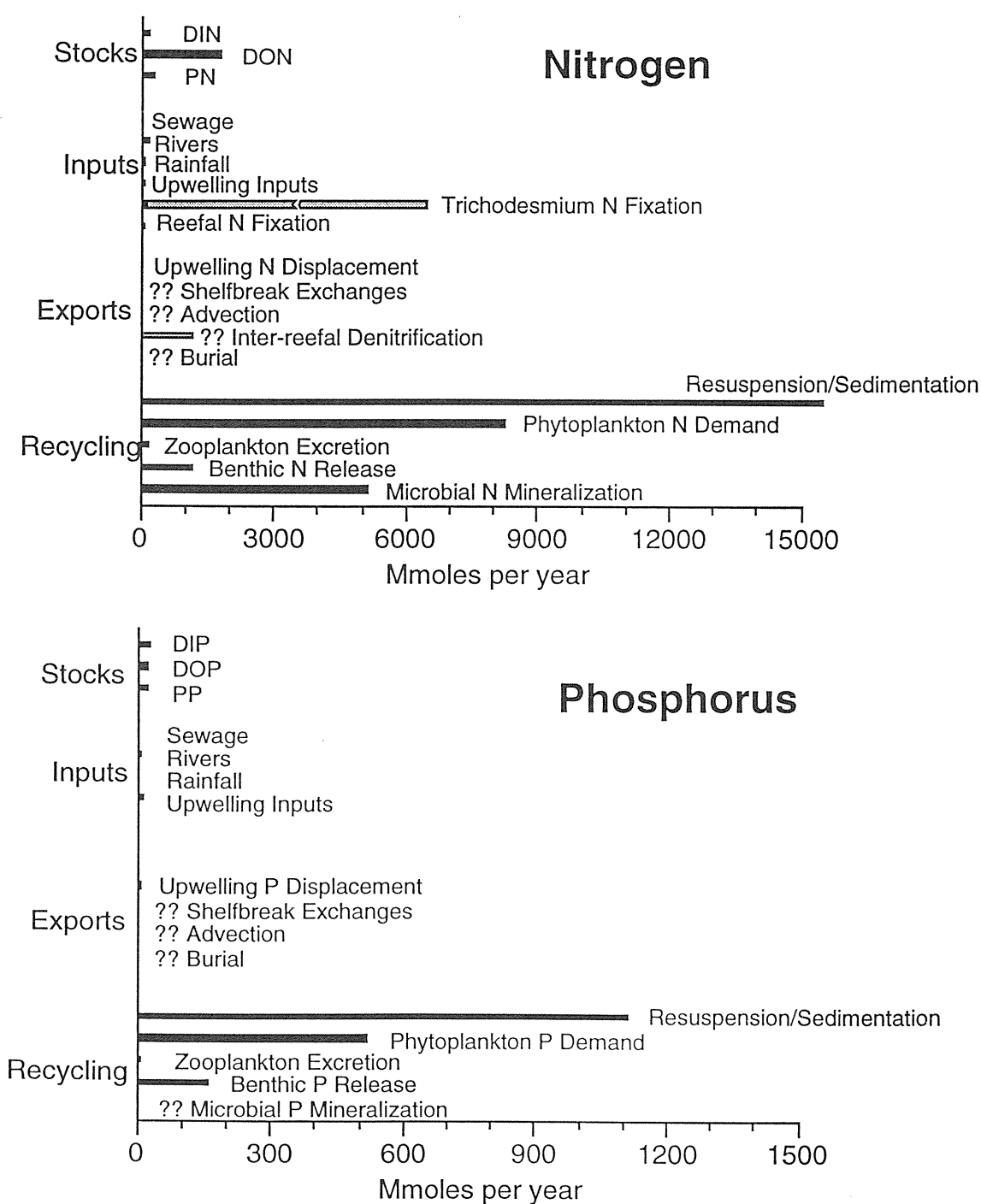


Figure 84. Calculated stocks of nitrogen and phosphorus in the Tully box in relation to system-scale input, export and recycling fluxes where they could be measured or estimated. All fluxes are for annual periods and are integrated over the area of the box. Question marks indicate significant fluxes for which no estimates have been made.

In the case of *Trichodesmium*, the very large potential range of nitrogen inputs from fixation of atmospheric N_2 reflects current estimates of variability in seasonal ranges of trichome abundances (seasonal arithmetic means vs. seasonal medians) extrapolated from one set of samples collected near Low Isles over one year (Marshall, 1933) and the wide range of measured N_2 fixation rates reported in the literature (Carpenter et al., 1987; Carpenter and Capone, 1992).

Conservatively estimated inputs of external ("new") nitrogen to the Cairns box (503 Mmol p.a.) equal 22 percent of the existing nitrogen stock (DIN+DON+PN) within waters of the box. Concurrent phosphorus inputs (18 Mmol p.a.) equal 24 percent of the existing water column phosphorus inventory. Terrestrial nitrogen inputs (sewage, rivers) account for 35 percent of the external inputs identified in Table 39. As will be discussed below, this may well be an underestimate. Shelfbreak upwelling accounted for 10 percent of the quantified inputs, with the remaining 55 percent (rainfall, N_2 fixation) using the low end of estimated *Trichodesmium* inputs being distributed over the area of the box. In the case of phosphorus, identified terrestrial, oceanic and distributed phosphorus sources accounted for 52, 12 and 36 percent of calculated inputs to the Cairns box.

Identified total nitrogen and phosphorus inputs to the Tully box (790 and 28 Mmol p.a.) were, respectively, 33 and 13 percent of the estimated water column inventories. Terrestrial sources accounted for 46 and 59 percent of nitrogen and phosphorus inputs, oceanic sources 10 and 30 percent and distributed sources, 44 and 10 percent. DON and DOP made up a significant proportion of the total water column nitrogen (70-80 percent) and much of the phosphorus (16-30 percent) in either box. The complex composition of these dissolved organic nutrient pools and their cycling dynamics are virtually unknown. Phytoplankton and pelagic bacteria are capable of using DON and DOP (Antia, 1991; Orrett and Karl, 1987). Experimental (e.g. Glibert et al., 1991; Tranvik et al., 1993) and geochemical evidence clearly suggests that oceanic DON and DOP pools are active (Jackson and Williams, 1985). The most active cycling of organic nutrients is associated with low molecular weight compounds such as amino acids (e.g. Andersson et al., 1985; Fuhrman, 1987; Fuhrman and Ferguson, 1986).

Estimates of nitrogen and phosphorus inputs from municipal sewage systems are calculated from data given by Brodie (1991). Brodie's estimates do not include sewage inputs through septic systems, some of which would be included in the river input estimates. The remaining, small, nutrient inputs from septic systems will enter coastal waters, either directly through groundwater or indirectly through ungauged streamflow. Relative to municipal sewage discharges, sewage from boats is an insignificant source of nitrogen and phosphorus at the regional scale. Considering both the Cairns and Tully boxes, sewage is currently a minor component (0.1 to 3.8 percent) of external nitrogen inputs to shelf waters. The imprecision of this estimate is largely due to the considerable uncertainty associated with the estimation of *Trichodesmium* nitrogen fixation rates. The higher relative input from sewage is based on the lower end of nitrogen inputs from *Trichodesmium*. Sewage inputs of phosphorus are relatively more important to shelf budgeting (3 to 13 percent of total P inputs), but are still quantitatively small compared to inputs from riverine sources and upwelling processes.

It is important to remember, however, that essentially all of the sewage and river inputs are delivered directly into the nearshore zone (0-20 m depth) which comprises < 11 percent of shelf area and < 6 percent of shelf volume, depending upon the individual box. These inputs can therefore have a significant local effect on water quality within this depth band (Figures 20-23). The annual sewage-related nitrogen and phosphorus inputs to the Cairns box are equal to 23 and 79 percent of existing nitrogen and phosphorus stocks within the 0-20 m depth band. Percentages of similar order would likely apply to the Tully box, but cannot be calculated due to the lack of DON data for inshore waters.

