Long-term changes to Mackay Whitsunday water quality and connectivity between terrestrial, mangrove, and coral reef ecosystems:

Clues from coral proxies and remote sensing records

Synthesis of research from an ARC Linkage Grant

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This report represents a synthesis of results from research conducted during an ARC Linkage Grant (2004 – 2007), by chief and partner investigators at:

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ACKNOWLEDGEMENTS

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EXECUTIVE SUMMARY

This report describes results from an integrated catchment to reef study conducted as part of an ARC Linkage Grant between the University of Queensland, the Australian National University, Stanford University, the Great Barrier Reef Marine Park Authority, the Mackay Whitsunday Natural Resource Management Group and the Mackay City Council. The study focused on identifying linkages between downstream changes to coastal water quality and upstream changes in land use practices in the Pioneer River catchment, which covers ~1570 km^2 within the Central Queensland Coast Bioregion. Of the four major catchment areas within the 9031 km^2 of Mackay Whitsunday regional management area, the Pioneer region was selected for intensive study because the catchment has:

- a high proportion of cropped lands with globally high rates of fertiliser application;

- unique topography that causes higher average annual rainfall than adjacent catchments;

- modelled high rates of runoff and high sediment export per unit area; and

- a large urban and industrial centre in Mackay through which the Pioneer River flows.

The research programme contained a four-phased approach to evaluate whether changes to measured nearshore water quality since European arrival were coincident with expanding catchment agricultural activities and land management practices, and then to assess the likelihood that declining water quality has impacted nearshore coral reef communities.

(1) A timeline of changes to catchment land cover was compiled both through literature review and mapping from remote sensing data (e.g. aerial photographs and satellite imagery).

(2) End-member input sources of nitrogen to the nearshore were identified using a tri-tracer approach with $\delta^{15}N$, $\delta^{13}C$ and C:N measurements of particulate organic matter (POM) collected from representative freshwater and marine sites.

(3) Long-term (1824 to 2005) records of changes to nearshore water quality were created by measuring tracers of nutrient ($\delta^{15}N$) and sediment (trace elements) delivery contained in long-lived *Porites* coral skeletons.

(4) Surveys of coral communities were conducted at sites along a gradient of distance (5 – 128 km) from the Pioneer River mouth to establish major differences between sites.

Results

Land Cover Change

Land clearing to expand the nascent sugarcane industry proceeded rapidly after settlement of Mackay in 1862, and by 1902 most lands available for sugarcane were already cropped. Agricultural production increased in intensity through the 20th century with the use of fertiliser (from the 1930s) and mechanical harvesters (from the 1960s). Between 1972 and 2004, the total area of cleared land (including cropped, fallow, pasture, residential and industrial lands) increased by only 16.5 km^2, as some previously cleared areas experienced secondary forest regrowth. Meanwhile, there was a net decline of 56.4 km^2 (32%) in forested area within sensitive riparian zones lining catchment waterways as sugarcane paddocks encroached on stream margins. In the Pioneer River Estuary, there was a net 22% decline in mangrove area between 1948 and 2002, principally due to losses from clearing, alteration of channel hydrology and dieback that primarily affected the grey mangrove (*Avicennia marina*).

Catchment End-Member Identification of Nitrogen Sources

Five main catchment end-members were identified from POM filtered from catchment and coastal water samples:

(1) "terrestrial" plant detrital matter in forest streams located 77 – 87 km upstream, representing fixed atmospheric N sources ($\delta^{15}N$ = 3.65‰, $\delta^{13}C$ = -27.50‰, C:N = 17.9);

(2) "upper river" terrigenous soil matter located 42 – 70 km inland ($\delta^{15}N$ = 3.22‰, $\delta^{13}C$ = -25.535‰, C:N = 12.1);

(3) "lower river" freshwater phytoplankton and algal-dominated matter from 12 – 22 km upstream in stratified reservoirs adjacent to catchment weirs, with highly enriched $\delta^{15}N$ likely caused by microbial remineralisation and denitrification ($\delta^{15}N$ = 8.99‰, $\delta^{13}C$ = -27.48‰, C:N = 8.9);

(4) "estuarine" planktonic and algal matter from sites located 3 – 8 km upstream ($\delta^{15}N$ = 3.65‰, $\delta^{13}C$ = -23.58‰, C:N = 7.6); and

(5) "marine" planktonic and algal dominated matter from the river mouth and coastal waters located 5 – 33 km offshore ($\delta^{15}N$ = 4.97‰, $\delta^{13}C$ = -18.70‰, C:N = 11.1).

These sources and transformations of N were defined in order to explain the $\delta^{15}N$ values of the organic content measured from massive *Porites* corals growing in a gradient of exposure to discharge from the Pioneer River. The enriched organic matter of nearshore coral skeletons from Round Top Island (mean $\delta^{15}N$ = 7.8 ± 1.2‰) is reflective of POM composition in coastal waters that is enriched with fertiliser-derived N during flood pulses from the Pioneer River. The precise isotopic "fingerprinting" of the Pioneer catchment using this tri-tracer approach

provided the essential contextual evidence necessary to interpret spatial and temporal δ^{15}N trends in nearshore *Porites* coral skeletons.

Long-term Trends in Coral δ^{15}N and Trace Elements

Measurements of coral δ^{15}N (a proxy for N in coastal waters) and coral trace element ratios of barium to calcium (Ba/Ca) and yttrium to calcium (Y/Ca; proxies for suspended sediment delivery to the nearshore) were both positively correlated to discharge from the Pioneer River, particularly during flood events. Variability in long-term records of coral δ^{15}N and Ba/Ca from an inshore Round Top Island coral (1824 to 2005) was influenced both by land use practices and climate fluctuations:

- Long-term inshore coral δ^{15}N measurements revealed a 10 to 16 fold increase in accumulation rates of nitrogen delivered in river floods compared to natural baseline values.

- The increases in N accumulation occurred over the past 40 – 50 years and were closely correlated with rapid increases in fertiliser application rates since the mid-1950s.

- A 4-fold increase in nearshore N accumulation since 1824 occurred even under ambient, non-flood conditions, providing clear evidence of chronic nutrient stress on inshore coral reef environments compared to baseline periods.

- Cycles in coral δ^{15}N since 1946 have significant periods of 3.0, 3.7, 10.0 and 12.8 years, which are synchronous with El-Niño Southern Oscillation (ENSO)-related (and possible Pacific Decadal Oscillation, PDO-related) temperature and precipitation cycles in the Great Barrier Reef (GBR) region.

- Cycles in coral Ba/Ca since 1946 have significant periods of ~19.5 years, which are likely related to overlap of strong positive Southern Oscillation Index (SOI) cycles (a measure of ENSO strength) and strong negative Interdecadal Pacific Oscillation (IPO) cycles in the 1950s and 1970s, which produced very wet decades and high runoff from Queensland rivers. Meanwhile, cycles in coral Y/Ca since 1946 have significant periods at approximately decadal resolution which may be a response to decadal modes of the SOI or PDO.

- Sediment flux and accumulation in the nearshore Mackay region escalated rapidly around the period of early-European land clearing (1862 – 1890), whereby average coral Ba/Ca increased by 37% over pre-clearing baseline values.

- There was a significant 16% reduction in average Ba/Ca levels between the mid-1990s and early 2000s, though a longer observation period is required to determine whether this reduction is associated with the adoption of green cane trash blanketing (GCTB) as a harvesting practice

or with low natural sediment delivery as a consequence of drier conditions since 1992. Coral δ^{15}N records, however, showed no diminishing effect on nutrient accumulation rates into Mackay nearshore waters since farmers switched to GCTB.

Mackay Coral Community Structure

The percent cover of live coral measured along an inshore to offshore gradient was consistent with cross-shelf trends in the GBR, with low cover inshore and higher cover and diversity offshore. Corals of the family Acroporidae were dominant at all reef locations surveyed, including the inner reef sites at Keswick and St. Bees Islands. The reef assemblages at Keswick and St. Bees were distinguished from other sites by the dominance of large stands of brown macroalgae, which occupied >60% cover at each location. A synthesis of coral community data with coral proxy records of water quality revealed that:

- δ^{15}N and total abundance of rare earth elements and yttrium (which are related to terrestrial exposure) are highly enriched in annual and flood bands from Keswick corals in 1951, 1974 and 1990-1991;

- The Keswick corals have bright luminescence bands during those years which are reflective of three of the largest flood seasons since 1950;

- Extreme flooding has been previously related to large-scale death of coral assemblages in the southern GBR, such as in the Keppel Islands following Cyclone Joy in 1990;

- Macroalgal growth is often the initial successional stage following large disturbance to coral reef, and has often been cited as an indicator of land-based eutrophication; and

- Fast-growing acroporid corals often dominate at repeatedly disturbed sites.

It is therefore possible that the community assemblages observed at Keswick and St. Bees Islands represent an early successional stage following large disturbance from recent, extreme flooding events bearing elevated nutrient loads from the Pioneer River. However, further research is needed to determine the exact timing of coral death and to assess whether macroalgae are a seasonal or perennial component of the system.

Sugarcane paddocks on the alluvial floodplain of the upper Pioneer River catchment, fringed by hills of the Clarke Range to the north.

Chapter One

The Pioneer River Catchment: Regional Setting

Introduction

The Pioneer River catchment (Figure 1; 21° – $21^o25'S$; $148^o30'$ – $149^o15'E$) covers ~1570 km^2 within the Central Queensland Coast Bioregion and the 9031 km^2 of the Mackay Whitsunday regional management area (QDNRM 2001, Furnas 2003). While the catchments of the Mackay Whitsunday area represent only a small proportion (2.1%) of the 423,070 km^2 of catchment land draining into the Great Barrier Reef (GBR) World Heritage Area, the region is particularly at risk from changes to catchment water quality, due to the proportion of land dedicated to intensive agriculture production, and from expanding population and industry pressures. Before draining into the GBR lagoon, the Pioneer River flows through the urban centre of Mackay, with a current population of 78,000 (http://www.mackay.qld.gov.au/about_mackay). Currently,

the Pioneer catchment is classified as "more than slightly disturbed" based on ongoing water quality surveys by the Queensland Department of Natural

Regional and Local Geography of the Pioneer Catchment
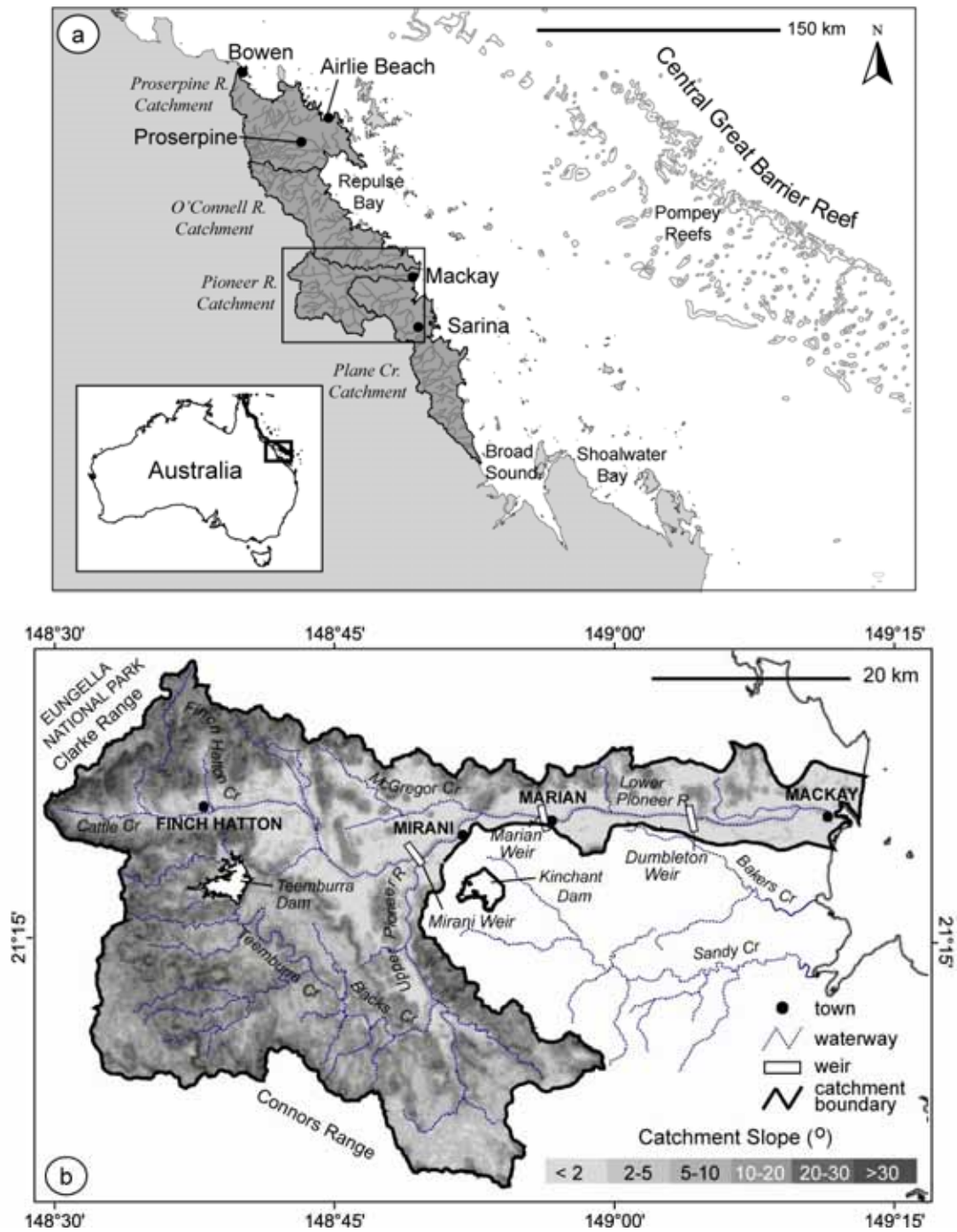
Figure 1. (a) Catchments of the Mackay-Whitsunday management region (dark grey) within central Queensland. Inset shows location within Australia. (b) Topographic and hydrologic features of the Pioneer River catchment.

Resources Mines and Water (QDNRMW), in which baseflow measurements of total nitrogen (N) generally exceeded trigger values for aquatic system protection (Brodie 2004, Mitchell et al. 2005).