The retention of sewage-derived nutrients within the nearshore band depends upon interactions between a number of oceanographic, geochemical and biological processes including: sedimentation, sediment-water exchange rates; burial in sediments; denitrification (nitrogen only); incorporation into insoluble minerals (phosphorus only); and lateral mixing into deeper waters of the GBR lagoon. With the exception of some benthic mineralization rates (Alongi, 1989, 1990) magnitude and variability of these processes in the nearshore region are essentially unknown. King and Wolanski (1991), through modelling, suggest that lateral current shear in the GBR lagoon creates a frontal zone between nearshore and outer-lagoon waters which dynamically traps a band of water against the coast. The importance of such dynamic features is likely to vary considerably with time and spatially along the coast due to changes in forcing processes such as coastal inputs of freshwater (buoyancy) and wind stress. There is abundant evidence that most terrigenous sediments (Gagan et al., 1989; Wolanski and van Senden, 1983) and a significant proportion of the more refractory components of terrestrial organic material entering the GBR lagoon are retained near the coast (e.g. Johns, 1988; Gagan et al., 1987).

River runoff is the major external source of external nitrogen and phosphorus to both the Cairns and Tully boxes, contributing N[P] equivalent to 7[9] percent of total stocks in the Cairns box and 15[7] percent of total stocks in the Tully box. As with sewage, all of these inputs flow into the nearshore zone. In the case of the Cairns box, river inputs are equivalent to 189 and 526 percent of water column nitrogen and phosphorus stocks within the 0-20 m depth band. The estimates given are based on water-borne inputs (dissolved + suspended particulates) only and are based solely upon gauged flow from two major rivers. As yet, no quantitative measurements have been made for nitrogen and phosphorus fluxes associated with gross sediment transport by rivers (discussed below) or for freshwater and nutrient inputs from ungauged coastal watersheds. Nor is there any estimate of groundwater nutrient inputs, either directly to the coastal zone (e.g. Johannes, 1980) or to the lower reaches of rivers below the gauging and sampling stations used for river monitoring.

Three of the gauged rivers (Herbert, Murray, Tully) regarded as making nutrient inputs to the Tully box do not, strictly speaking, discharge directly into the Tully box. Combined geostrophic and buoyancy effects (e.g. LeBlond et al., 1986; Pettigrew and Murray, 1986), however, would ensure that most of the freshwater discharged from these rivers travels northward against the coastline and enters the Tully box along its southern boundary. The transport of suspended particulates or sediments and the time frames associated with sediment associated nutrient cycling processes are complex and are not quantified at this time. It is highly likely that a significant proportion of the nutrients coming from the Murray and Tully rivers which eventually enter the Tully box as individual nutrient species, are geochemically and biologically processed/cycled near the river mouths. Some fraction of the water-borne nutrients exiting from the Herbert river, however, are likely stored within coastal sediments and the extensive mangrove forests of the Hinchinbrook channel system before reaching the Tully box. The budget calculations herein do not take this explicitly into account, so the total river nutrient inputs to the Tully box are likely over-estimated to some degree.

The estimated fluxes of nitrogen and phosphorus from north Queensland rivers to the shelf are based solely on the extrapolation of volume-weighted exports from the So. Johnstone River. Statistical and geographical limitations to this extrapolation are uncertain. The integrated annual discharges from the South Johnstone River for the two years quantified in detail (0.80 and $0.87 \times 10^9 \text{ m}^3$) are very close to the long-term average discharge from this river ($0.81 \times 10^9 \text{ m}^3$) with both years in question having one major cyclone related flood. There is no *a priori* reason to assume that discharge-weighted average nutrient concentrations in all of the rivers considered should be similar. Catchment sizes, soils and land use characteristics differ between the rivers involved, though most of the catchments considered herein are relatively small and receive high average annual rainfalls (Hausler, 1991). Mean concentrations of at least three constituents (Table 22) measured under low-flow conditions differ significantly between the

eight rivers. The high within-season variability of flow-rates and nutrient concentrations observed in the So. Johnstone River data clearly indicates that rigorous comparisons will require multi-year data sets with high temporal (daily) resolution. The Russell River catchment above the highway bridge sampling site is most likely the closest to being in a pristine state. In contrast, the Herbert River, the largest river directly affecting the study region, has significant areas of drier grazing lands in the upland portion of its catchment.

Interestingly, the discharge-weighted mean concentration of nitrogen in So. Johnstone River waters (27.3 mmol m^{-3}) is quite close to the discharge-weighted mean concentration of nitrogen for a global suite of large tropical rivers ($29.4 \text{ mmol N m}^{-3}$; Ittekkot et al., 1983). Based on their data, the discharge-weighted mean nitrogen concentration in the So. Johnstone River is only slightly higher, than the mean for the nominally pristine tropical rivers considered (e.g. the Amazon River, mean = $19.6 \pm 10.7 \text{ mmol N m}^{-3}$), but is considerably lower than mean nitrogen concentrations in several of the large rivers of southern Asia (e.g. Ganges, Indus - $46 \pm 27 \text{ mmol N m}^{-3}$). With the exception of the Amazon River, nitrogen fluxes from these large tropical rivers tend to be dominated by particulate nitrogen species, which is not surprising, given the high sediment loads coming from southern Asian rivers (Milliman and Meade, 1983). Based on the slopes of a GM functional regression (Ricker, 1973), the PN/suspended solids ratio for suspended matter in the pooled Herbert, Tully and So. Johnstone River samples was $118 \text{ } \mu\text{mol nitrogen per gram}$ (=moles per tonne) or 0.165% by weight. This ratio was largely weighted toward the ratio for the Herbert River which normally carries a greater suspended sediment load. At present, there are too few suspended sediment samples from other rivers to attempt to draw meaningful between-river comparisons.

In most cases, dissolved phosphorus is not the major form of phosphorus present in river waters. Most river phosphorus remains bound to soil particles (Froelich, 1988). Meybeck (1982) suggested that as a global average, riverine particulate matter contains 37 moles of phosphorus per tonne of sediment (= 0.115 percent of dry weight). The aggregate PP/suspended solids ratio for the Herbert, Tully and So. Johnstone Rivers (again based on a GM functional regression slope) was $11.6 \text{ } \mu\text{moles P per gram}$ (=moles per tonne) of suspended sediment (0.036 percent of dry weight).

Total nitrogen exports from the So. Johnstone River catchment (Figure 38) are dominated by dissolved inorganic species (DIN: 55 percent), most of which are exported during brief flood events. Dissolved organic nitrogen species comprised 38 percent of the total nitrogen exported, while PN contributed only 8 percent. In contrast, 81 of the total phosphorus exports from the So. Johnstone River were in particulate forms (PP), with dissolved inorganic phosphorus (11 percent) and dissolved organic phosphorus (8 percent) contributing nearly equally to the remainder. In both the So. Johnstone (Figure 36) and Herbert Rivers (Figure 43), PN and PP were strongly correlated with suspended solids concentrations. Concentrations of both the PN and PP at the most upstream sampling site on the Herbert (above the floodplain) were very similar to concentrations measured at lower floodplain sites, suggesting that under low flow conditions, agricultural activity on the floodplain contributes relatively little to PN and PP exports from the Herbert River. The sampling program on the Herbert River did not resolve major flood events when considerable amounts of sediment, PN and PP are likely to be mobilized within and exported from the lower catchment. The absence of a pronounced longitudinal gradient in the Herbert River, however, does indicate that the dry hinterlands are a significant source of particulate nitrogen and phosphorus. In contrast, concentrations of dissolved nitrogen and phosphorus species in both the So. Johnstone and Herbert Rivers were weakly correlated, if at all, with discharge. Of the dissolved nitrogen and phosphorus species, NO_3 was the best correlated with flow rates as it is not bound to soil particles and tends to be mobilized during flood events.

The existing data on river nutrient concentrations and export fluxes does not provide a complete picture of nitrogen and phosphorus inputs to the shelf, as nutrient delivery associated with total river sediment fluxes (e.g. Belperio, 1979) have not been resolved. The present river sampling program does not include an estimate of total sediment fluxes from individual catchments. Sediment discharge rates from north Queensland rivers and their impact on reefs are known to be highly episodic and are particularly associated with cyclone-related flooding in individual catchments (e.g. Davies and Hughes, 1983). Between such events, relatively little sediment is discharged onto the shelf, with significant amounts of sediment being accumulated within watersheds and estuaries (Arakel et al., 1989). Overall, most of the sediment exported to the shelf appears to be delivered as suspended material rather than by bedload transport (Belperio, 1979), but the proportion of PN and PP transported has not been apportioned between suspended and bedload fluxes for the rivers in the study region.

As the proportion of PN and PP transported by the So. Johnstone River is relatively large (ca. 40 and 80 percent of total nitrogen), inaccuracies in transport estimates arising from the distribution of sediment nitrogen transport between suspended and bedload fractions may be significant. This is obviously an important topic for future research.

Belperio (1983) estimated long-term average sediment fluxes to the area encompassing the Cairns and Tully boxes to be 2.1 and 4.9×10^6 tonnes per year, respectively. In this calculation, sediment carried by the Herbert and Murray Rivers is presumed to remain outside of the Tully box. The extent to which the sediment-associated nitrogen and phosphorus also remains bound to the sediment is unclear. A range of estimates of potential nitrogen and phosphorus inputs to waters of the Cairns and Tully boxes can be made from these global sediment transport rates. Meybeck (1982) reported that the nitrogen content of river particulate material ranged between 0.1 and 1.3 percent of dry weight (71 - 928 mol N tonne^{-1}). Pristine tropical rivers without sharp relief are likely at the lower end of this range. The slope of the PN vs. suspended solids GM regression for the Herbert, Tully and So. Johnstone rivers was 0.165 percent of dry weight (118 mol tonne^{-1}). Again, on a global scale, Meybeck (1982) estimated that phosphorus associated with river particulates averaged 37 mol tonne^{-1} . No range was given. The local phosphorus content of river particulates, based on the GM regression slope is 11.6 mol tonne^{-1} . For the sediment delivery rates given above, assuming that 87 percent of the sediment transported was in the fine fraction (Belperio, 1979), the measured PN/suspended sediment composition would translate to a nutrient flux of 216 Mmol into the Cairns box and 486 Mmol into the Tully box. Concurrent phosphorus fluxes based upon Meybeck's ratio would be 68 and 157 Mmol per year into the Cairns and Tully boxes, respectively. The sediment-associated phosphorus fluxes into the Cairns and Tully boxes based on the locally derived P/sediment ratio would be 21 and 50 Mmol per year. The lower end of the ranges for sediment-associated nitrogen fluxes overlap with the estimates of riverine nitrogen inputs based on extrapolations of the So. Johnstone River data set (dissolved + particulate), but the calculated phosphorus inputs with sediment are far greater than that based on the locally measured concentrations. Two assumptions can be made, firstly that most sediment transport is of the fine fraction and secondly that the nitrogen and phosphorus content of sediment coarser than silt is likely to be minimal. Therefore the accuracy of the estimate of river fluxes depends upon the extent to which the collections of suspended material for PN and PP measurements reflects the cross-sectional averaged flux of fine particulate material down the river. Nutrient fluxes based on reliable sampling of the fine sediment concentrations should therefore reliably capture the sediment associated nitrogen and phosphorus fluxes.

The fate of sediment associated nitrogen and phosphorus, once out of the rivers, is not known with certainty. Both nitrogen and phosphorus are susceptible to long-term burial in coastal and deltaic sediments. The nominal phosphorus composition of nearshore and mid-shelf sediments (0.03-0.04 percent dry weight) is similar to that measured for suspended particulate matter collected in the freshwater section of rivers. Sediment accumulation rates along the coast have

only been measured at a few sites (e.g. Gagan, 1990) and subsurface profiles of nitrogen and phosphorus are equally scarce (see Alongi, 1989, 1990). Some fraction of both the nitrogen and phosphorus associated with particulate material in river sediments will be mobilized when the sediments move from freshwaters to saline coastal waters (Fox et al., 1986). In the case of nitrogen, most of this mobilization will be due to biological activity with some fraction of the mineralized nitrogen being subsequently removed by denitrification (e.g. Seitzinger, 1987, 1988). Phosphorus availability is in large part related to adsorption-desorption reactions occurring within the estuarine zone (Froelich, 1988; Fox et al., 1986). The magnitude and kinetics of these processes and subsequent biologically mediated redeposition of phosphorus in coastal and shelf waters are not quantified at this time.

With regard to present and future research, there is a priority need to extend the program of daily sampling begun with the So. Johnstone River to the other major rivers in the region in order to quantify discharge-weighted nutrient export and between-river differences in export. Such detailed data sets are required to compare nutrient fluxes from different catchment types and to develop numerical models relating nutrient export to instantaneous and lagged flow rates in the various rivers. The present estimate is based on the assumption that nitrogen and phosphorus concentrations in all rivers are similar to the value established for the So. Johnstone River. A similar approach was taken by Cosser (1988), who used phosphorus loading curves established for the So. Pine River (SE Queensland: Cosser, 1989) to estimate phosphorus inputs to the Cairns region. Cosser's estimate of 2060 tonnes of phosphorus per year into the Cairns box region considered herein (66 Mmol) is ca. 10 times the estimate derived from extrapolation of So. Johnstone River discharge data, but very close to the upper estimate derived from sediment phosphorus composition ratios and estimated sediment delivery rates to the shelf (21-68 Mmoles). The potential magnitude of phosphorus (and possibly nitrogen) imports associated with river sediment transport to the shelf clearly merits increased research effort to refine estimates of fine sediment inputs and the nitrogen and phosphorus composition of that sediment. In the end, quantification of sediment delivery rates may be the most appropriate way to estimate phosphorus inputs to the shelf. Much remains to be done regarding the geochemistry of phosphorus and nitrogen in newly delivered and established shelf sediments. Also, the present river data sets give little indication regarding the extent to which land use practices within catchments influence the nitrogen and phosphorus content of sediments discharged from rivers.

As given, fixation of atmospheric N_2 by *Trichodesmium* in the water column could easily be the largest external source of nitrogen to both the Cairns and Tully boxes. These estimates, however, must be taken with considerable caution as they rely upon a number of untested assumptions about the spatial and temporal distribution of *Trichodesmium* colonies, their size and rates of N_2 fixation by *Trichodesmium* in the GBR environment.

Trichodesmium abundances in GBR waters are known to be highly variable (Marshall, 1933; Revelante and Gilmarin, 1982). At present, there is no appropriate data published which indicates how extensively the large surface aggregations seen in nearshore and GBR lagoon waters are distributed across the shelf or the limits to which quantitative abundance data from one or two sites can be spatially extrapolated. Information on the temporal and depth-related variability in the distribution of N_2 fixation rates within the water column is also lacking. A sampling program was recently established to quantify *Trichodesmium* colony abundances in the water column and to quantify regional-scale variability in abundance. The initial data suggests that colony numbers decrease with distance from shore and that significant temporal and regional-scale fluctuations occur (Furnas, unpubl.). As a result, shelf-scale estimates of *Trichodesmium* abundance based on nearshore or lagoon sites likely overestimate shelf-scale abundances, but it is uncertain by how much. Considerable data needs to be collected to constrain estimates of regional *Trichodesmium* abundance, spatial and temporal variability.

Concurrent sampling is also required to estimate the number of trichomes per colony. *Trichodesmium* rate processes given in the literature are usually scaled to the trichome. Literature values regarding the number of trichomes per colony currently span a 7-fold range (30-200+).

As a result, there is good reason to believe that the given ranges of nitrogen inputs from atmospheric fixation by *Trichodesmium* are far too high. Stoichiometric considerations alone reinforce this. At the nominal N:P ratio (44) measured for *Trichodesmium* colonies (Mague et al., 1977), “new” nitrogen fixation inputs of 140-6,500 Mmol p.a. and 188-8,700 Mmol p.a. for the Cairns and Tully boxes would require concurrent phosphorus inputs of 3-148 and 4-198 Mmol, respectively to sustain “balanced” growth. As no phosphorus is fixed from an atmospheric source, *Trichodesmium* N₂ fixation could consume 13-600 and 11-493 percent of estimated phosphorus inputs to the Cairns and Tully boxes taking the higher end of the upwelling input estimates, but not potential river sediment inputs. The high fixation values are given at this time because they illustrate the present uncertainty regarding the role of *Trichodesmium* in shelf nutrient budgets.