Geography and Geology

The Pioneer catchment is bounded by the steep slopes of the Clarke Range to the north and west and the Connors Range to the southwest, both of which are composed largely of granites and granodiorites of the Carboniferous-Mesozoic Urannah Complex, the dominant geological unit within the catchment (Figure 2). While the upper tributaries of the Pioneer River originate at relatively high altitude (>1000 m), resulting in fast-flowing creeks with short water residence times, the main branches of the Pioneer flow over lower elevation floodplains stretching 75 km from the ranges to the sea (Gourlay & Hacker 1986).

The Pioneer catchment has four main sub-basins varying in topography, lithologies, vegetation, and land use: (1) Cattle Creek, (2) Upper Pioneer, (3) McGregor Creek, and (4) Lower Pioneer (QDNRM 2001). The headwaters of Cattle Creek begin at 700 m in Eungella National Park and drain rainforests on the steep terrain of the igneous Urannah Complex before reaching heavily cropped regions in the valley floor. The main tributaries of the Upper Pioneer subcatchment, Teemburra and Blacks Creeks, extend into the Clarke, Connors and Pinnacle Ranges where they drain open grassy to closed woodlands dominated by species of *Corymbia* and *Eucalyptus*. The lower portion of Blacks Creek passes through heavily grazed lands and carried a sandy sediment load from weathering of the granitic Urannah Complex source (QDNRM 2001). McGregor Creek, in the north central region of the catchment, drains *Corymbia/Eucalyptus* woodland and rainforest on the Urannah Complex and on the Permian volcanic and sedimentary units of the Middle Plains Range down to a valley floor that has been extensively cleared for sugarcane. Finally, the Lower Pioneer River, extending east from the confluence of Cattle Creek and the Upper Pioneer River, drains small catchments to the north with remnants of rainforest and open to wooded *Corymbia/Eucalyptus* areas largely on Permian volcanic and metamorphosed sediments. The Lower Pioneer River once overflowed across the floodplain (now largely converted to agriculture) into Sandy and Bakers

Creeks during major flooding, but this has not occurred within the past 150 years (QDNRM 2001).

Pioneer Catchment Region Geology
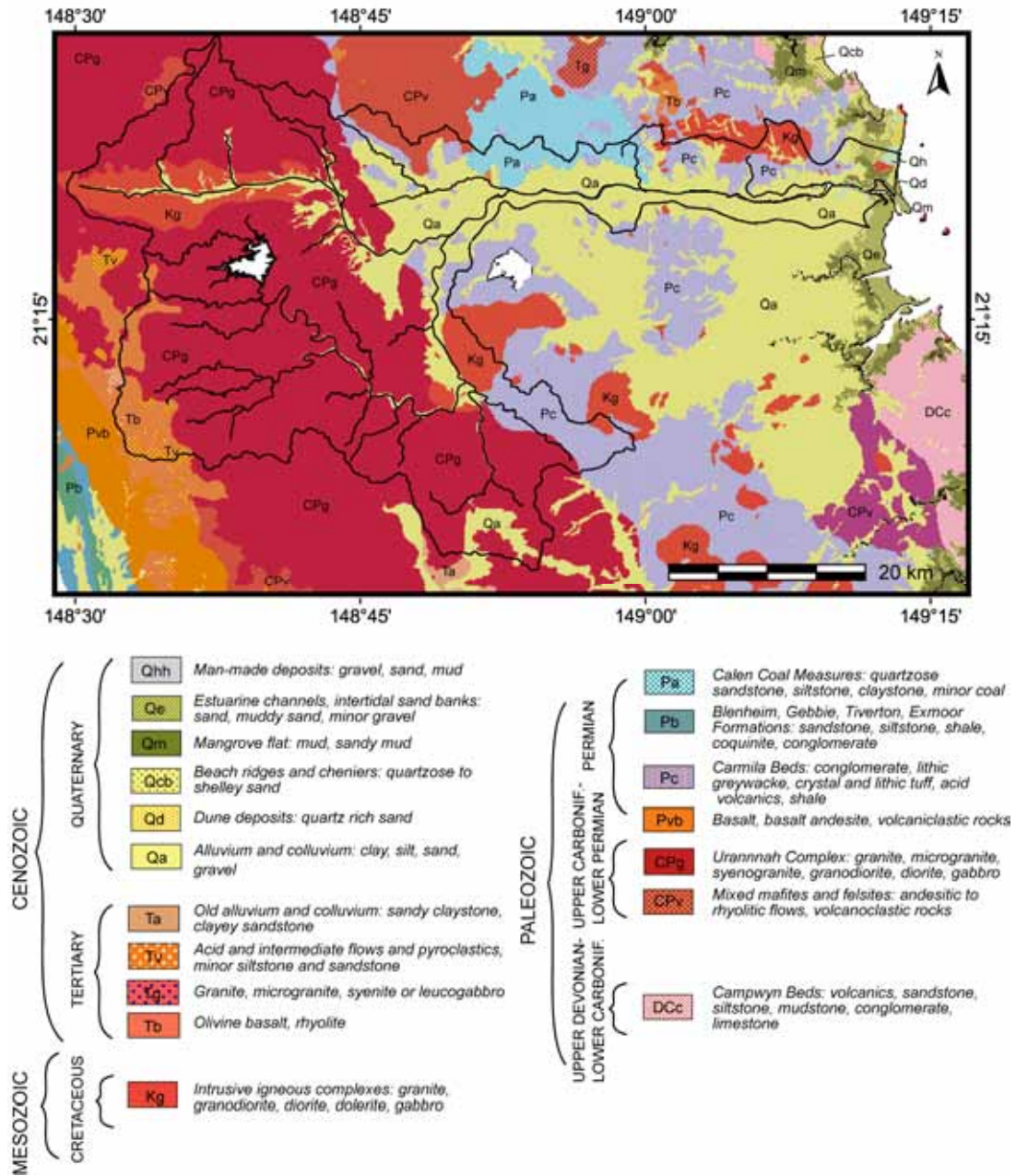
Figure 2. Geologic map of the Pioneer catchment region with major rock units. (Constructed using digital data from Geosciences Australia).

Climate and Hydrology

Climate in northeast Australia is controlled by the westerly monsoon circulation during the warm, wet summer season (October – March) and by the southeasterly trade wind circulation during the cooler dry winter period (April to September) (Lough in-press). Most rainfall (80%) occurs during the summer monsoon (Lough in-press), while regional precipitation and river flow patterns are strongly influenced by the El Niño Southern Oscillation (ENSO) (Power et al. 1999, Verdon et al. 2004). As a consequence, Queensland catchments have high inter-annual variability in rainfall, streamflow, and, to a lesser extent, wind fields (Lough 1994).

Although the Pioneer catchment in located within the "dry tropics" band of central Queensland, its unique topography causes higher average annual rainfall than adjacent catchments. Both the funnel shape of the lower catchment and the abrupt rise in slope contribute to orographic uplift, causing elevated rainfall on the ranges that drain mainly into Cattle Creek and its tributaries (Gourlay & Hacker 1986). The southwestern part of the Pioneer catchment has a much drier climate: although the Upper Pioneer branch of the river system drains over half of the total catchment area, it produces only ~20% of the discharge (Credlin 1973).

Mackay's tropical, humid climate exhibits seasonal wet/dry variability, with ~75% of rain (annual mean = 1634 ± 517mm yr^{-1}; Australian Bureau of Meteorology Station precipitation stations 33046, 33064, and 33119 over the period 1871-2002) falling between the austral summer months of October and March (Brodie 2004). As a consequence, Pioneer River flow is characterised by highly episodic flow patterns: floods accounted for 89 ± 8% of the average 807,917 ± 725,829ML of freshwater discharged annually between 1916 – 2003 (composite record from the Pleystowe Mill gauge, QDNRW station 125001A, Oct 1916-Aug 1978 and the Mirani Weir gauge, QDNRW station 125600A, Nov 1977-Nov 2003; Figure 3). Much of the river system is regulated: three weirs at Marian, Dumbleton and Mirani (constructed in 1952, 1982 and 1987 respectively) plus two dams at Kinchant and Teemburra (built in 1977 and 1997) can store 226,400 Ml of water (~25% of mean total annual runoff), primarily for irrigation (Gourlay & Hacker 1986, QDNRM 2001, Brodie 2004).
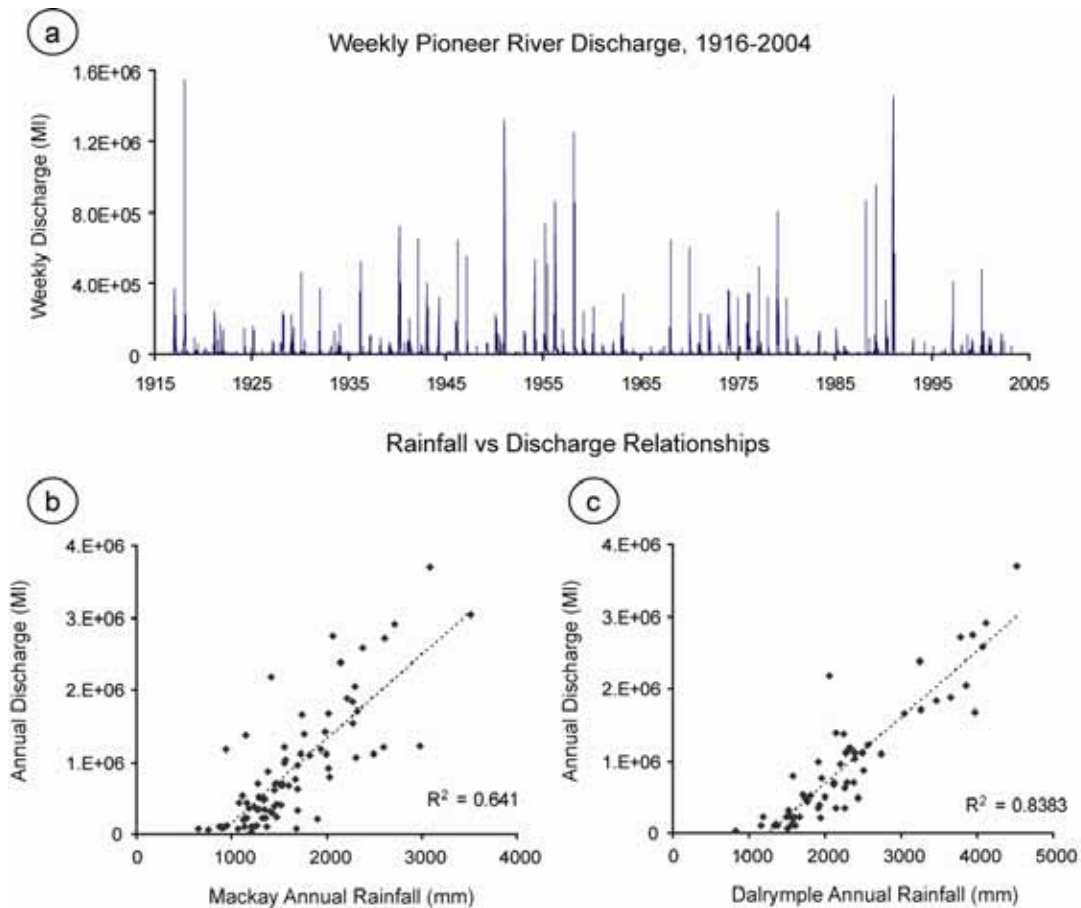
Figure 3. (a) Composite weekly Pioneer River discharge between 1916 and 2004 measured from QDNRW station 125001A at Pleystowe Mill and 125600A at station Mirani Weir. (b) Relationship between annual rainfall at Mackay (from BOM stations 33046, 33064 and 33119) and annual Pioneer River discharge between 1917 and 2003. (c) Stronger correlation between annual rainfall at Dalrymple Heights (BOM station 33016), at the headwaters of Cattle Creek, and annual Pioneer River discharge.

Land Use

The Pioneer catchment has the second highest proportion of cropped land among all GBR catchments (Rayment & Neil 1997), with ~362 km^2 (23% of catchment area) dedicated to sugarcane cultivation mapped in 1999 by QDNRW (Figure 4, Table 1). Sugarcane production accounts for 99.8% of all agriculture and covers 71% of floodplain area on slopes >1 degree (Figure 5a). While livestock grazing is the dominant land use in the Pioneer catchment by area (30.6%; Figure 5b), intensive agricultural production is more likely to influence Pioneer streamwater quality parameters: soil erosion rates from cropped lands in Australia (<5 - >500 t ha^{-1} yr^{-1}) can be as much as 25 times greater than erosion from grazed paddocks (2.6 – 20 t h a^{-1} yr^{-1}) and > 100 times greater than

estimates for forested catchments (<0.1-5 t ha^{-1} yr^{-1}) (Douglas 1967, Sallaway 1979, Matthews & Makepeace 1981, Capelin & Prove 1983, Mullins et al. 1984, Prove et al. 1986, Prove & Hicks 1991, Prove 1992). Upper catchment slopes are primarily forested (64% of remnant native vegetation occurs on slopes >10 degrees; Figure 5c), though a large portion of this area is designated for production forestry (Figure 5d). Other anthropogenic modifications to the catchment likely to affect water quality include: urban runoff from impermeable surfaces; port and harbour industrial waste (Figure 5e); secondary sewage treatment from the estuarine Mt. Bassett wastewater treatment facility (Figure 5f); and reduction in area of riparian zones, freshwater wetlands and estuarine forests (see Chapters 2 and 8).

Mackay Section of the Great Barrier Reef World Heritage Area

The Great Barrier Reef (GBR) World Heritage Area is the world's largest protected marine reserve, covering a total area of 422,000 km^2 between 9°S and 24°30'S and including over 3200 coral reefs (Haynes et al. 2001). Reefs and islands of the Mackay Whitsunday region fall within the Mackay-Capricorn management section of the GBR (20°S and 24°30'S), which occurs along a broad section of the continental shelf (> 200 km) and contains ~47% of reefs within the entire GBR system (Kleypas & Hopley 1992). The dense, outer reef networks of

Table 1. Area of land cover classes in the Pioneer Catchment mapped from Queensland Land Use Mapping Program data (1 : 50 000 scale), based on interpretations from 1999 aerial photographs and Landsat satellite imagery. Individual polygons were classified according to the Australian Land Use and Management Classification (ALUMC) and merged into the 10 broad classes below.