Rainfall was a surprisingly large source of nitrogen and phosphorus to GBR shelf waters. Most of the annual rainfall comes during the summer when northerly monsoonal winds and tropical depressions associated with cyclones have greater importance. For annual, area-averaged rainfalls close to 2.1 meters, calculated rainfall inputs of freshwater to the Cairns and Tully boxes (collectively, 28.9 km³) would be twice the gauged inflow of freshwater from local rivers (15.8 km³) and on the order of 5-6 percent of the total volume of shelf waters. Calculated annual nitrogen inputs from rainfall are of similar order to net nitrogen inputs from shelfbreak upwelling. Phosphorus inputs from atmospheric deposition are considerably smaller: similar to phosphorus inputs from sewage.

Several aspects of the rainfall nutrient fluxes need to be followed up to confirm or refine the estimates made herein. First and most significantly, the high apparent concentrations of organic nitrogen (=total N - DIN) in rain need to be confirmed. The relatively few reported measurements of organic nitrogen in marine rainfall samples suggest that organic nitrogen can be relatively significant. The estimate of DON and PN concentrations in rain is currently based on a very small number of samples (9-12). It is unclear how representative these samples are for the central GBR as a whole or what potential levels of contamination associated with sampling might be. In particular, the rainfall collections were not accompanied by meteorological data that would shed light upon marine or terrestrially influenced upwind sources of the nitrogen and phosphorus (e.g. Graham and Duce, 1981).

The relative importance of rainfall as a source of nitrogen and phosphorus to plankton populations in the ocean has been the subject of some debate (e.g. Paerl, 1985; Knap et al., 1986; Duce, 1986; Paerl et al., 1990). While rainfall inputs appear to be regionally unimportant relative to the annual nutrient demand driven by phytoplankton primary production (Knap et al., 1986), individual rainfall events may be locally significant over short time scales (Paerl, 1985; Willey and Paerl, 1993). The nitrogen loading flux onto the GBR shelf from atmospheric precipitation (14 mmol m⁻² year⁻¹) is approximately half the flux measured in the air pollution influenced Sargasso Sea (29 mmol m⁻² year⁻¹), but similar to that recorded in the central North Pacific Ocean (9.5-19 mmol m⁻² year⁻¹; Duce, 1986). Area-averaged rainfall phosphorus inputs (0.37 mmol m⁻² year⁻¹) to the GBR are 75-180 times greater than recorded in the central south Pacific Ocean, and still 30-40 fold greater than that recorded off the SE United States.

After river inputs, shelfbreak upwelling is the second largest external source of phosphorus to waters of both the Cairns and Tully boxes. The magnitude of nutrient inputs through intrusive upwelling activity is clearly dependent upon both the magnitude and frequency of intrusion

events. During the period of this study, only one significant intrusion event per year was recorded by the shelfbreak TDR moorings in the Cairns region. During a previous study (Andrews and Furnas, 1986), three major intrusion events were recorded over the course of one summer period. The lengths of shelfbreak temperature records are currently too short to resolve the magnitude of inter- and intra-annual variability in the occurrence and frequency of intrusion events. Whether the frequency and magnitude of intrusive activity varies on an inter-annual basis in response to ENSO events is unknown, but is certainly of interest.

The empirical, linear modelling approach taken to convert shelfbreak temperature minima during intrusion events to estimates of intruded water volumes and nutrient inputs, is based on the assumption that the layered vertical structure of water masses observed in the relatively deep, but open waters of Palm Passage also occurs in the shallower, reef strewn waters of the Cairns and Tully boxes. This assumption is likely simplistic. Estimates of the maximum volume of intruded SLW likely to come into either the Cairns or Tully boxes (15-20 percent of total shelf volume) are of similar order to that calculated for the SE continental shelf of the United States (11-36 percent; Atkinson et al., 1980). The linear modelling approach does not include either positive or negative effects of topographic steering and 3-dimensional wake mixing upon the distribution of intruded water. For example, the masking technique used, which employs box-average bathymetric sections, would suggest that intruded water rarely penetrates to the vicinity of Green Island. Recently obtained near-bottom temperature records from the vicinity of Green Island (Furnas, unpubl.) do however show the presence of intruded water near the reef. Obviously, a more comprehensive approach to modelling the behaviour of intrusion events is needed, but the effort will almost surely require multi-layered hydrodynamic models to achieve realistic simulations.

The magnitude and variability of dissolved and particulate nitrogen and phosphorus concentrations in outer shelf waters is a major constraint upon our ability to quantify both the size and the accuracy of net upwelling nitrogen and phosphorus inputs. The calculated net upwelling inputs to the Cairns box are based on the assumption that 86 percent of the nitrogen and 37 percent of the phosphorus in displaced surface waters are DON and DOP. Obviously, the magnitude of displacement fluxes is strongly dependent upon the calculated mean (or median) DON or DOP concentration in outer-shelf waters. PN and PP contributed an additional 11 percent of the nitrogen and 26 percent of the phosphorus exported. DON exports from the Cairns box, based on the median summer DON concentration in outer shelf waters were only 1.5 times the imports of DON in the intruded water and 44 percent of the NO_3 stock intruded. No net input of nitrogen to the Cairns box would occur if DON+PN concentrations in displaced outer shelf surface waters were $2.3 \mu\text{mol N l}^{-1}$ greater (a 37 percent increase). In the case of phosphorus, however, the necessary increase of DOP+PP concentrations in displaced water would have to be on the order of 400 percent. Coefficients of variation (CVs) for seasonal depth-weighted mean water column concentrations of DON on the outer shelf ranged from 12 to 49 percent (Tables 5-8). Seasonal CVs for outer shelf PN stocks ranged between 26 and 33 percent.

The validity of the estimate of atmospheric N_2 fixation by coral reefs revolves around three key assumptions: that the estimate of structural habitat areas derived from analysis of a whole-GBR sample of reefs is applicable to the population of reefs in the central GBR; that the extrapolation of measured nitrogen fixation rates by Larkum et al. (1988) to structural habitat areas is appropriate for the GBR; and that the N_2 fixation rates and seasonal variability measured by Larkum et al. (1988) at One Tree Reef (23°S) are appropriate to conditions in the central GBR (16-18°S).

At present, while there are good estimates of reef areas (GBRMPA Reef Gazetteer) and reef structural taxonomy (Hopley et al., 1989), there are no published shelf-scale estimates of reef

structural habitat areas at a scale useful for extrapolating regional biological and geochemical rate processes. A very preliminary examination of the classified satellite imagery indicates that reef-top (< 2 m depth) and shallow sand habitat areas are only roughly proportional to reef size (Figure 2). The error for individual reefs is quite large and inversely proportional to size (Figure 3). These two habitats are the primary classified shallow habitat types, with deeper sandy lagoonal or deep slopes making up much of the remaining classified area of the reefs observed. Steep slopes, while supporting concentrated biological populations and high area-specific rate processes, contribute relatively little to total reef area. Classified slope areas are subject to greater uncertainty due to their narrow vertically projected areas relative to pixel sizes.

The present estimate of reef flat area (Table 2) emphasizes the shallow hard substrate zone with the greatest contribution to reef-scale nitrogen fixation. The highest area-specific N_2 fixation rates are consistently recorded on hard substratum types characteristic of reef flats and reef crests (Larkum et al., 1988), contributing an estimated 80-85 percent of whole-reef nitrogen fixation. Similar habitat types and sand at deeper depths have a much lower fixation potential (Wilkinson et al., 1984; Larkum et al., 1988; Capone et al., 1992).

The area-specific nitrogen fixation measurements given by Larkum et al. for hard substrata on One Tree Reef ($5-10 \text{ nmol cm}^{-2} \text{ hr}^{-1}$; $11-23 \text{ kg ha}^{-1} \text{ year}^{-1}$) are of similar order to those reported by Wilkinson et al. (1984) for the central GBR (19° S ; $2-4 \text{ nmol cm}^{-2} \text{ hr}^{-1}$, mean = $20 \text{ kg km}^{-2} \text{ year}^{-1}$) for similar small pieces of substratum. Larkum et al. (1988) made a more comprehensive attempt to resolve methodological, temporal, spatial, roughness and habitat related effects on reef-scale nitrogen fixation rates. The relatively low degree of seasonal variation in measured rates (ca. 20 percent) suggests that latitude may not be an important factor and that the data from One Tree Reef (annual temperature range $18-30^\circ \text{C}$) can be reasonably extrapolated to the central GBR (annual temperature range $22-30^\circ \text{C}$). A significant component of variability in the measurement and extrapolation of nitrogen fixation rates to larger scales is associated with short-term (day-to-day) and local (several m^2) effects. This is understandable in that the highest fixation rates are associated with disturbed (grazed) substrates. The variability likely reflects local grazing and disturbance processes necessary for the development of the actively fixing cyanobacterial communities.