Land Use Class	km^2	% Cover
Services and Transportation	4.8	0.3
Residential/Urban	27.6	1.7
Reservoirs, rivers, streams, ponds	31.1	2.0
Agriculture	362.9	23.0
Park/conservation, remnant native forest	290.9	18.4
Marsh/wetland	6.9	0.4
Manufacturing/industrial	4.8	0.3
Livestock grazing	482	30.6
Production forestry	341.4	21.6
Other minimal uses	25.1	1.6
TOTAL	1577.5	100.0
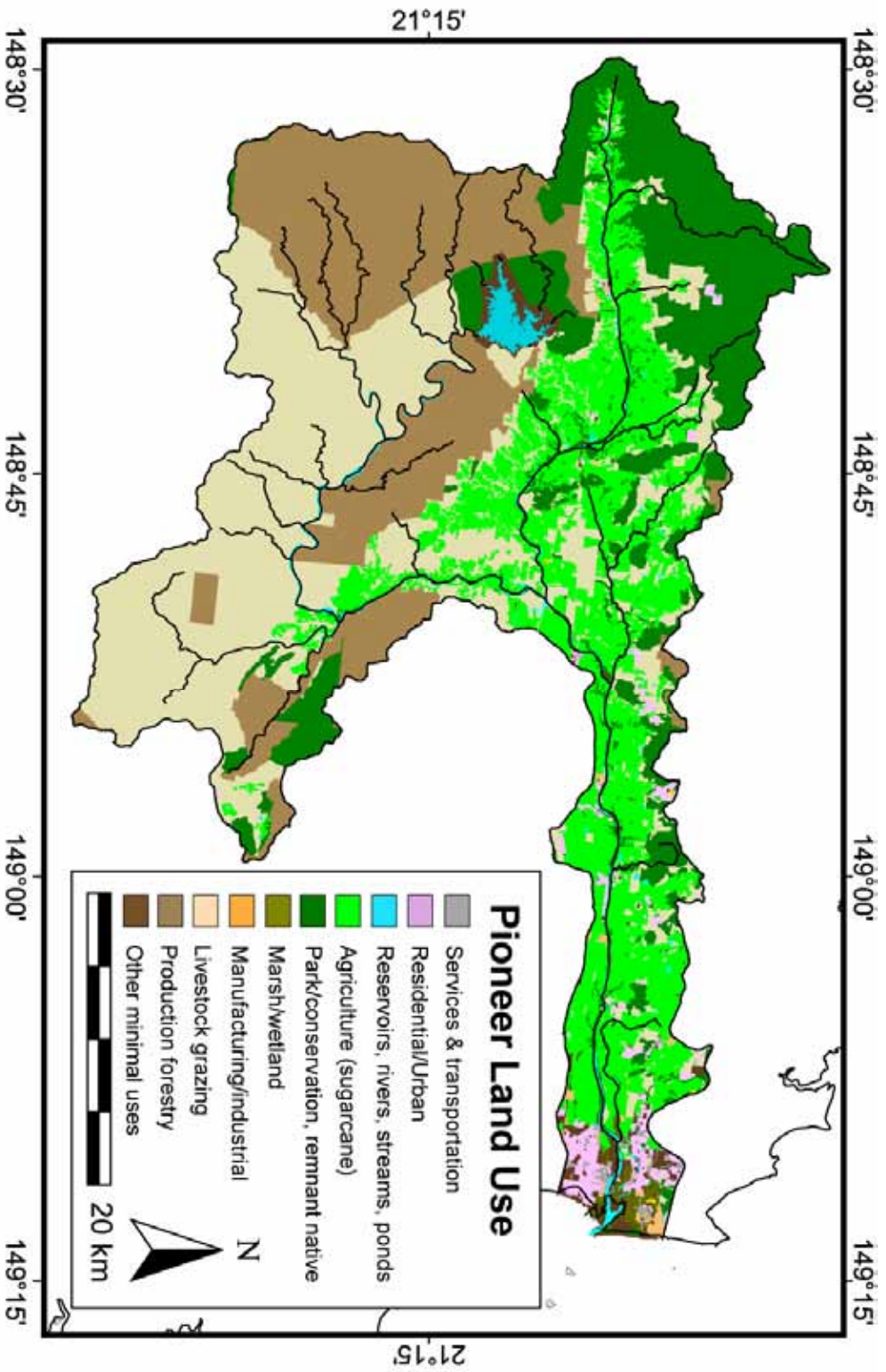
Figure 4. Dominant land use categories in the Pioneer River catchment mapped using Queensland Land Use Mapping Program data.

Pioneer Land Use

- Services & transportation
- Residential/Urban
- Reservoirs, rivers, streams, ponds
- Agriculture (sugarcane)
- Park/conservation, remnant native
- Marsh/wetland
- Manufacturing/industrial
- Livestock grazing
- Production forestry
- Other minimal uses

N

20 km
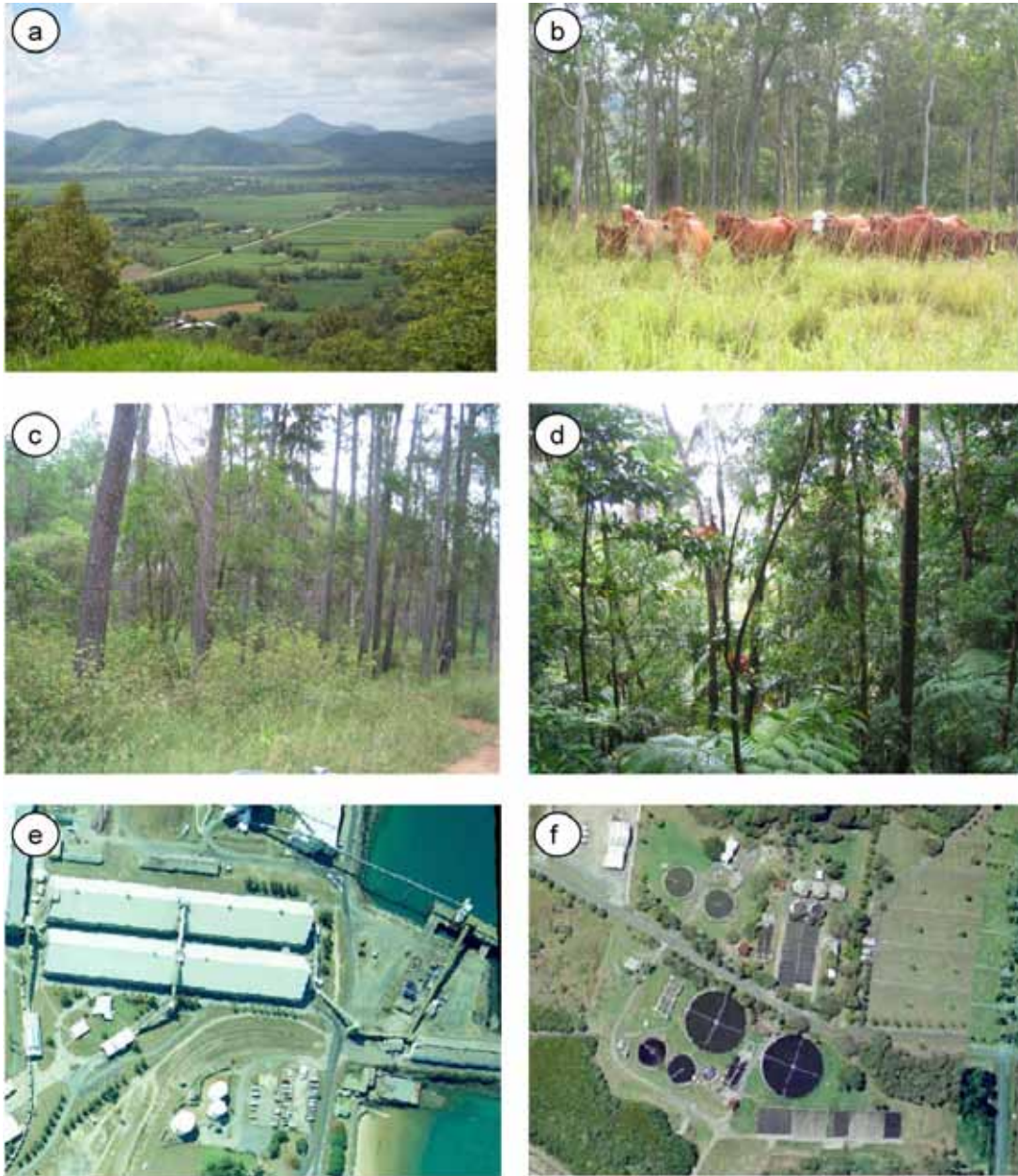
Figure 5. Main types of land use and land cover in the Pioneer catchment. (a) Sugarcane paddocks dominating the alluvial plains. View looking north from Teemburra Dam, photographed 16 March 2006. (b) Cattle grazing adjacent to riparian forest strip near Upper Pioneer River, photographed 15 March 2005. (c) Managed forest in the Mia Mia State Forest, photographed 15 March 2005. (d) Rainforest of Eungella National Park, photographed 14 March 2005. (e) Subset of 2002 aerial photograph (captured 1 May) showing port industry at Mackay Harbour. (f) Subset of same aerial photograph over Mt. Bassett wastewater treatment plant.

the Pompey and Swain Groups are separated from the midshelf reefs and continental islands by a deep (>30 m) channel used as a major shipping route for coal exported from the Dalrymple Bay/Hay Point loading facility ~30 km south of Mackay.

The limited inner reef development between Mackay and Broad Sound has been attributed to elevated turbidity caused by high current speeds associated with large tidal ranges (Kleypas 1996). Maximum spring tides at Mackay reach 6.4 m, while tides at the head of Broad Sound can exceed 10 m, yielding currents up to 3 ms^{-1} (Kleypas 1996, QEPA 2004). The tidal range declines eastwardly across the shelf to 4.5 - 5.0 m in the Cumberland Islands and to 4.0 m in the Pompey Reefs, where tidal currents exceed 4 ms^{-1}, the highest in the entire GBR province (Kleypas & Hopley 1992, Hopley 2006).

North of Broad Sound, which receives no river inputs, nearshore reef development may have also been limited by freshwater exposure. In the GBR lagoon, the dispersal of flood plumes is governed by wind stress, tidal currents, wind-driven currents and geostrophic forces (Wolanski 1994, Devlin & Brodie 2005). Strong prevailing southeasterly winds, such as observed at Mackay with average winds of 18.4 ± 8.4 km/hr from 154 ± 58° (Bureau of Meteorology Station 33119 at Mount Bassett), produce longshore movement of inner shelf waters that usually cause northward spreading of flood plumes largely restricted to within 20 km of the coast (King et al. 2001). The behaviour of plumes within the Mackay region and their delivery of sediments and nutrients to the nearshore environment is addressed in detail in Chapters 5, 6 and 7.

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Workers manually harvesting sugarcane on steep slopes in the Mackay district, c. 1910-1912. Photograph courtesy of John Oxley Library, Brisbane, Queensland.

Chapter Two

Historical Land Cover Change in the Pioneer Catchment

Introduction

The transformation of coastal landscapes to support human activities, primarily agriculture and urban development, threatens freshwater and marine systems worldwide. Croplands and pastures now occupy ~40% of Earth's land surface, representing a 466% increase in cultivated land cover between 1700 and 1980 (Foley et al. 2005). Over half of Queensland's 117 million hectares of woody vegetation has been cleared since European arrival (QEPA 1999), and nearly 80% of the 422,000km^2 Great Barrier Reef (GBR) catchment is dedicated to agriculture, primarily cattle grazing for beef production (77% of land area), and cultivation for sugarcane cropping (1%) (Devlin & Brodie 2005, Furnas et al. 2005). When land is grazed or tilled, soil compaction leads to increasing erosion and runoff as infiltration declines (Pimentel et al. 1993), while fertilisers and pesticides applied to cultivated areas leach into ground and surface waters

(Matson et al. 1997). Of all land uses, conversion of natural forest to sugarcane cropping exerts the greatest impact on wetland and riparian habitat and ecosystem function (Johnson et al. 2001).

Intact riparian zones are important for maintaining healthy ecosystem linkages between terrestrial, aquatic and marine systems. Riparian zones are defined as the vegetation at the interface between terrestrial and aquatic systems, and may occupy a variety of landforms and communities across sharp environmental gradients (Gregory et al. 1991). While riparian zones provide important habitat for terrestrial and aquatic fauna, they additionally perform critical functions of trapping sediments and filtering nutrients from catchment runoff (Arthington et al. 1997, McKergow et al. 2003). In Queensland, recent land clearing over the past 50 years has resulted in a large losses of riparian and wetland habitat (Johnson et al. 2001), which is likely to affect the buffering of material entering the GBR lagoon.

In this portion of the study, we combine historical accounts of land clearing with more recent assessments of land cover change from satellite imagery in order to describe patterns of vegetation loss in the Pioneer River catchment. These records are vital in order to assess whether long term changes water quality from coastal waters adjacent to Mackay can be linked to catchment land management practices.

Sugarcane Expansion in Mackay

While there are no accurately documented records of early land clearing in the Mackay region, histories from the sugarcane industry provide insight into periods of rapid expansion. European exploration of the Pioneer River began in 1860 during a cattle run led by John Mackay (Gourlay & Hacker 1986). Mackay returned to settle the region in 1862, and by 1865, native grasslands and woodlands were burned by John Spiller to clear land for the first experimental sugarcane plot (Kerr 1980, Manning 1983). As Spiller noted, "The first grass I burned was on the Pioneer and it was 12 ft. and over in height. . . . I could see the fire burning in the ranges for four days afterwards." (Manning 1983).

Figure 1. Cleared hillsides behind The Cedars plantation, c. 1878. Photograph courtesy of John Oxley Library, Brisbane, Queensland.

In 1870, 400 ha of sugarcane were farmed, and by 1872, the Mackay district led Australian sugarcane production (Kerr 1980). Land clearing of native vegetation for agricultural production continued rapidly: there were 25 operational mills in 1883, and by 1902, most lands available for sugarcane were already being cropped (Bolton 1963). Although the forested hillslopes were initially thought unsuitable for planting, lands north of the river were quickly cleared when the soil was deemed to be fertile (Manning 1983). Several mills such as The Cedars expanded into the higher country (Figure 1), where stones were used to form broken terraces for erosion control (Manning 1983). According to *The Daily Mercury*'s 1967 centenary feature on the sugar industry, "most of the steep hillside paddocks were thrown out of cultivation . . . late in 1902, when field cultivation techniques made weed and moisture control on the flat country more positive."

Beginning in the late 1930s, applying fertiliser to sugarcane paddocks led to rapid development of the industry (Rolleston 1987). By 1999, ~24,000 tonnes of N and P fertilisers were applied to the 123,954 ha of cropped cane paddocks in the broader Mackay region at rates of 148 – 220 kg ha^{-1} and 16 – 37 kg ha^{-1} respectively (Simpson et al. 2001, Brodie 2004). Similar heavy applications of

pesticides and herbicides also permitted increased harvest yield, and by 1996, the Central Queensland region (including Mackay) had the highest statewide application rate per ha of the herbicides diuron, ametryn and glyphosate (Brodie 2004).

Recent Catchment Land Clearing

Images from the series of sensors on the Landsat satellites were used to map recent changes in forest cover on both a basin-wide scale and within the riparian zones of the Pioneer River catchment. Specific details on mapping methods can be found in Jupiter (2006) and Jupiter & Marion (2007). Between 1972 and 2004, the major change in catchment land cover was a net loss of 56.4 km^2 (32%) of forested area within riparian zones adjacent to catchment waterways (Table 1). Most losses resulted from reductions in width of the riparian zone as agricultural areas encroached on streambanks (Figure 2), though other changes followed hydrologic manipulations, such as the construction of Teemburra Dam in 1997 (Figure 3). Over the same time period, total catchment cleared area increased by 16.5 km^2, as new clearing along riparian zones was offset by secondary forest growth in other areas (Figure 3). There was no general trend of expansion or contraction of agriculture on upper catchment slopes.

The regional ecosystems (REs) within the Pioneer catchment most affected by land clearing between 1972 and 2004 include: open forests dominated by *Eucalyptus tereticornis*, *Corymbia intermedia* and *Lophostemon suaveolons* on alluvial levees and lower terraces (8.3.6a); semi-deciduous vine

Table 1. Changes in riparian forest cover and catchment land clearing (to nearest 0.1 km^2) mapped from Landsat satellite data between 1972 and 2004. Average annual rates of riparian forest change are reported for each time interval.

Year	Riparian Zone		Catchment	
	Forest (km^2)	Change km^2/yr	Forest (km^2)	Cleared (km^2)
1972	175.0		1064.0	507.5
1978	185.6	+1.8		
1984	158.9	-4.5		
1990	138.9	-3.3		
1995	133.5	-1.1		
2000	126.2	-1.5		
2004	118.6	-1.9	1046.1	524.0
Net Change 1972-2004	-56.4		- 17.9	+16.5
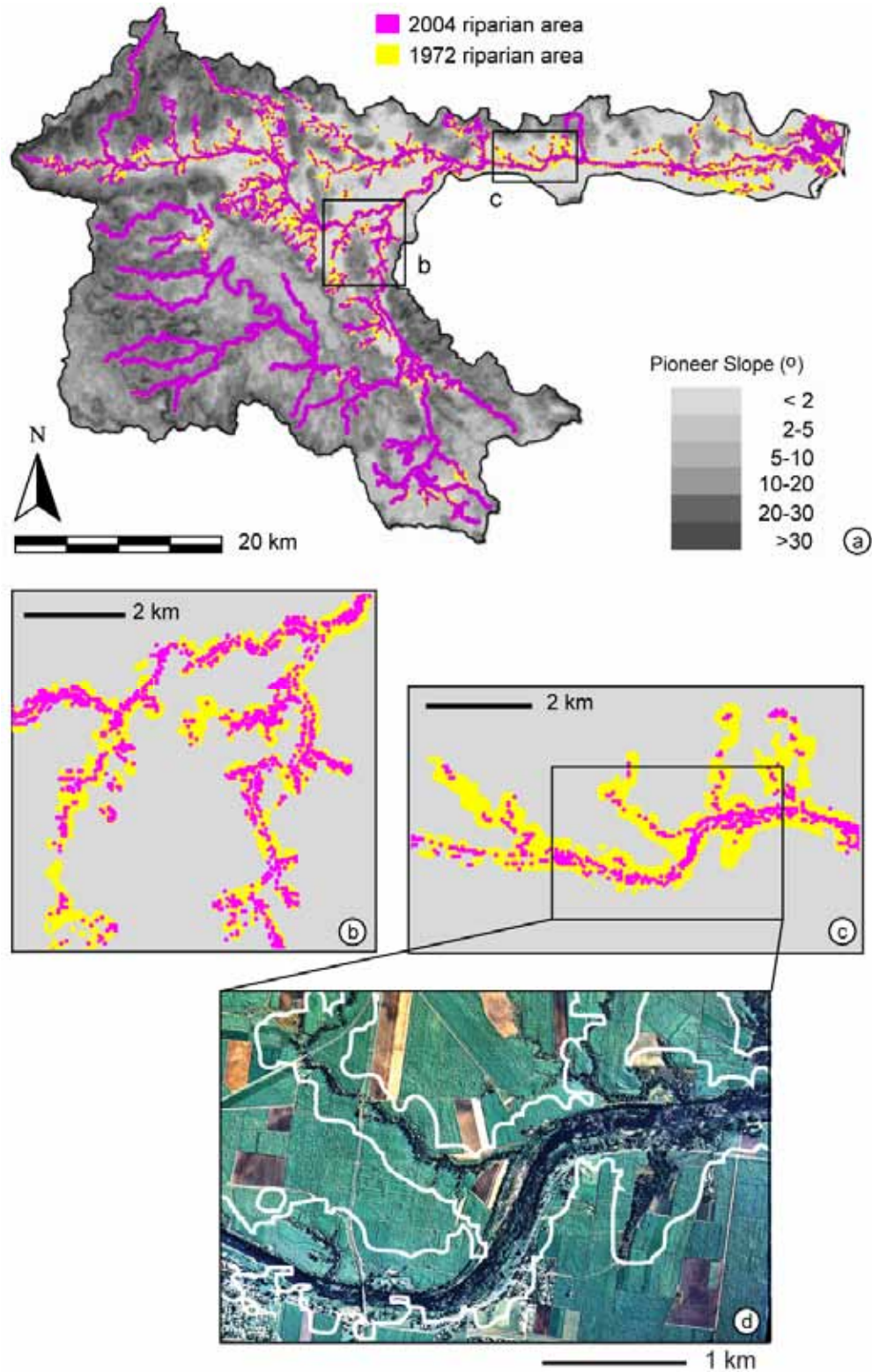
Figure 2. (a) Forested area within the riparian zone of the Pioneer catchment mapped from 1972 (yellow) and 2004 (magenta) Landsat images. Enlarged subsets (b and c) show reduced width of the riparian zone on the alluvial plains between 1972 and 2004 due to encroachment of sugarcane paddocks, which can be seen clearly on the 1998 aerial photograph around the town of Marian in (d), where the outer extent of the mapped 1972 riparian zone is shown in white.

A. 1972 cleared area

30 km

C. Finch Hatton region

3 km
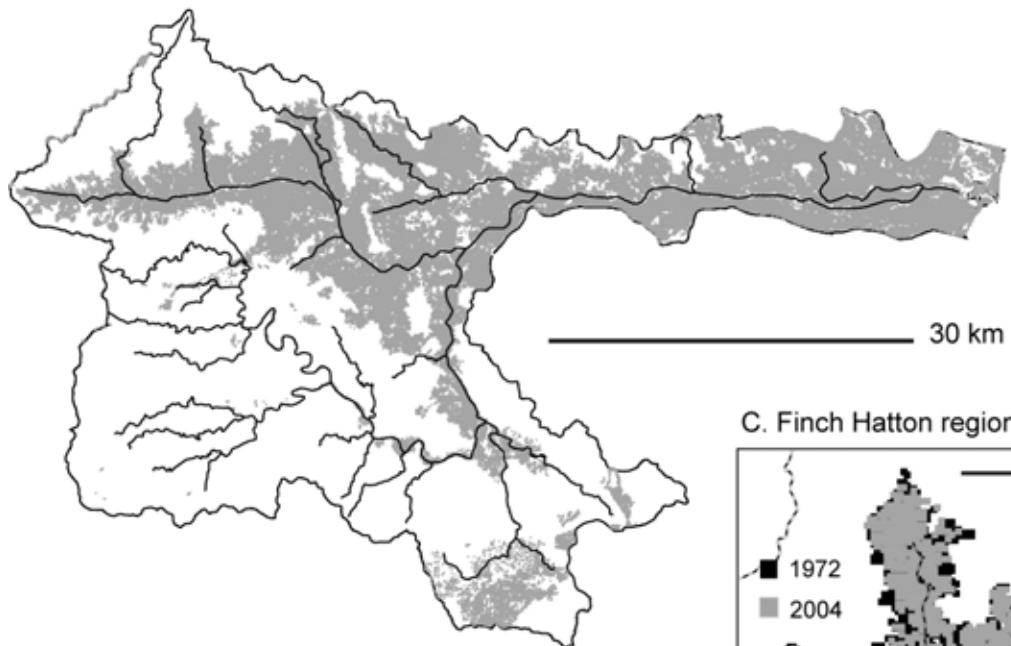
■ 1972
■ 2004

B. 2004 cleared area

30 km
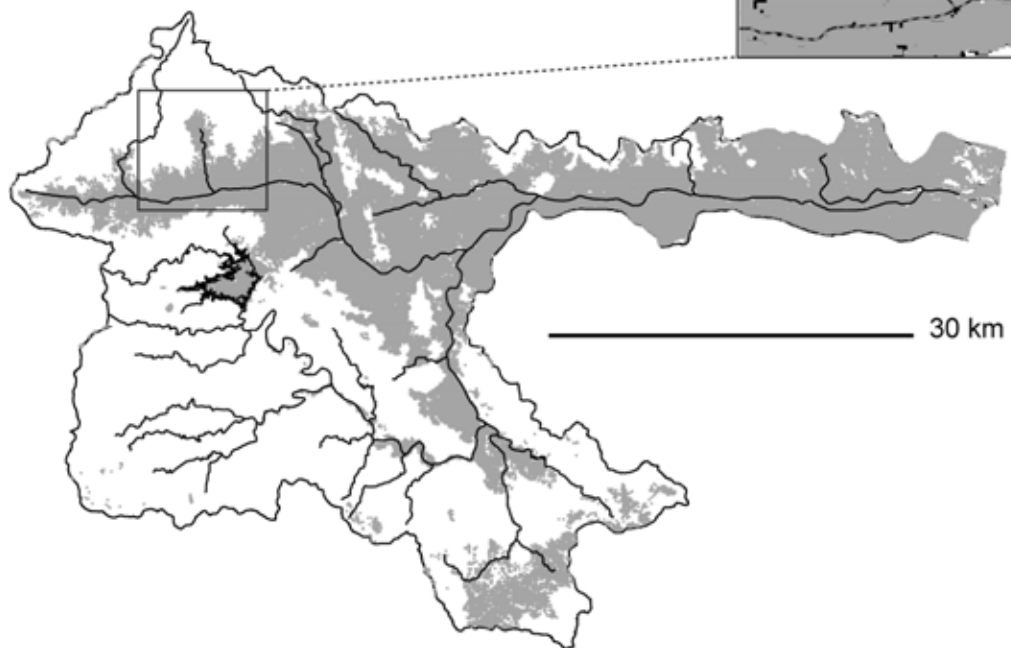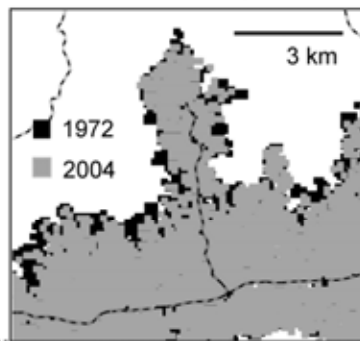
Figure 3. Total cleared area (grey), including cropped, fallow, pasture, urban and residential lands, within the Pioneer catchment boundary in (a) 1972 and (b) 2004, mapped at ~90 m resolution from Landsat satellite images. (c) Inset showing 2004 cleared area (grey) overlaid over 1972 cleared area (black) in the Finch Hatton region where previously cleared areas were likely replaced by secondary forest growth.

forests (8.3.10) and native grasslands (8.3.12) fringing watercourses on alluvial plains; woodlands dominated by *C. clarksoniana*, *L. suaveolon*s, and *E. platyphylla* on alluvial plains (8.3.5); and *Melaleuca viridiflora* woodlands on seasonally inundated alluvial plains (8.3.2; Table 2, Figure 4). Disturbed REs within the lower catchment estuary, freshwater wetlands and coastal dunes include: mangroves (8.1.1); *Sporobulus virginicus* grassland (8.1.3); *Paspalum spp* and *Fimbristylis ferruginea* sedgeland/grassland (8.1.4); samphire open forbland (8.1.2); closed forests of *Melaleuca spp* (8.3.11); and open to closed forests of coastal dune species (8.2.7a, 8.2.9, 8.2.13a; Table 2).

Consequences of Riparian Forest Loss

While rapid and widespread land clearing occurred in the Pioneer River catchment following European settlement, recent land use change has disproportionately affected the critical riparian zone. The losses observed in the Pioneer catchment are consistent with recent changes in riparian and wetland vegetation in other parts of Queensland, such as the Herbert River and Johnstone River catchments, where 80% and 60% of riparian and freshwater wetlands, respectively, have been lost since 1943 and 1951 (Johnson et al. 1999). In all the above cases, sugarcane is now planted on alluvial floodplains formerly occupied largely by *Melaleuca* stands (Arthington et al. 1997, Johnson et al. 1999). The *Melaleuca viridiflora* regional ecosystem (8.3.2), highly disturbed by recent Pioneer land clearing since 1972, is currently classified "of concern" as it has been reduced to 10-30% of its pre-European extent, while two other types of woodlands dominated by *Corymbia spp.* and *Eucalypt spp.* (8.3.5, 8.3.6) on alluvial plains are now considered "endangered" (<10% of former extent) (Werren 2001).