A significant question revolves around the accuracy of the extrapolation of rates measured on small, geometrically simple samples to structurally complex reef habitats. At present, this conversion is subject to considerable uncertainty and will likely remain so until something more rigorous like 3-dimensional fractal surface modelling becomes practical. Reef-scale geochemical processes must be quantified at areal scales between m^2 and km^2 . Nitrogen fixing assemblages operate and are affected by biological and physical processes at scales between mm^2 and m^2 . The extrapolations from measurements made on individual samples to habitat areas must therefore be tempered with some caution.

Overall, nitrogen fixation by reefs is a noticeable, though minor, contributor of nitrogen to each shelf-scale box. It is unclear how much of this fixed nitrogen is actually exported from reefs to the surrounding waters of the Cairns and Tully boxes. Overall, Kinsey (1991b) estimated that reefs may export one percent (1%) of their gross primary production. Whether similar exports of nitrogen occur remains to be fully tested. Zones within reefs appear to export fixed nitrogen (Wiebe et al., 1975), but at this time the magnitude of nitrogen storage or loss processes such as burial and denitrification occurring at the whole-reef scale is unknown. Export processes removing fixed nitrogen from reefs vary seasonally and in response to specific events (Barnes, 1989). At some times, however, nitrogen losses from individual reef systems can be very small (e.g. Crossland and Barnes, 1983). Such variability will require that detailed temporal and spatial sampling be carried out to resolve export events. Unifying principles to deal with the structural and hydrodynamic heterogeneity of reefs will likely have to be included as well.

Even then, other as yet undefined techniques will be needed to resolve whether the nitrogen exported was initially fixed by reef organisms or was merely trapped from surrounding waters by reef assemblages which can efficiently remove dilute nutrients from solution (Atkinson, 1992).

A number of key system processes are unquantified at this stage and can only be roughly estimated. These processes include nitrogen fixation, utilization and denitrification in coastal and open shelf sediments, burial of fixed nitrogen and phosphorus, longshore advection out of the study boxes for significant local inputs and lateral exchanges of water and nutrients with the oligotrophic East Australian Current. The denitrification and long-term burial fluxes are accessible to direct measurement. Longshore advection and lateral exchange fluxes must be estimated by differences from known and quantifiable fluxes, or by modelling approaches. Under the assumption of long-term steady state taken in developing this budget, net longshore advection of nutrients into and out of the boxes is therefore assumed to be negligible. Andrews and Pickard (1990) calculated a range of residence times for shelf waters (2-20 weeks) based on estimated values of long-shelf current shear, wind-band forcing of intrusions and tidal exchange. The extent to which these processes are additive or exclusive was not resolved, though most likely they are on episodic time scales.

It is unclear to what extent the existing direct measurements of nitrogen fixation in reefal sediments (Capone et al., 1992) can be extrapolated to open shelf sediments. If the mean rate ($7.9 \mu\text{mol m}^{-2} \text{hr}^{-1}$) is extrapolated to the area of shelf in the two boxes, it would suggest that an additional 411 and 542 Mmol (5750 and 7600 metric tonnes) of nitrogen are fixed annually within the Cairns and Tully boxes. These inputs are very large relative to other system inputs such as rivers and upwelling and must be viewed with caution until verified. Active nitrogen fixation was measured to depths of at least 4-8 cm in reef sediments, though most was measured at the sediment surface. If the surficial rates are related to light input, nitrogen fixation by sediments at deeper depths can be expected to be considerably lower.

At present, there is no direct measurement of sediment associated denitrification in GBR reef or open shelf sediments (Capone et al., 1992). These measurements were carried out at shallow depths (< 20 m). Central GBR sediments vary greatly in texture (e.g. Maxwell, 1968; Alongi, 1989). The anaerobic conditions normally presumed necessary for denitrification are commonly observed at depths ranging from < 1 cm in muddy coastal sediments to 5-10 cm in granular outer-shelf carbonate sands and gravels (Alongi, pers. comm.). However, Capone et al. (1992) commented that locally significant rates of denitrification were measured in nominally aerobic reef sediments.

Field measurements of denitrification rates in subtropical estuarine (Seitzinger, 1987), coral reef sediments (Seitzinger and D'Elia, 1985; Capone et al. 1992) and elsewhere clearly indicate that denitrification processes are significant in sediment nutrient budgets. Seitzinger (1987) calculated that denitrification in estuarine sediments removed an amount of nitrogen equivalent to the DIN returned to the water column by benthic mineralization processes (ca. 1200 and 1600 Mmol for the Cairns and Tully boxes, respectively). Seitzinger and D'Elia (1985) measured denitrification rates in slurries of sediments from a Caribbean reef lagoon equivalent to an areal rate of $50 \mu\text{mol N m}^{-2} \text{hr}^{-1}$. Extrapolated to the areas of the Cairns and Tully boxes, this rate would lead to potential annual shelf-scale denitrification fluxes of 2600 and 3400 Mmol. Such extrapolations must be viewed with caution as denitrification rates are very dependent upon NO_3 production and availability, supply of carbon and the physical setting. The rate measured by Seitzinger and D'Elia is likely an overestimate as the sediment used came from a backreef seagrass bed where elevated organic inputs could increase microbial denitrification rates (Seitzinger and Nixon, 1985). The average of actual sediment denitrification rates ($0.25 \mu\text{mol m}^{-2} \text{hr}^{-1}$) measured at deeper reef sites (20 m) by Capone et al.

(1992) is considerably lower and if applicable to the total area of central GBR shelf sediments would result in estimated denitrification fluxes of 13 and 17 Mmol for the Cairns and Tully boxes. As yet, no denitrification measurements have been made in nearshore sediments. Due to the smaller area involved, denitrification in reef sediments (Capone et al. (1992) mean value = $0.51 \pm 64 \mu\text{mol m}^{-2} \text{ hr}^{-1}$) is a relatively small nitrogen sink in either box ($1.1 \text{ Mmol N year}^{-1}$).

On a short term (< 1 week) basis, shelf-scale denitrification fluxes are not likely to be closely linked to organic production and sedimentation rates. First, as will be discussed below, organic materials on the benthos are subject to recurring resuspension and redeposition. Deposition events involving freshly produced, as opposed to recycled organic matter, will be temporally blurred. Inshore and offshore sediments also contain substantial stocks of organic matter and associated nitrogen (e.g. Capone et al., 1992) relative to denitrification fluxes. It is likely that most of the denitrification occurring in GBR shelf sediments will occur through the processing of nitrogen stocks already within the sediment. The uptake of NO_3 from the water column by outer-shelf sediments (Alongi, 1989; Table 30) and its ready transformation ($0.34 \mu\text{mol m}^{-2} \text{ hr}^{-1}$; Capone et al., 1992) is indicative of both the permeability of the sediments and the high activity of denitrifying bacteria. Alongi identified denitrification as the likely reason for the observed discrepancy of sediment-water column O:N:P flux ratios (350:9:1) from values expected if living or newly dead plankton were the source of organic matter (276:16:1). Nitrogen mineralization, nitrification and denitrification rates in muddy sediments are known to be closely coupled, both spatially and in magnitude (Jenkins and Kemp, 1984; Capone et al., 1992).

If, as a first approximation, the magnitude of shelf-scale denitrification is taken as being equal in magnitude to benthic excretion of DIN (Seitzinger, 1987), then the potential removal of nitrogen by denitrification exceeds the summed external inputs from all quantified sources, river sediment inputs included, taking the lower end of the range of *Trichodesmium* fixation estimates for reasons given above. This would indicate that either inputs have been vastly under-estimated, or that sediment denitrification rates must be considerably lower than benthic DIN excretion rates. If the much lower shelf denitrification rates extrapolated from direct measurements made on reef sediments are appropriate, the amount of nitrogen removed by denitrification (13 and $17 \text{ Mmol year}^{-1}$ for the Cairns and Tully boxes) is roughly equivalent to the relatively small inputs from sewage (19 and $10 \text{ Mmol year}^{-1}$; Brodie, 1991).