Loss of these types of natural forest canopy can alter ecosystem condition and function through: (1) increased light penetration and stream temperature, which may increase biological activity and lead to anoxia (Bunn & Davies 1996, Arthington et al. 1997, Boothroyd et al. 2002); (2) reduced leaf litter and woody debris export to support in-stream food chains and invertebrate habitat (O'Connor 1991); (3) increased susceptibility of fish to predation (Pusey & Arthington 2003);
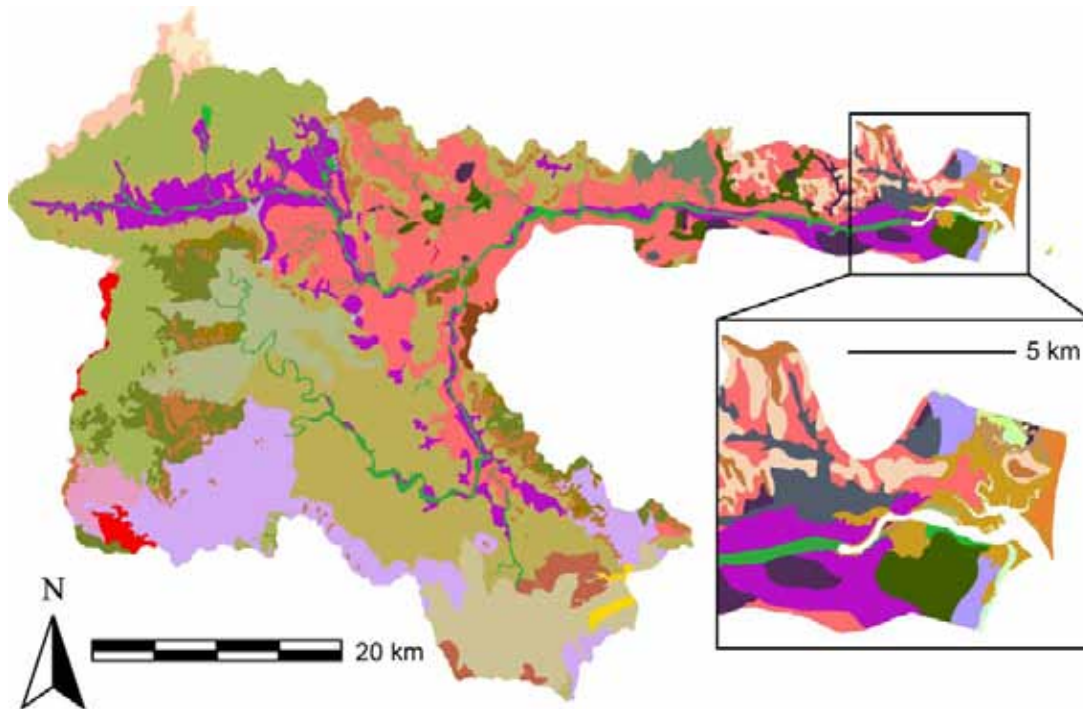
Regional Ecosystem Classes

8.1.1 *	8.3.5 *	8.12.1a	8.12.31a,b	
8.1.2 *	8.3.6a *	8.12.2	8.12.32	
8.1.3 *	8.3.10 *	8.12.3a	11.3.4	
8.1.4 *	8.3.11 *	8.12.5a	11.3.25b	
8.2.6a *	8.3.12 *	8.12.7a,c	11.12.1a	
8.2.7a *	8.3.13a	8.12.9	11.12.3	
8.2.9 * *	8.8.1a,b	8.12.11a	11.12.6a	
8.2.13a	8.11.1	8.12.12a		
8.3.1a *	8.11.2	8.12.13a		
8.3.2 *	8.11.3a	8.12.17a		
8.3.3a,x1 *	8.11.4	8.12.23		
8.3.4	8.11.5a	8.12.27a		

Figure 4. Pre-clearing distributions of regional ecosystems (RE) within the Pioneer catchment (constructed using digital data from QEPA, who determined classes by extrapolation guided by landforms present in 1962 aerial photographs, Neldner et al. 2005). Asterisks denote REs most affected by recent (1972 to 2004) land clearing. Descriptions of the dominant vegetation types, land forms and underlying geology of REs affected by land clearing are listed in Table 2. A full description of Pioneer Catchment REs can be found in Jupiter (2006) or in the QEPA Regional Ecosystem Description Database (QEPA 2005), which can be downloaded at: http://www.epa.qld.gov.au/nature_conservation/biodiversity/regional_ecosystems/

Table 2. Regional ecosystems (REs), defined by QEPA, most affected by recent riparian forest loss between 1972 and 2004. RE class codes and descriptions were assigned by QEPA based on their regional ecosystem description database (QEPA 2005), and represent the dominant RE within the area. Total estimated pre-clear and remnant 2001 areas are reported, as well as the % remnant for REs in 2001.

Regional Ecosystem	Dominant vegetation	Land form	Pre-clear area (ha)	2001 area (ha)	% remnant
Catchment					
8.3.1a	Semi-deciduous vine forest	Fringing watercourses on alluvial plains	3416.2	1768.4	51.8
8.3.2	Melaleuca viridiflora woodland often with emergent eucalypts and grassy/herbaceous ground cover	Seasonally inundated alluvial plains with impeded drainage	2618.6	90.4	3.4
8.3.3ax1	Melaleuca leucadendra or M. fluviatilis ± Casuarina cunninghamiana open forest to woodland	Fringing watercourses	2199.3	3000.0	136.4
8.3.5	Corymbia clarksonia + Lophostemon suaveolens + Eucaplyptus platyphylla woodland, or E. platyphylla woodland	Alluvial plains	24661.3	1375.4	5.6
8.3.6a	Eucalyptus tereticornis, Corymbia intermedia and Lophostemon suaveolens (or C. tessellaris dominant) open forest	Alluvial levees and lower terraces	11078.4	1038.2	9.4
8.3.10	Notophyll vine forest with variable dominants	Gently sloping alluvial fans next to ranges	300.3	27.1	9.0
8.3.12	Native grassland	Alluvial and old marine plains	1621.8	25.2	1.6
Estuary/Coast					
8.1.1	Mangrove vegetation	Estuarine wetland	973.2	729.3	74.9
8.1.2	Samphire open forbland to isolated clumps of forbs	Saltpans and plains ajacent to estuaries	12.9	12.6	97.8
8.1.3	Sporobolus virginicus grassland	Estuarine wetland	48.4	41.8	86.4
8.1.4	Papsalum spp. and Fimbristylis ferruginea sedgeland/grassland	Estuarine wetland	199.8	128.1	64.2
8.2.6a	Corymbia tessellaris + Acacia leptocarpa + Banksia integrifolia + Melaleuca dealbata + beach scrub species open forest	Coastal parallel dunes	99.0	38.7	39.1
8.2.7a	Melaleuca spp. ± Lophostemon suaveolens ± Eucalyptus robusta open woodland to open forest	Wetlands associated with parabolic dunes	64.8	55.6	85.9
8.2.9	Heteropogon triticeus, Imperata cylindrica and Themeda triandra grassland	Coastal dunes	226.4	87.2	38.5
8.2.13a	Corymbia tessellaris, Melaleuca spp., Livistona decipiens ± Acacia spp. ± Lophostemon suaveolens open to closed forest	Dune sands mixed with alluvium and marine sediments	430.0	28.9	6.7
8.3.11	Melaleuca spp. aff. viridiflora closed forest to woodland	Broad drainage areas (wetlands)	1155.2	70.7	6.1

and (4) reduced habitat and corridors for terrestrial flora and fauna (Johnson et al. 1997, Naiman & Decamps 1997). Werren (2001) lists 18 plants, 19 birds, 7 reptiles, 4 amphibians and 1 mammal, classified as endangered, rare, or vulnerable, that currently utilise threatened riparian habitat in the Pioneer catchment.

Lastly, because most losses of riparian vegetation within the Pioneer catchment have occurred adjacent to sugarcane paddocks, and because the widths of these filter strips have narrowed, water draining from these regions is likely to have higher suspended sediment and nutrient loads (Dillaha et al. 1989, Norris 1993). Although this study did not attempt to quantify in-stream sediment and nutrient concentrations in relation to riparian condition or width, other reports from the region provide evidence of elevated sediment and nutrient concentrations in runoff from heavily cleared regions with only narrow, remnant riparian strips: in a comparison of sub-catchments from the Mackay and Whitsunday regions, average storm maximum and ambient baseflow levels of total suspended solids (TSS) in January 2005 were two and eleven-fold greater, respectively, from sub-catchments cleared for sugarcane than from forested sub-catchments (Rohde et al. 2006). Simultaneously, maximum storm levels of total N and P in runoff from sugarcane sub-catchments were approximately twice as high as those from forested sub-catchments, while ambient levels were four to six-fold greater from the cultivated areas (Rohde et al. 2006). Future studies are still needed to assess whether there is a causal relationship with reduced riparian width and elevated sediment and nutrient concentrations, particularly during high flow conditions when water is likely to be channelised before it can be filtered during overland wash (Norris 1993).

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Pioneer River reservoir waters downstream of the Dumbleton Weir. Photographed 8 March 2006.

Chapter Three

Nutrient Dynamics in Pioneer Catchment Waters

Introduction

Estuaries, shallow coastal areas, and continental shelf waters collectively account for almost half of total marine primary production, despite covering only 15% of the Earth's ocean surface (Paerl 1997). Today, however, anthropogenic nitrogen (N) inputs in runoff from highly populated and/or modified coastal lands exceed natural sources, and are having widespread impacts on water quality and coastal ecosystems worldwide (Matson et al. 1997, Vitousek et al. 1997, Beman et al. 2005). Therefore, establishing clear linkages between anthropogenic sources of nitrogen pollution and eutrophic estuarine and marine waters is critical for the design of water quality remediation programs.

One approach is to trace N sources directly into coastal food webs by analysis of natural abundance ratios of nitrogen stable isotopes ($\delta^{15}N$). During biologically-mediated reactions, the preferential uptake of ^{14}N and its removal via

the excretion of waste products such as urea and ammonia produces distinctive isotopic signatures that can be used to identify catchment sources and processes that influence nearshore marine $\delta^{15}N$ values (McClelland et al. 1997, Yamamuro et al. 2003). A typical river system receives both natural and anthropogenic N-inputs. Natural C3 plant detrital material has low $\delta^{15}N$ values (-2 to 2‰) reflecting its primary source of N from the atmosphere ($\delta^{15}N$ = 0‰ by definition; Owens 1985). Synthetic N fertilisers, which are fixed industrially from atmospheric nitrogen, range from -2 to 2‰ (Heaton 1986, Kendall 1998). Dissolved inorganic nitrogen (DIN) $\delta^{15}N$ values from septic tanks and urban wastewaters typically exceed 10‰ due to ammonium nitrification and volatilization and nitrate denitrification into ammonia and N_2 (Jordan et al. 1997, McClelland & Valiela 1998). In secondary and tertiary sewage treatment systems, effluent $\delta^{15}N$ values range from 2 to 4‰ (Sweeney & Kaplan 1980).

However, in tidal estuaries which are characterised by long residence times (days to weeks), the $\delta^{15}N$ of DIN and particulate matter is often altered by biological (usually microbial) processes (Cifuentes et al. 1988, Middelburg & Nieuwenhuize 2001). Aquatic algae that assimilate DIN from the water column discriminate against ^{15}N, depleting residual $\delta^{15}N$ by a fractionation factor (ε) of -9‰ for nitrate, and depending on concentrations, by 0 to -25‰ for ammonium (Pennock et al. 1996, Middelburg & Nieuwenhuize 2001). Denitrification by facultative anaerobic bacteria in sediments increases DIN $\delta^{15}N$ by a rate dependent factor of up to +20‰, depending on the ambient temperature, supply of substrate, and O_2 concentrations (Middelburg & Nieuwenhuize 2001). Remineralisation of senescent plankton or detrital matter by heterotrophic bacteria enriches ^{15}N substrates by 3.5 to 9.6‰, while nitrifying organisms transform $^{14}NH_4^+$ into nitrate, lowering $\delta^{15}N$ values by -18‰, (Mariotti et al. 1984, Minagawa & Wada 1986).

The isotopic and elemental composition of suspended particulate organic matter (POM) offers broad insights into the sources and transformations of nitrogen within river, estuarine and marine sources. POM is composed of both terrestrial (allochthonous) sources of organic detritus, such as terrigenous soil matter and leaf debris, and in-stream (autochthonous) sources, including freshwater and marine phytoplankton, macrophytes and algae (Cifuentes et al. 1988, Kendall et al. 2001). The composition of particulate matter is most clearly

distinguished by its elemental ratio of carbon to nitrogen (C:N). Terrestrial plant matter originating from natural ecosystems has C:N values of 15-20, while arable terrigenous soils range from 10-12 and freshwater and marine plankton have ratios of <8 (Kendall et al. 2001). Using POM or nitrate $\delta^{15}N$ values, most stable isotope studies focus either on: (1) characterising end-member inputs and progressive mixing within watersheds; (2) quantifying non-conservative transformations of N species during passage through riverine and estuarine waters; or (3) identifying temporal and/or spatial gradients in nearshore marine waters by analysing producer $\delta^{15}N$ values. In the present study, we use POM $\delta^{15}N$, $\delta^{13}C$ and C:N ratios to investigate linkages between land-derived sources of N in the Pioneer River catchment and nearshore *Porites* coral skeletons. Although we focus on nitrogen, which is a limiting nutrient in the world's oceans, $\delta^{13}C$ and C:N values are used to constrain N sources and transformation pathways. In this chapter, $\delta^{15}N$ values calculated for catchment end-members are compared with those of organic material extracted from the skeletons of massive *Porites* corals collected across a 50 km tract of the south central Great Barrier Reef, reflecting a gradient of exposure to discharge from the Pioneer River.