At the simplest level, net burial rates of nitrogen and phosphorus in shelf sediments are equal to the average concentration (mol cm^{-1}) of these elements in a thin layer at a depth below the horizon of sediment mixing, biological activity and active diffusion, multiplied by the long-term average sediment accumulation rate (cm year^{-1}). This approach assumes that the current net nitrogen and phosphorus deposition rates and current sediment accumulation rates equal the long-term average rates. Whether sediment accumulation rates, particularly in nearshore waters, have altered in recent times due to human activities is a topical management question. A variety of information (e.g. Prove and Hicks, 1990) suggests that modern sediment fluxes from coastal watersheds have increased due to agricultural activity (Arakel et al., 1989). There are not, at present, any reliable measurements of the nitrogen and phosphorus content of central GBR shelf sediments at depths greater than 20 cm (Alongi, 1989). In a number of reef and shelf habitats, the bioturbation horizon is deeper than 20 cm. Likewise, tropical cyclones are known to resuspend shallow reef and some shelf sediments to depths up to 20 cm (Gagan et al., 1989).

Shelf sediment accumulation rates, particularly within the last 100 years, are poorly quantified (e.g. Gagan, 1990). Belpiero (1983) estimated net sediment accumulation rates in the inshore zone near Townsville (ca. 19°S) which are influenced by Burdekin River sediments are on the

order of 0.2-0.4 mm year⁻¹. Gagan (1990) found maximal sediment accumulation rates on the order of 0.5 cm year⁻¹ near river mouths. Sediment accumulation rates were calculated to be ≤ 0.1 mm year⁻¹ on the mid and outer shelf where total sediment accumulation away from the immediate vicinity of reefs was often < 1-2 m over the last 10,000 years (Belperio, 1983; Scoffin and Tudhope, 1985). These estimates are largely based on the interpretation of shallow seismic profiling data. With the exception of Gagan's results, the available estimates have not been corrected for sediment mixing by isotopic methods. Almost all sediment cores taken by Gagan near the mouths of rivers show evidence of penetration of the short-lived natural isotope, ²¹⁰Pb, to depths of at least 40 cm, indicating vertical mixing in the sediment. Vertical profiles of solid phase sediment nitrogen and phosphorus in the upper 20 cm show no vertical structure. Some seasonal variability is apparent (Alongi, 1989).

Using the above estimates of sediment accumulation rates, it is possible to make a first-order estimate of long-term nitrogen and phosphorus burial rates on the shelf. Shelf sediments (Alongi, 1989) have a water content of 33 percent (= 67 percent dry matter). The dry matter has a bulk density on the order of 1.5 g cm⁻³. While some seasonal and cross-shelf differences in the nitrogen and phosphorus content of shelf sediments are apparent, the differences are relatively small. Shelf sediments in the northern and central GBR have a nitrogen content generally falling between 0.06-0.1 percent of dry weight and a nominal phosphorus content between 0.02-0.04 percent of dry weight (Alongi, 1989; Furnas et al., 1990a,b). By way of comparison, material collected in the moored sediment traps had a mean nitrogen and phosphorus content of 0.8 and 0.07 percent of dry weight, respectively.

For a sediment with a dry weight composition of 0.1 percent nitrogen, a volume of surficial sediment 1 m² in area and 1 cm thick (10⁴ cm³) would contain 714 mmol nitrogen (= 10 g) and 97 mmol phosphorus (= 3 g). A long-term deposition rate of 0.1 mm year⁻¹ would therefore be 1 percent of this rate on an areal basis (7.1 mmol N m⁻² year⁻¹; 0.97 mmol P m⁻² year⁻¹). If one takes the mean sediment deposition rate within the 20 m isobath as being 0.4 mm year⁻¹ (Belperio, 1983) and 0.1 mm year⁻¹ at depths deeper than 20 m (ignoring reefs for convenience), the annual sediment burial fluxes for the Cairns box would be 58 Mmol nitrogen and 12 Mmol phosphorus. Corresponding box-scale annual burial fluxes for the Tully box are calculated to be 67 Mmol nitrogen and 14 Mmol phosphorus. Obviously, these estimates are subject to uncertainty and need to be improved with better estimates of net sediment accumulation rates and more detailed areal and seasonal weighting of sediment nitrogen and phosphorus content.

Estimates of long-term nutrient removal by burial are of similar order to inputs from shelfbreak upwelling processes and are more consistent with the river nutrient delivery rates calculated herein than with the higher estimates given by Cosser (1988). Considerably higher local rates of nutrient deposition and burial would be expected for areas near river mouths, but as the inshore region comprises only a small fraction of total shelf area, the overall effect of high burial rates in the nearshore will be reduced by the much larger area of the outer shelf with little net deposition.

Calculated estimates of *in situ* mineralization and recycling processes, though indirect, are very, very large in comparison to most known or estimable nitrogen and phosphorus inputs to, and losses from, the two boxes (Figures 83 and 84 Bottom). The disparity between the magnitudes of quantified inputs and estimates of recycling fluxes clearly indicates that on a regional, time averaged basis, external nutrient inputs exert only an incremental influence on nutrient stocks or availability in GBR shelf waters. Under conditions approximating the equilibrium conditions assumed for the budgeting exercise, the bulk of daily phytoplankton and algal demand for nitrogen and phosphorus would be met by water column recycling processes mediated by macrozooplankton, microzooplankton, heterotrophic flagellates and bacteria. Likewise, net fluxes of nitrogen (and likely phosphorus) into and out of sediments appear to be small relative to natural recycling fluxes within the sediments (Capone et al., 1992). All of the important

fluxes affecting dissolved nutrient species occur within a very large background of sedimenting and resuspending particulate material which is itself subject to continual consumption and mineralization in the water column and benthos.

The very high fluxes of mass, carbon and nutrient (N, P) sedimentation measured in both the Cairns and Tully boxes are unlikely to result from sedimentation of freshly formed particulate materials generated either within the water column or advected laterally away from reefs, though these sources are ultimately the major sources of particulate material in shelf waters. Rather, most of the particulate organic matter collected by the sediment traps, whether moored or free-drifting, is resuspended from the benthos. The coarse nature of mid- and outer-shelf sediments (e.g. Scoffin and Tudhope, 1985; Alongi, 1989) clearly implies the presence of sufficient turbulent energy within the system to remove fine sediment particles. This fine particulate material appears to be deposited on the continental slope (Alongi and Pichon, 1988), though the organic content of slope sediments is very low (Alongi, 1987).

The elemental composition of material collected in the moored sediment traps at the southern end of the Tully box (0.8 percent N, 0.07 percent P by weight) reflects dilution of water column particulate material (median nitrogen composition = 1.81 percent of dry weight, median phosphorus composition = 0.32 percent) by resuspended sediments. Using the nitrogen content, the trapped material appears to be a mixture consisting of 40-45 percent water column particulates and 55-60 percent resuspended sediment. If phosphorus is used, however, the trapped material appears to be 88-91 percent resuspended material. For the drifter traps deployed on the mid- and outer-shelf in the Cairns box, the higher median nitrogen content of trapped material suggests a 50 percent dilution of water column particulates by resuspended material. On the basis of phosphorus, however, it would appear that ca. 95 percent of the material collected is resuspended sediment. Reasons for the discrepancy are not clear. Other elements or isotopes may give a clearer picture. It may in part be due to the analytical procedure for phosphorus used herein for sediment trapped material (acid-persulfate digestion followed by colorimetric phosphorus quantification) compared to the method used by Alongi (1989) for sediments (perchloric acid digestion followed by inductively coupled plasma emission quantification). The operational fractionation of phosphorus species in natural soil and sediment samples is largely dependent on the digestion procedures used to extract phosphorus from the matrix (Froelich, 1988).

The occurrence of large amounts of resuspended material means that measured sedimentation fluxes of carbon, nitrogen and phosphorus bear little relationship to short-term (day-to-day) temporal variability of primary production in the water column. While it is known that outer-shelf phytoplankton biomass and productivity responds to nutrients delivered by upwelling events (Furnas and Mitchell, 1986, 1987), the sediment trapping program to date has not observed any coupling between intrusion events and deposition. Rather, the amount of material collected by sediment traps appears to be influenced by regional levels of weather mediated sediment resuspension and time averaged regional fluctuations in primary production. Particulate organic matter in the water column is continuously subject to processes of aggregation, disaggregation, decomposition and feeding by planktonic organisms. Further analysis of this data set will include examination of sedimentation dynamics in relation to current and prior wind stress conditions.

Mineralization of nitrogen and phosphorus by macro- and microzooplankton (tintinnids and larger) was a minor, but not insignificant source of nutrients to the water column (Figures 83 and 84 Bottom). The general similarity between weight-specific nitrogen and phosphorus excretion rates of copepods and copepod assemblages from a number of tropical regions (e.g. Ikeda et al., 1982a,b; Smith et al., 1981; Verity, 1985) suggests that the estimates of macrozooplankton nutrient excretion fluxes derived from community biomass (dry weight) measurements and literature derived excretion rates are likely to be reasonable. Net

zooplankton (> 73 μm fraction) assemblages throughout the GBR are dominated by copepods at most times of the year (Liston, 1990). Net zooplankton contributed 5-10 percent of nitrogen demand in the Cairns and Tully boxes, respectively (Table 39). Phosphorus mineralization was similarly calculated to be between 5 and 10 percent of demand. Where ecosystem input and mineralization fluxes have been more comprehensively budgeted (e.g. Smith et al., 1981; Harrison et al., 1983; Furnas et al., 1986), the contribution of pelagic zooplankton tends to fall within this general (low) range. The low proportion of nitrogen and phosphorus demand cycled by macro- and microzooplankton is consistent with the observation that 50-90 percent of the water column primary production in GBR shelf waters is attributable to picoplankton sized algae (< 2 μm) which are largely unavailable to net zooplankton consumers (Johnson et al., 1982). The magnitude of the estimated zooplankton nitrogen and phosphorus mineralization fluxes relative to demand derived from primary production implies that zooplankton consume a similar fraction of the organic material produced: 5-10 percent plus that going into fecal pellets (ca. 2 percent; Small et al., 1983) and secondary production (as yet unquantified).

At present, the accuracy of zooplankton excretion fluxes are largely constrained by the magnitude of spatial and temporal variability in the estimations of macrozooplankton biomass within the central GBR, and to an unknown, but likely lesser extent, by estimations of the biomass and community structure of larger microzooplankton (e.g. tintinnids, juvenile crustaceans, larger protozoans). The excretion flux estimates calculated herein assume that the biomass of larger microzooplankton and coupled excretion fluxes are a constant, small percentage of macrozooplankton biomass and excretion fluxes (Ikeda et al., 1982b). This assumption has not as yet been examined in detail within the Cairns and Tully boxes.

Microbial mineralization of dissolved and particulate organic matter in the water column is clearly the major source of inorganic nitrogen (e.g. Harrison, 1978) and likely the major source of inorganic phosphorus (e.g. Smith et al., 1985) as well. Harrison (1978) showed that very small organisms (< 1 μm) are responsible for much of the water column mineralization. This observation has been largely borne out elsewhere, but the proportion varies from system to system. The microbial nitrogen mineralization flux is calculated from what is admittedly a very small number of direct measurements (Hopkinson et al., 1987) and its extrapolation from these measurements is based upon a number of untested assumptions regarding local variability in rates, cross-shelf gradients and seasonal fluctuations in mean rates. The obvious question is whether mineralization rates measured during winter in and close to a coral reef are truly applicable to open shelf waters. Questions regarding short-term temporal variations in microbial mineralization rates cannot be addressed at this time. It is known that mineralization rates vary with the physiological state of micro-flagellate populations and the chemical composition of their prey (Andersson et al., 1985; Goldman et al., 1987). There are at present, no comprehensive estimates of microzooplankton and microflagellate abundances or biomass in GBR shelf waters, growth rates or data providing functional connections with microbial abundance/growth and feeding rates. Ayukai (1992), however, has recently provided some limited estimates from a coral reef lagoonal environment. Given the rapid growth rates of microflagellate and bacterial populations, considerable short-term temporal and local spatial variability in biomass and rates are to be expected. Despite their limitations, Hopkinson et al.'s measurements likely put a proper order of magnitude on the estimate of microbial mineralization inputs.

With the possible exception of Dunlap's (1985) measurements of external phosphatase activity in waters flowing over coral reefs, no equivalent measurements are available for microbial mineralization of phosphorus in the GBR water column. Dunlap measured substrate hydrolysis rates between 1 and 2 $\text{nmol P l}^{-1} \text{ hr}^{-1}$ ($= 8.8\text{-}17.5 \text{ Mmol P km}^{-3} \text{ year}^{-1}$). As these rates were derived from enzyme assays with artificial additions of an unnatural substrate, the rates obtained must be regarded as being potential rates. Assuming that DOP mineralization occurs

at the rates given by Dunlap and is distributed uniformly throughout the water column (all Dunlap's measurements were done with surface waters), this range would translate to annual phosphorus turnover fluxes of 1700-3450 Mmol and 2700-5500 Mmol for the Cairns and Tully boxes, respectively. These calculated turnover fluxes are clearly far in excess of estimated phosphorus demand from primary production. The distribution of phosphatase activity away from reefs is unknown as are the factors which control its magnitude. These high rates provide a mechanism for the observation that dissolved inorganic phosphorus (PO_4) is virtually always detectable in shelf waters regardless of the concentration of inorganic nitrogen. The apparent high potential for DOP mineralization indicates that pelagic bacteria and other micro-organisms can readily supply phytoplankton demand for phosphorus in the presence of a suitable DOP source.

As no microbial phosphorus mineralization measurements have been made in the GBR, the most appropriate results are those from the phosphorus mineralization experiments carried out in coastal and oceanic waters near Hawaii (Smith et al., 1985; Orrett and Karl, 1987). There, phytoplankton (including bacteria) phosphorus demand and microbial phosphorus mineralization appear to be balanced when considered on time scales of 24 hours. In fact, it is likely that phytoplankton phosphorus uptake is constrained by the *in situ* mineralization rate. As elsewhere, mineralization by larger zooplankton (and benthic sources) is insufficient to meet instantaneous phytoplankton demand. Because of the tendency of nutrient-limited phytoplankton to take up dissolved nutrients at high rates when available, potential demand for nitrogen and phosphorus almost surely exceeds production by mineralization.

19. THE BALANCE BETWEEN UPTAKE DEMAND AND SOURCES OF NITROGEN AND PHOSPHORUS

Added together, estimated inputs of nitrogen to the water column from benthic mineralization, macro- plus microzooplankton excretion and water column microbial mineralization account for 87 and 82 percent of the nitrogen demand arising from calculated phytoplankton primary production in the Cairns and Tully boxes, respectively. External sources of nitrogen (taking the low end of the potential *Trichodesmium* fixation rates) account for 6-7 percent of phytoplankton nitrogen demand. For the sake of this calculation, it is assumed that reefs export little nitrogen to surrounding shelf waters. This may not be the case (Kinsey, 1991b). In any case, the contribution of reefs would be negligible. River and sewage inputs of nitrogen would account for 2-3 percent of the nitrogen demand. Collectively, recycling and external sources do not meet phytoplankton demand because of the potentially large losses of nitrogen from the shelf system through denitrification in sediments, burial in shelf sediments and lateral mixing/advection to the EAC. Either inputs have been underestimated or in fact, the primary production measurements over-estimate phytoplankton nutrient demand. Quite clearly, an expansion of the contribution of nitrogen fixation by *Trichodesmium* could meet and exceed the shortfall in nitrogen, however, such an increase would also be readily apparent through an increase in primary production. This would have to be confirmed by extensive field sampling and experimental measurements of both carbon and nitrogen fixation by *Trichodesmium*. There is some scope for additional nitrogen inputs via sediment which were not fully accounted for in the extrapolation of So. Johnstone River nutrient fluxes, but this is also likely to be small.