Defining End-members from the Pioneer Catchment System

N inputs into the Pioneer River catchment waterways were characterised by analysing $\delta^{15}N$, $\delta^{13}C$ and C:N ratios of particulate organic matter (POM), and the concentrations of fluvial N species, from 18 freshwater, estuarine and marine sites located throughout the Pioneer River and tributaries (Figure 1). The sites selected included exposure to: marine particulates (sites 1-2); river mouth N (site 3); urban wastewater and effluent from Mackay's secondary wastewater treatment facility at Mt. Bassett (sites 4-5); agricultural leachate from adjacent sugarcane fields distributed through the alluvial floodplain (sites 6-7, 10-16); stagnant reservoir waters adjacent to flood-controlling weirs (sites 8-9); and terrigenous soils and terrestrial plant matter from native forests in the Clarke Range (sites 17-18). All field sampling was conducted during low flow conditions in March 2005 and March 2006 from mid-stream waters outside of eddies or pools. POM was sampled by scooping 1 L of water from 50 cm below the surface and vacuum filtering through a 47 mm, pre-combusted glass fibre filter and analysed at the Stanford Stable Isotope Laboratory. In order to constrain
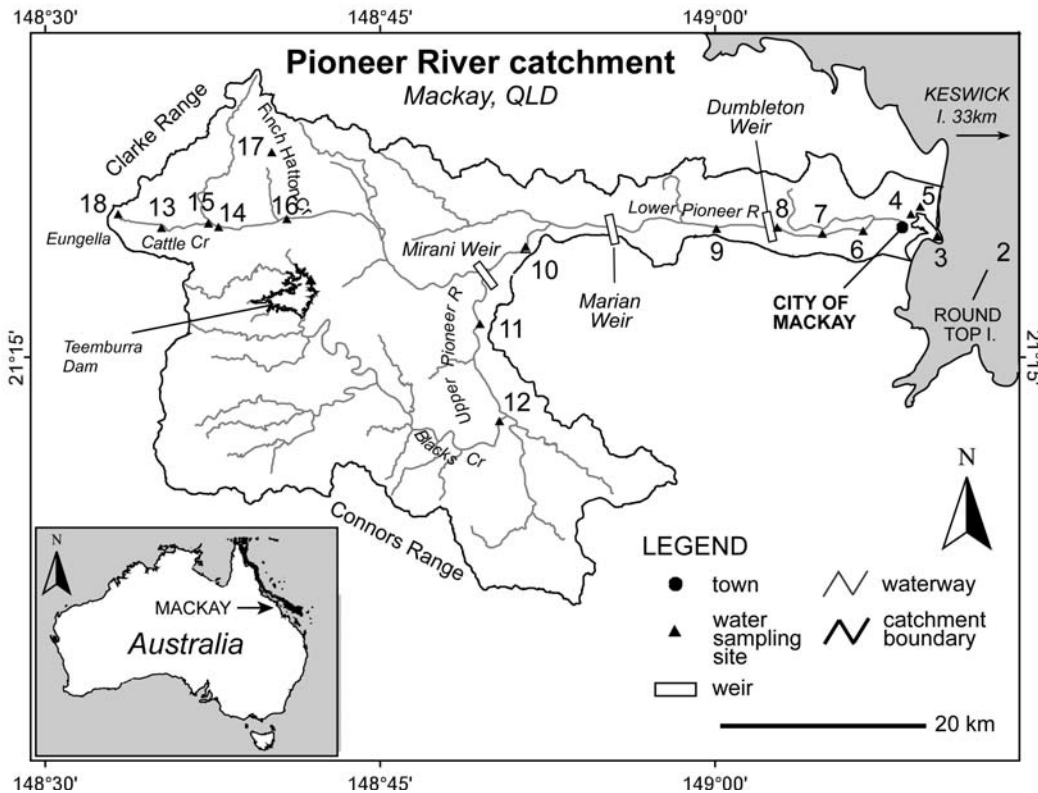
Figure 1. The Pioneer River catchment covers 1570 km^2 and is located in the agricultural Mackay region of central Queensland, Australia. The adjacent Great Barrier Reef Lagoon extends 220km to the east across the broad continental shelf.

biological processes acting to fractionate N within the river system, nutrient concentrations (particulate, dissolved inorganic, dissolved organic nitrogen and phosphorus) were additionally analysed from separate 750 ml water samples at the Australian Centre for Tropical Freshwater Research. Further details on sample collection, preparation and analyses can be found in Marion (2007).

Table 1 summarises values of δ^{15}N, δ^{13}C and C:N ratios measured from 76 POM samples, of which 70 were used as inputs into a principal components analysis (PCA) to separate the samples into coherent end-member groupings (Figure 2). PCA conducted using any two of the three variables did not clearly differentiate the end-members, emphasising the value of using a tri- instead of a dual-tracer approach. In the tri-tracer PCA, the "factor loading" reflects the distance of each data point from a linear line of best fit through the data. The factor of the first principal component explained 48.9% of the variance

Table 1. $\delta^{15}N$, $\delta^{13}C$, and C:N values of particulate organic matter collected from the Pioneer River catchment and inner Great Barrier Reef lagoon of Queensland, Australia.

Collection date	Site #	Site Name	Land Use	Km upstream	Salinity (ppt)	n	$\delta^{15}N$ (‰ AIR)	$\delta^{13}C$ (‰ PDB)	C:N
13/3/06	1	KIW	Marine	-33*	34.5	6	4.90	-15.44	12.73
14/3/06	2	RTW	Marine	-5*	34.5	3	5.11	-17.85	10.55
17/3/06	3	PRM**	Estuarine	0.25	32.8	8	6.06	-21.46	10.08
17/3/05	4	BSB	Urban	3	32.8	4	5.50	-24.27	8.50
16/3/05	5	STP	Sewage	3	ND	6	2.95	ND	6.20
17/3/06	6	PNR- 1**	Cane fields	8	28.9	3	6.98	-22.65	9.05
17/3/06	7	PNR-2**	Cane fields	12	21.2	3	8.09	-24.98	9.58
16/3/06	8	PNR-DBW**	Weir	16	0.1	9	9.46	-26.67	8.85
16/3/06	9	PNR-3**	Weir	22	0.1	3	8.46	-32.41	8.20
16/3/06	10	PNR- MRI**	Cane fields	42	0	3	3.22	-28.27	8.97
16/3/06	11	PNR-4**	Cane fields	52	0	3	1.46	-25.86	9.29
15/3/05	12	BLC	Cane fields	64	0	3	0.69	-31.19	12.57
16/3/06	13	CC**	Cane fields	82	0	3	4.02	-25.25	12.40
17/3/06	14	CC-FCH**	Cane fields	77	0	7	3.96	-23.75	14.47
14/3/05	15	CC-UB**	Cane fields	77	0	2	2.95	-21.44	11.99
16/3/06	16	CC-UA	Cane fields	70	0	4	4.88	-23.14	12.65
16/3/06	17	FHC	Forest	77	0	4	4.54	-27.49	17.24
14/3/05	18	EUN	Forest	87	0	2	1.87	-27.53	19.10

* Kilometers offshore (to the east)
**Sites from which water samples were also collected for nutrient concentration analyses.

in the data, and the second explained 33.3%. PCA revealed five distinct POM end-members (Table 2) with the following average values:

(1) "terrestrial" plant detrital matter in forest streams located 77 – 87 km upstream ($\delta^{15}N$ = 3.65‰, $\delta^{13}C$ = -27.50‰, C:N = 17.9);

(2) "upper river" terrigenous soil matter located 42 – 70 km inland ($\delta^{15}N$ = 3.22‰, $\delta^{13}C$ = -25.535‰, C:N = 12.1);

(3) lower river" freshwater phytoplankton and algal-dominated matter from 12 – 22 km upstream ($\delta^{15}N$ = 8.99‰, $\delta^{13}C$ = -27.48‰, C:N = 8.9);

(4) "estuarine" planktonic and algal matter from sites located 3 – 8 km upstream ($\delta^{15}N$ = 3.65‰, $\delta^{13}C$ = -23.58‰, C:N = 7.6); and

(5) "marine" planktonic and algal dominated matter from the river mouth and coastal waters located 5 – 33 km offshore ($\delta^{15}N$ = 4.97‰, $\delta^{13}C$ = -18.70‰, C:N = 11.1).
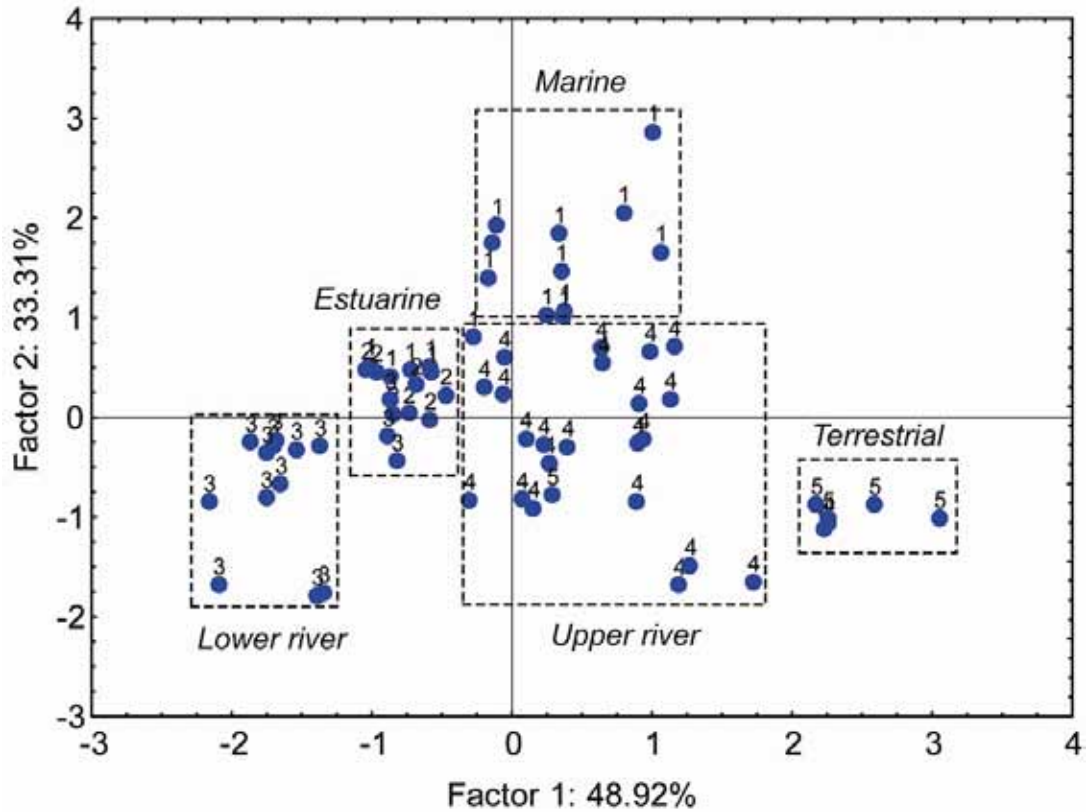
Figure 2. PCA loadings of raw $\delta^{15}N$, $\delta^{13}C$, and C:N data of particulate organic matter (POM) collected from the Pioneer River catchment and in the inner Great Barrier Reef (GBR) lagoon. Five distinct end-members are evident, based on similarity of isotopic and elemental composition, from marine (1), estuarine (2), lower river (3), upper river (4), and terrestrial (5) environments.

Table 2. $\delta^{15}N$, $\delta^{13}C$, and C/N values and concentrations of end-members identified in the Pioneer River via principal components analysis.

End-member	Sites	n	$\delta^{15}N$ (‰ AIR)	$\delta^{13}C$ (‰ PDB)	C:N	PN (uM)	DON (uM)	NH4 (uM)	NO3 (uM)
Marine	1-3	17	5.48	-18.70	11.1	1.5	7.5	0.7	0.6
Estuarine	4-6	9	6.13	-23.58	7.6	4.3	8.4	0.4	5.2
Lower river	7-9	15	8.99	-27.48	8.9	13.9	27.0	0.4	3.3
Upper river	10-16	24	3.22	-25.35	12.1	3.8	10.4	0.4	0.6
Terrestrial	17-18	6	3.65	-27.50	17.9	-	-	-	-
Total	1-18	70	5.17	-24.18	10.9	6.7	14.9	0.4	1.9

In the sections below, exogenous (terrestrial) and endogenous (riverine) input sources and transformations of N responsible for the end-member values are discussed in order to explain the $\delta^{15}N$ values of the organic content measured from massive *Porites* corals growing in a gradient of exposure to discharge from the Pioneer River.

Upstream Sources of ^{15}N-depleted Particulate Matter

The depleted ^{15}N composition (3.7 ± 1.1‰) of the Pioneer "terrestrial" end-member sites are indicative of plant-derived allochthonous inputs in natural forest runoff, where fixation of atmospheric N provides the majority of nitrogen used within the ecosystem (Owens 1985). The high C:N ratios (17.9) and depleted POM δ^{13}C (-27.50‰) indicate that the detrital matter originated from C3 plants, which dominate in natural vegetative and forest systems (Kendall et al. 2001). The low dissolved inorganic and organic nitrogen concentrations in these tributary streams suggest that the Pioneer River is naturally depleted in nutrient availability (Figure 3).
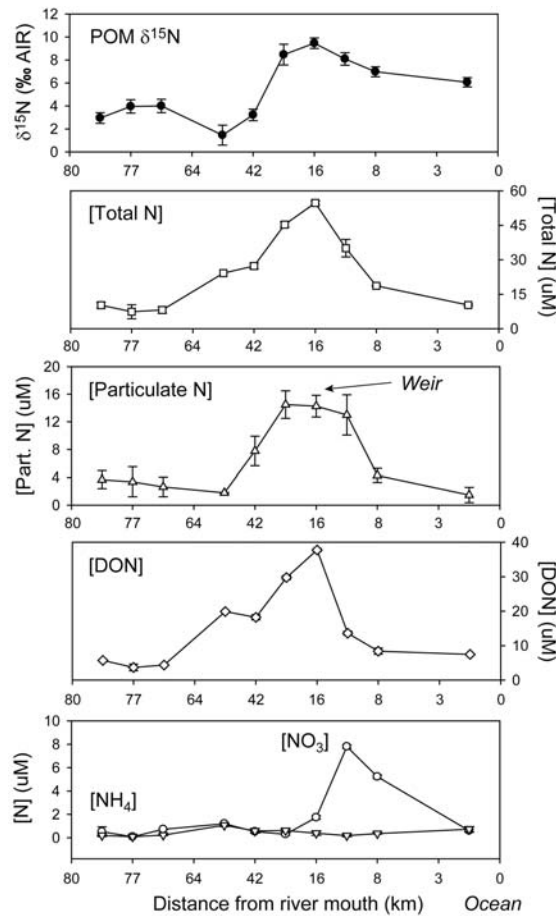
Figure 3. Mean δ^{15}N values (a) and concentrations of particulate and dissolved nitrogen (b-e) at sites collected in the Pioneer River. The highest N concentrations were observed in slow-flowing and stagnant reservoir waters near to lower Pioneer's primary flood and irrigation control dam, the Dumbleton Weir ("weir"). Error bars represent mean ± 2 std error (SE).