In making these comparisons, it should be borne in mind that carbon and nutrient uptake are not always in balance, whether at the scale of individual cells (Goldman et al., 1981), ecosystem (Smith and Kinsey, 1989) or oceans. Over time scales of 24-hours, primary production rates appear to be a reasonable estimator of phytoplankton biomass production (Furnas, 1982). Within shorter time scales, however, it is readily possible that the primary production estimates may over-estimate nutrient demand. At present, there are no concurrent measurements of phytoplankton carbon and nitrogen [or phosphorus] uptake to calibrate nutrient demand to midday primary production rates. Obviously, there is a clear need to do so.

A similar comparison cannot be made for phosphorus at this time due to a lack of a reasonable estimate for water column phosphorus mineralization rates. As shown above, external sources are likely small relative to internal recycling fluxes which hold demand in check. Sewage and river inputs of phosphorus are on the order of 2 percent of the estimated phytoplankton phosphorus demand. The continual presence of PO_4 in shelf waters at virtually all times and the low DIN/DIP ratio of shelf waters (Furnas and Mitchell, 1986) suggests that biomass levels in the pelagic ecosystem of the central is nitrogen limited. This conclusion requires future examination (Smith, 1984) as better estimates of the magnitude of nitrogen fixation by *Trichodesmium* become available.

20. SUMMATION

This report presents the first quantitative estimates of nutrient pool sizes and nutrient fluxes for a shelf-scale section of the Great Barrier Reef. The region between Cape Tribulation and Dunk Island, adjoining Cairns, is characterized by the close proximity of outer-shelf reefs to the coast, the highest regional level of reef-based tourism and a high level of agricultural, urban and hinter-land development. The budgets developed indicate that instantaneous nutrient availability within central Great Barrier Reef shelf waters is still largely controlled by natural input and recycling processes. Human-related inputs remain at low incremental levels. This is almost always the case for large natural ecosystems. What we wish to learn is how systems of this scale and type respond to such incremental inputs and where the perceived desirable qualities of the ecosystem become endangered by them.

The budgets for the nutrient elements nitrogen (N) and phosphorus (P), as presented, are not complete or balanced. The magnitude of several important system fluxes remain to be verified by direct measurement or other means. In particular, rates of cross shelf diffusion (turbulent mixing), lateral exchanges between outer shelf waters and the East Australian Current (EAC), denitrification in shelf sediments and microbial mineralization in the water column need to be measured or estimated in a manner which will allow a more fully verified description of system-scale fluxes to be made. Of the above, sediment denitrification rates and water column mineralization rates are open to direct measurement. In contrast, lateral mixing and exchange fluxes will almost certainly have to be modelled to estimate their magnitude. It is essential that cross-shelf mixing rates be determined as this process will be a major determinant of shelf water quality, particularly within the nearshore zone.

The high intrinsic growth, nutrient uptake and production potential of phytoplankton in well-lit, warm tropical seas will almost always ensure that concentrations of dissolved inorganic nutrients remain low in central Great Barrier Reef waters. If pronounced increases in dissolved nutrient levels occur for some reason, these increases will be ephemeral as phytoplankton rapidly take up the nutrients. Changes in water quality will therefore be most apparent through regional increases in phytoplankton biomass and suspended particulate materials. Monitoring programs need to focus on collecting high quality estimates of phytoplankton biomass and population status over periods long enough to cancel biases arising from short-term variability.

A significant proportion of both the nitrogen and phosphorus in the water column was present in particulate and dissolved organic form. The high sedimentation fluxes of particulate nitrogen and particulate phosphorus measured in both inner and outer shelf waters relative to external inputs imply equally large resuspension fluxes and indicates that a substantial proportion of the particulate nitrogen and particulate phosphorus within the water is detrital in nature. The general correlation between particulate nitrogen, particulate phosphorus and chlorophyll clearly suggests that almost all of this material is of marine origin (Gagan et al., 1987). The dynamics of particulate detrital materials form a back-drop against which biological flux measurements must be made. Very little is known regarding the composition of dissolved and particulate organic nutrient pools in Great Barrier Reef waters or of their internal dynamics. It is likely that the mineralization of water column and sediment organic nitrogen and phosphorus pools substantially buffers fluctuations in phytoplankton biomass and dissolved inorganic nutrient concentrations.

Putting the very large uncertainty in nitrogen fixation by *Trichodesmium* aside, considerable disparity between the magnitude of external inputs from the land, atmosphere and sea and the likely magnitude of internal recycling fluxes of nitrogen and phosphorus in shelf waters is evident. The largest proportion of these internal recycling fluxes are mediated by water column microbial populations. The estimates presented herein are derived from a very tenuous base as

the dynamics of microbial populations in Great Barrier Reef waters are virtually unknown. Much of what is known about water column microbial dynamics in tropical marine waters is based upon experiments in "clear water" oceanic systems. The limits to the extrapolation of such results to a shelf and coastal system with extensive coral reefs and resuspension fluxes is uncertain. Research activities by the Biological Oceanography group over the next few years will focus upon quantifying local recycling fluxes and putting reasonable bounds on their magnitude.

It is tempting to conclude that the water quality status of the central Great Barrier Reef is not at immediate risk and that at current nutrient input rates, external sources will have little future impact on water quality within the central Great Barrier Reef region. For the moment, this may be the case. Human related nutrient inputs comprise only a few percent of the total nutrient (nitrogen, phosphorus) fluxes which sustain the Great Barrier Reef ecosystem. Dissolved and particulate nutrient concentrations will remain low in outer shelf waters and will continue to be largely controlled by natural processes. However, the estimates of stocks and fluxes given herein are strongly weighted toward the larger areas and volumes of the outer shelf. The initial impact of changes in water quality will be most apparent in the near-shore zone and inner Great Barrier Reef lagoon and will be most strongly felt by the coastal fringing reefs. These nutrient-related changes in water quality will be closely connected to alterations in coastal sediment inputs and sedimentation dynamics. The magnitude of terrestrial inputs of sediments and nutrients are directly linked to regional populations levels, economic activity and development patterns. It is still unresolved to what extent water quality and sediment related factors control the cross-shelf distribution of reefs and of biological communities on reefs. Deleterious changes in water quality on the mid- and outer shelf, much like the rise in global human populations will happen imperceptibly at first. When changes to mid-shelf reefs that can be clearly related to water quality become evident, they will be difficult to arrest. Unlike parts of the well-studied Kaneohe Bay system (Smith et al., 1981), significant human-related nutrient inputs to the central Great Barrier Reef cannot be reduced by turning off or diverting one or a few discrete sources. The largest external inputs, mainly from river runoff, are diffuse in nature with multiple sources within watersheds which are largely unmanaged and therefore difficult to identify and control.

If the lessons from the experience in Kaneohe Bay, Hawaii are transferable to the Great Barrier Reef, incremental increases in nutrient inputs to the Great Barrier Reef will progressively increase stocks of nutrients in both nearshore waters and sediments. Increases in sediment nutrient pools will subsequently be reflected in increased stocks of detrital nitrogen and phosphorus being resuspended into the water column to become available for mineralization by bacteria and zooplankton. Nutrient-related changes in water quality will therefore represent a balance between resuspension mediated sediment-water column exchanges, mineralization by water column populations making use of this resuspended material, phytoplankton demand and physical cross-shelf dispersion processes.

The challenge for oceanographers is to delve into the natural variability which characterizes shelf systems like the Great Barrier Reef, both to understand its magnitude and causative mechanisms and to tease out definitive trends in the state of waters, sediments and biological communities. In parallel, it is essential that coral reef scientists work to understand how nutrient concentrations, supply rates, speciation and mineralization processes directly and indirectly affect the structure and function of coral reefs. Both efforts will require a long-term commitment of time and resources.

The challenge for reef managers is to turn this information into sound programs for the conservation of the Great Barrier Reef that have broadly based community and political support. In the first instance, there is a great need to educate the public and the political/bureaucratic system about the magnitude of changes in water quality which will

ultimately lead to a degradation of the Great Barrier Reef and its value to Australia, the time scales over which such changes occur, the mechanisms involved and the long-term dynamics of the process. The changes will initially be subtle, localized and easy or tempting to ignore.

The alternative is a Great Barrier Reef that is less than the Great Barrier Reef we have now.

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This report is dedicated to the late John Wellington. We shall miss him.

This is AIMS contribution 628.

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