The sites representing the "upper river" end-member (located 42-70 km upstream of the river mouth) pass through sugarcane fields that collectively cover >70% of the Pioneer alluvial floodplain (Jupiter & Marion 2007). Particulate matter collected from these streams and irrigation waterways bordered by sugarcane includes a high proportion of terrigenous soil organic matter, indicated by its average C:N ratio of 12.1 (Kendall et al. 2001). POM δ^{15}N values (3.2 ± 0.4‰) were similar to the ^{15}N composition of DIN-based fertilisers (-3 to 2‰), which are applied in the Pioneer catchment at mean rates of 173 kg N ha^{-1} (Simpson et al. 2001, Brodie 2004). Meanwhile, POM δ^{13}C values (-23.35 ± 0.69‰) are indicative of terrigenous soil export from cultivated fields, as the sugarcane plant (*Saccharum* spp.), with δ^{13}C values of -10 to -12‰, does not contribute greatly to the riverine detrital pool of organic carbon (Bunn et al. 1997, Kendall et al. 2001, Udy & Bunn 2001). Species of green algae have also been observed to lower Queensland riverine δ^{13}C values (Bunn et al. 1997). In the Pioneer River where filamentous green algal components were sampled and verified by microscopy, the low DIN concentrations and depleted POM δ^{15}N values also suggest algal activity whereby N is rapidly assimilated by the freshwater algae without experiencing further biological processing.

Microbial Transformations and δ^{15}N Enrichment in the Lower Pioneer

The most striking feature of the Pioneer River transect is the +6‰ increase in particulate δ^{15}N values over the 20 km distance between the narrow agricultural waterways of the upper Pioneer, and the broad banks (site 7) and stagnant reservoir pools (sites 8 and 9) of the lower river (δ^{15}N = 9.0 ± 0.4‰; Figure 4a). Three fixed-crest concrete irrigation and flood-control weirs interrupt normal river flow along this stretch (Figure 5): the Mirani Weir (42 km upstream) was constructed in 1987, the Marian Weir (32 km upstream) was constructed in 1952, and the Dumbleton Weir (16 km upstream) was constructed in 1982 and upgraded in 1992 and 1998 (QDNRM 2001). The combined capacities of the three weirs with other hydrological modifications further upstream (Teemburra Dam, off-stream storage at Kinchant Dam) is 226,000 Ml, or roughly 25% of the unregulated mean annual flow of the Pioneer (Brodie 2004). The sudden drop in
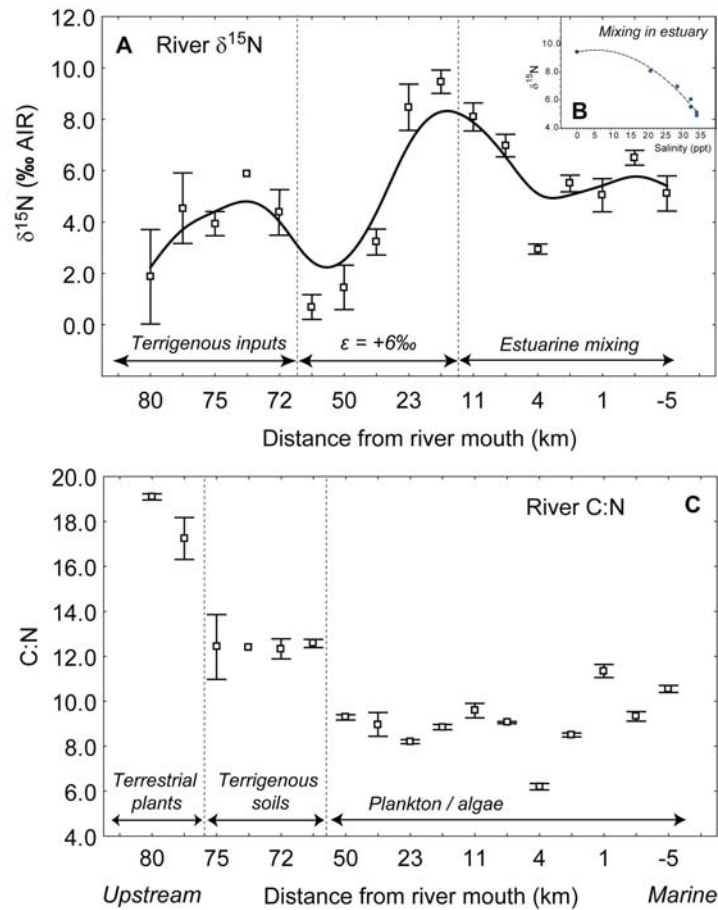
Figure 4. Average $\delta^{15}N$ of particulate organic matter (POM) samples (a) collected from tributary, reservoir, and river sites along an upstream-downstream transect of the Pioneer catchment, Mackay. Cross-plot of $\delta^{15}N$ vs. salinity (b) shows near-conservative mixing of N inputs across the estuarine salinity gradient. C:N values (c) are useful for discriminating algal from non-algal sources of POM in the same samples. Error bars represent mean ± 2 std error (SE).

the C:N values between the upper and lower river indicates that particulate matter in these slow flowing or stagnant lower river waters are composed mainly of freshwater phytoplankton and algae (Kendall et al. 2001), compared to predominantly terrigenous soils (C:N = 12) further upstream (Figure 4c).

Microbial remineralisation of decaying organic matter (the labile N pool) within the Dumbleton reservoir is consistent with the +6‰ rise in downstream POM $\delta^{15}N$ values (Owens 1985, Cifuentes et al. 1988, Middelburg & Nieuwenhuize 2000). The low ammonium concentrations and high dissolved organic nitrogen (DON) concentrations, both of which are byproducts of
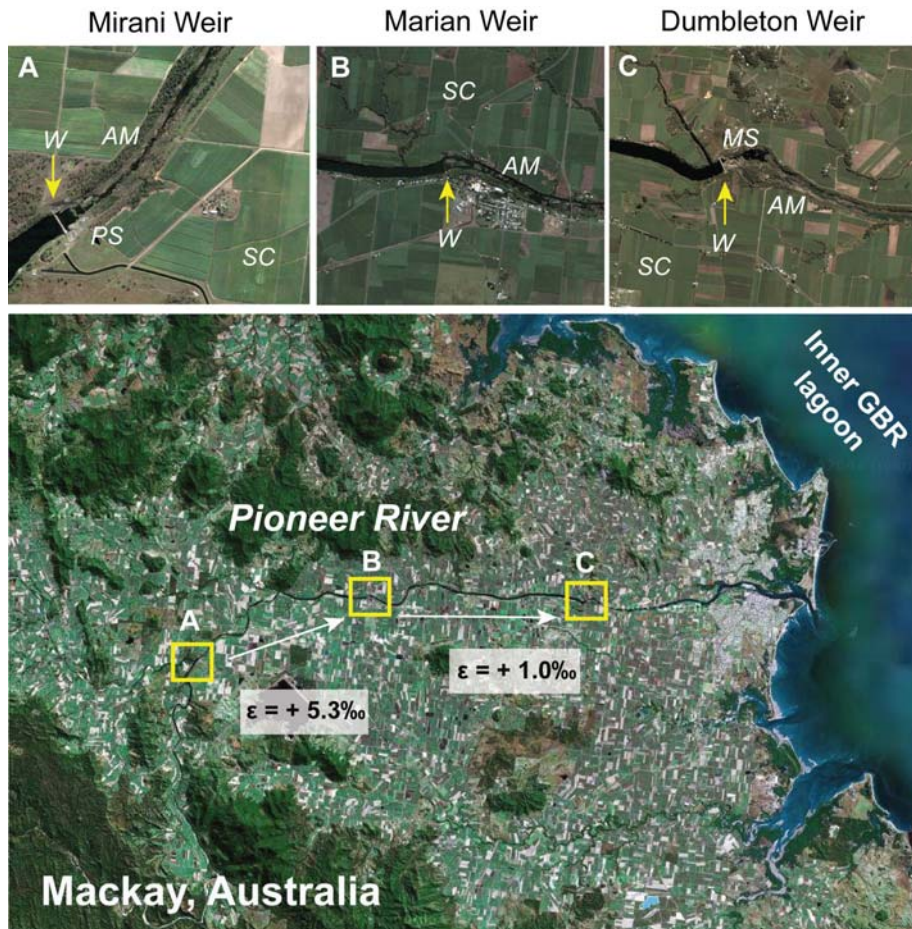
Figure 5. River weir systems at (a) Mirani, (b) Marian, and (c) Dumbleton in Mackay, Queensland interrupt normal river flow, leading to high algal biomass and low oxygen conditions in the benthic (hypolimnion) layers. These serve as principal loci for algal and microbial N transformations, increasing average δ^{15}N values by +6‰. Abbreviations: W= weir, AM = algal & microbial biomass, SC = sugarcane, PS = permanently thermally stratified, MS = monomictic (seasonal) stratification.

mineralisation, indicate that DIN is limiting in the stagnant pool weirs (Middelburg & Nieuwenhuize 2001). Veuger et al. (2004) found that up to 70% of the total DON pool (primarily urea and amino acids) is available biologically and limits productivity in Randers Fjord, Netherlands, in all but mid-summer months (August). In the lower Pioneer, DON is not limiting as it accounted for the highest concentration of all N species in the residual N pool (up to 37.8 µM N), suggesting DON release from remineralisation, although we cannot discount inputs of urea fertiliser leachate as another possibility for elevated DON values.

Denitrification is a cause of δ^{15}N enrichment in healthy and eutrophic river systems and is likely to also be accountable for some of the downstream enrichment seen here. Removal of 20% of ambient nitrogen concentrations

(mostly nitrate) from water bodies by denitrification can result in DIN $\delta^{15}N$ enrichment of +8‰, although enrichment of up to 20‰ has been reported (Middelburg & Nieuwenhuize 2001). Sediment-dwelling, facultative anaerobic bacteria utilise nitrate as the terminal electron acceptor during the oxidation or organic matter, producing N_2, NO or N_2O that is subsequently lost from the system (Seitzinger 1988). The process requires low concentrations (<0.2 mg L^{-1}) of oxygen, which are typically found in estuarine sediments or stagnant bottom (hypolimnion) layers, as are found in the Mirani and Dumbleton weirs (Meisenhelter 2006). Dumbleton reservoir is monomictic, being characterised by weak thermal stratification (<5°C difference between surface and bottom layers) during the warm summer months, while Mirani is permanently stratified. The bottom layers contain low dissolved oxygen concentrations of <3 mg L^{-1} (Meisenhelter 2006), which is sufficient to allow denitrifying anaerobic bacteria to live there. The elevated particulate nitrogen and DON concentrations reflect high biomass and remineralisation, while the low nitrate and ammonium concentrations, both of which are reactants in denitrification, suggest rapid attenuation rates producing the heavy lower Pioneer $\delta^{15}N$ values.

Conservative Mixing Through the Estuarine Salinity Gradient

The ^{15}N composition of the Pioneer estuary (6.1 ± 0.5‰) is on the low end of the published $\delta^{15}N$ values for estuarine end-members (Figure 6). Inputs of ^{15}N-depleted sewage effluent from Mackay's secondary sewage treatment facility ($\delta^{15}N$ = 3.0 ± 0.2‰, site 5) into the Pioneer estuary is one possible cause of the relatively light $\delta^{15}N$ signal. However, the annual N load released from the Mt. Bassett Wastewater Treatment facility (220 tonnes yr^{-1}) is minor compared to leachate from the ~21,000 T of nitrogenous fertilisers applied in the Mackay region (Simpson et al. 2001, Brodie 2004). For example, an estimated 242 T of N were exported from Dumbleton weir during a 3-day flood event in 2002, representing export rates of 1.5 kg N ha^{-1} from the 1570 km^2 Pioneer catchment (Simpson 2002). Since fertiliser-derived DIN in the Pioneer has a high ^{15}N composition by the time it reaches the estuary (due to
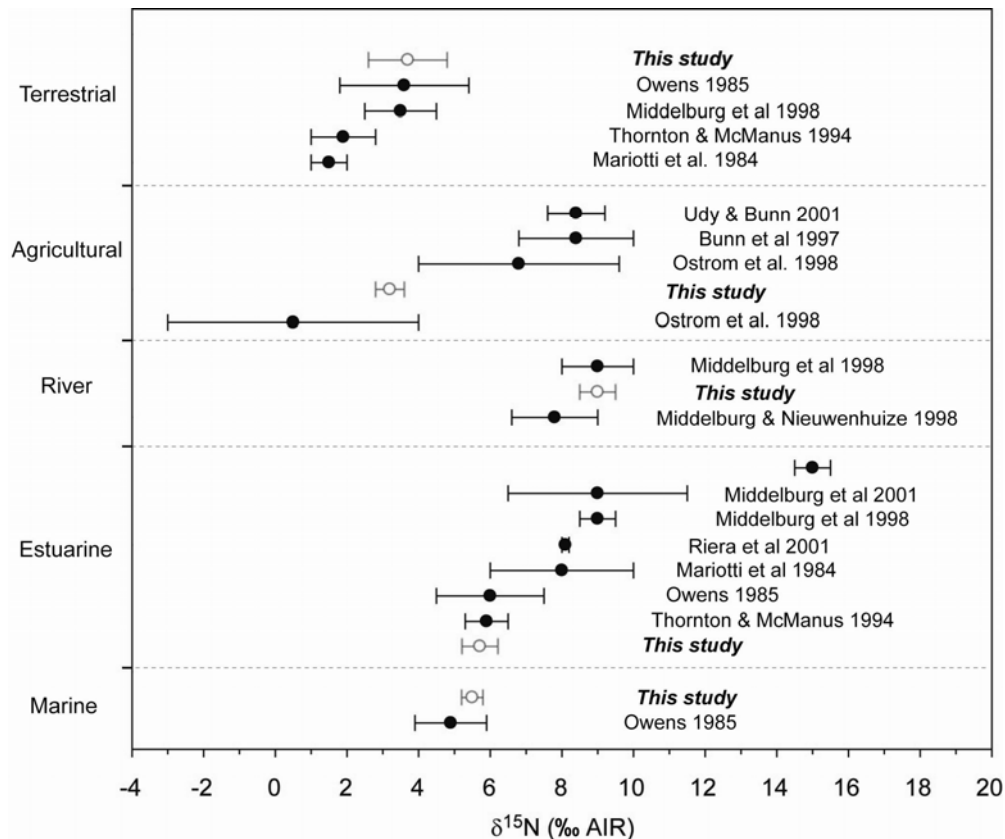
Figure 6. Published range of δ^{15}N values of particulate organic matter (POM) sampled in large, human-modified river systems in Australia, the U.S., and the Netherlands. Results from the current study are indicated by hollow circles.

non-conservative behaviour in the lower river), while the δ^{15}N values decrease in the estuary, it seems likely that physical, conservative mixing processes are responsible for the 5‰ decline in δ^{15}N values (Figure 4b). Meanwhile, the 9‰ decrease in δ^{13}C values between the lower river (-27.5‰), estuary (-23.6‰) and marine (-18.7‰) waters reflects the transition from POM dominated by freshwater plankton and mangrove detritus to waters dominated by marine plankton (Middelburg & Nieuwenhuize 1998, Kendall et al. 2001). This is clearly illustrated in the results of the PCA where the estuarine end-member cluster includes both terrestrial and marine samples, reinforcing that it is a hybrid class of adjacent freshwater and marine water bodies (Figure 2).

Additional non-conservative behaviour and enhanced biological processing of fluvial N species may also contribute to the 5‰ decline in δ^{15}N values between the lower sections of the river and estuarine sites. Interestingly, the highest nitrate concentrations observed in the Pioneer River were measured

in two estuarine sites 500 m downstream of Dumbleton weir (with salinities of 21.2 and 28.9 ppt respectively; Figure 3). Nitrification, which preferentially converts $^{14}NH_4^+$ into NO_3 in a well-oxygenated environment, enriches the biologically available pool of ammonium. Assimilation of the residual ammonium pool by algal and plankton species, which are the primary constituents of suspended particulate matter, can result in extreme ^{15}N enrichment (up to +18‰) in estuaries (Mariotti et al. 1984, Cifuentes et al. 1989). Alternatively, assimilation of low-^{15}N nitrate via progressive algal uptake has been observed to deplete POM pools by as much as -9‰ (Mariotti et al. 1984, Middelburg & Nieuwenhuize 1998), which is consistent with the low values observed in the present study.

Linking N in River Discharge with Nearshore Coral Skeletons

To determine whether nearshore *Porites* corals faithfully record sources of fluvial N discharged from the Pioneer River during flood pulses, massive *Porites* corals were analysed for $\delta^{15}N$, $\delta^{13}C$ and C:N ratios from cores collected from 3 sites (Round Top, Keswick and Scawfell islands) along a gradient of distance from the Pioneer River mouth. Sites and coral coring techniques are described in greater detail in Chapter 4, as well as in Marion (2007) and Jupiter (2006). Average coral carbonate $\delta^{15}N$ values decreased significantly with distance from land (Figure 7), while mean $\delta^{13}C$ values increased with distance. Elemental C:N ratios ranged from a minimum of 6.6 (in Round Top Island core F) to a maximum of 7.8 (Keswick Island core C).
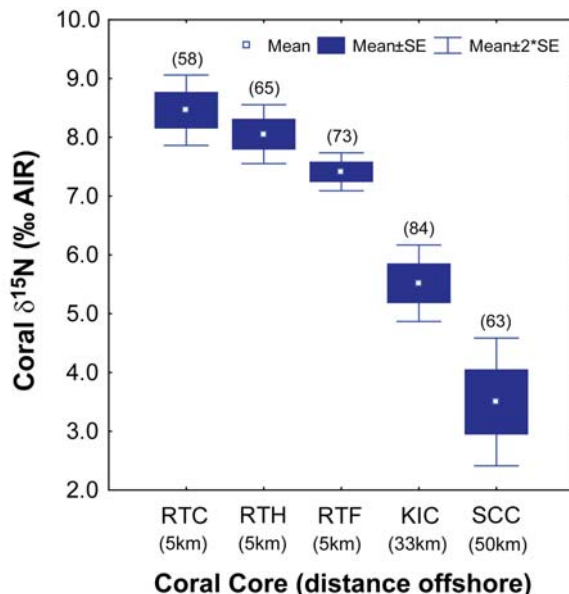
Figure 7. Average $\delta^{15}N$ values of insoluble nitrogen extracted from five *Porites* coral cores collected across an inshore to offshore transect of the southern Great Barrier Reef. The cross-shelf decline reflects decreasing exposure to ^{15}N-enriched discharge from the Pioneer River. Boxes represent the average (± 2 std error, SE) of annual increments of growth (density band couplets) sampled from each core; sample sizes are in parentheses.

The enriched organic matter of nearshore coral skeletons from Round Top Island is reflective of POM composition in river and coastal waters that are enriched during flood pulses from the Pioneer River, as illustrated in the schematic in Figure 8. Under ambient conditions, N concentrations increase dramatically between the narrow agricultural waterways located 42-77 km upstream and the reservoir waters that pool both upstream and downstream of the Mirani, Marian and Dumbleton weirs. As total N concentrations rise, they acquire a distinctively high ^{15}N signature that reaches a maximum value of 9.5‰ ~0.5 km downstream from Dumbleton weir (Figure 8a). The increase in average δ^{15}N values is most likely caused by the removal of ^{14}N$_2$ by denitrifying bacteria living in the anoxic bottom (hypolimnion) layers of the thermally stratified reservoir
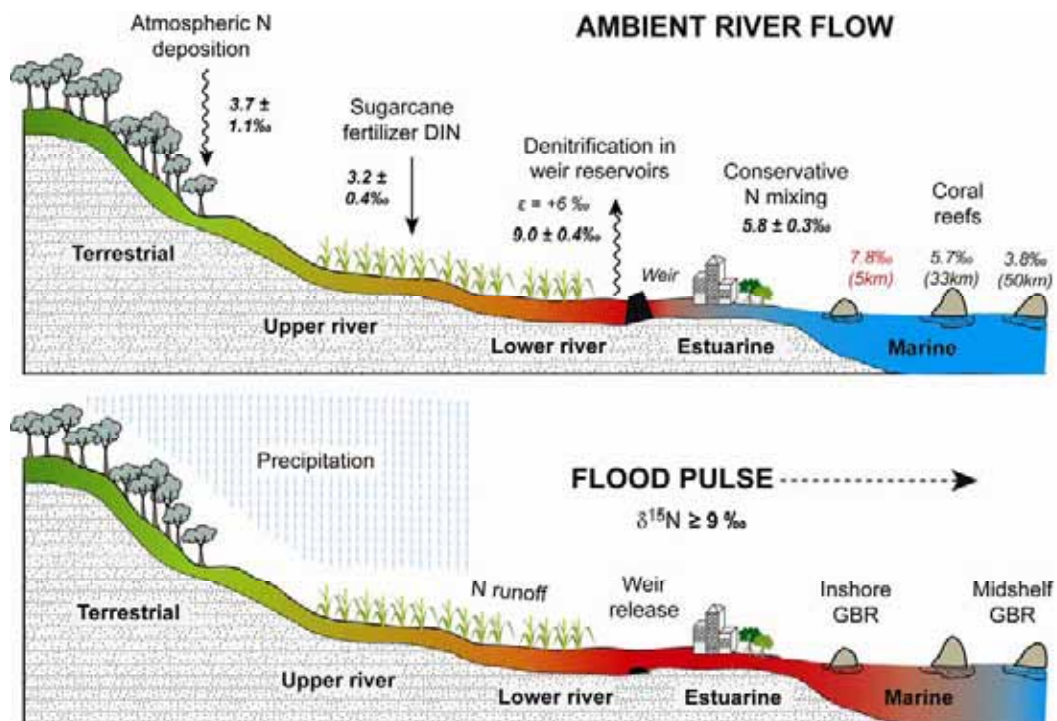
Figure 8. Schematic of nitrogen sources and transformations in the Pioneer River catchment during low-flow conditions (top). Microbial (non-conservative) processing of N species in lower river reservoirs are reflected by enriched particulate δ^{15}N values sampled from the river. Following heavy rainfall events (bottom), the ^{15}N-enriched (>9‰) reservoir waters are discharged as low salinity floods plumes that can extend 33km into the GBR Lagoon, causing enrichment of organic fractions in nearshore coral skeletons.

waters. During flood events (Figure 8b), which occur every 1-2 years in the Pioneer, average monthly discharge rates rise from 6,000 ± 5,000 Ml (ambient flow) to 102,000 ± 83,000 Ml (flood pulse). We hypothesise that the release of ^{15}N-enriched weir reservoir waters into the downstream estuary and nearshore GBR lagoon bears an enriched isotopic signature (>9‰) that is traceable in time-integrated substrates such as insoluble nitrogen fractions within the skeletons of reef-building *Porites* corals growing immediately offshore. Nitrogen incorporation into coral skeletons will be discussed in detail in Chapter 5.

The range of δ^{15}N values observed in the three *Porites* reef corals collected 5 km offshore and directly within the dispersal zone of the Pioneer River was enriched by 2 to 4‰ over the midshelf reefs. These results are consistent with a previous study of the ^{15}N composition of *Porites* coral tissue collected across the GBR shelf. Sammarco et al. (1999) observed a curvilinear decline in δ^{15}N values between the inshore (5.0 – 5.5‰) and midshelf reefs (3.8‰, 60 km offshore), followed by a slight increase offshore (5.2‰, 120 km offshore). The authors interpreted the inshore enrichment as a reflection of the ^{15}N-enriched terrigenous N inputs, including agricultural runoff, mangrove detritus, and secondary-treated sewage effluent. They related the depleted values from the midshelf to N-fixation by cyanobacterial mats in shallow reef environments, and the offshore enrichments to upwelling of deep water nitrate.

The inshore coral δ^{15}N values in the present study were 2 – 2.5‰ higher than those near Townsville (Sammarco et al. 1999) located 300 km to the north. One obvious explanation for the difference between the reported inshore δ^{15}N values is that the Sammarco et al. (1999) study focused on the δ^{15}N values of the bulk *Porites* tissue layer (coral host + algal fractions), while in this study we measured the decalcified organic matter extracted from the skeleton. Generally speaking, sample substrates that permit longer integration periods of environmental change correspond with higher δ^{15}N values when chronically exposed to ^{15}N-enriched sources. Here the value of inshore skeletal δ^{15}N (7.8 ± 1.2‰) > coral tissue δ^{15}N (6.9 ± 1.2‰) > POM δ^{15}N (5.1 ± 0.7‰). This suggests that in the nearshore reefs of Mackay, episodic periods of ^{15}N-enrichment in the coastal environment, for example during the flood-associated influx of enriched Pioneer river N, are reflected in multi-decadal skeletal record, but may be missed

by the shorter integration time of the coral tissue (6-12 months) or marine POM (1-2 weeks).

Episodic and chronic discharge of δ^{15}N-enriched lower river N sources, combined with ^{15}N fractionation associated with planktonic uptake of land-derived DIN and mineralisation, would account for the ^{15}N-enriched organic matter observed in inshore coral skeletons. For example, Pioneer flow rates of up to 290 m^3 s^{-1} triggered release of Mirani and Dumbleton weirs (present day end-member δ^{15}N = 9.0‰) during a minor, three day flood pulse in 2002. The resulting 125,900 Ml pulse of flood waters that entered the coastal ocean (representing 14% of the average annual discharge volume) was associated with maximum concentrations of 190 µM of nitrate + nitrite, of which 55% was sediment bound (Simpson 2002). At Round Top Island, nitrate and ammonium concentrations reached 7.4 µM and 1.6 µM after a separate minor flood pulse in 2005 (Rohde et al. 2005). However, only a small fraction of the terrestrial-derived DIN is likely to come in contact with the 8 m deep coral colonies, as the bulk of the DIN (mostly nitrate) is rapidly assimilated by blooming species of phytoplankton (dominated in nearshore GBR waters by *Synechococcus* and *Prochlorococcus*, Furnas et al. 2005). Extensive phytoplankton bloom formation is a noted feature in the nearshore Mackay and Whitsunday waters, where after 24 hrs following a discharge event in 2005, chlorophyll-a levels had doubled to 1.6 µg l^{-1}, while nitrate and ammonium concentrations returned to ambient concentrations (Rohde et al. 2006). These elevated concentrations of particulate N (algal biomass) have a lasting effect on the nutrient regimes of coastal marine environments due to the cascading effects of remineralisation, reuptake, and ultimately blanketing of the benthic communities during post-bloom senescence.

Conclusions

The organic matter entrained in nearshore coral skeletons living immediately offshore of the mouth of the Pioneer River bears an isotopic signature that reflects the cascading effects of multiple N transformations during passage of river POM to the ocean. The process begins with elevated anthropogenic inputs of biologically available (fertiliser-derived DIN) into the upper Pioneer River (Brodie 2004, Mitchell et al. 2005), followed by extensive microbial transformations in the lower river (+6‰), and ending with planktonic-

related δ^{15}N enrichment (0-9‰) in the coastal waters prior to settling on and being incorporated by benthic coral communities. The precise isotopic "fingerprinting" of the Pioneer catchment described here, using the tri-tracer approach, provides important contextual evidence for interpreting spatial and temporal δ^{15}N trends in nearshore *Porites* coral skeletons, which will be discussed at length in Chapter 5.

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Reef environment at Keswick Island with massive *Porites* colony in background, 1 April 2004.

Coral Environmental Records from the Mackay Section of the GBR: Background

Introduction

Coral reefs are among the richest and most diverse of all marine ecosystems. Reef-building corals belong to the order Scleractinia, which emerged during the mid-Triassic period about 237 Ma (Stanley & Fautin 2001). Scleractinian corals are similar in body plan to anemones, but secrete a calcium carbonate skeleton. In some species, budding by individual coral polyps leads to massive colonial structures, and over geologic time, calcium carbonate accretion by aggregates of colonial corals form reefs (Veron 2000). Coral reefs serve critical functions in the world's oceans, including: seeding and sheltering one quarter of marine species despite occupying only 0.25% of the world's oceans; sequestering atmospheric and oceanic carbon via calcification; supporting global

industries worth \$375 billion annually (including \$5.5 billion in the GBR); and protecting highly populated coastlines in tropical reef-containing nations (Bryant et al. 1998; Kleypas et al. 1999).

A defining feature of tropical and subtropical Scleractinian corals is their ability to live and support daily productivity rates that are thousands of times higher than surrounding nutrient-poor ocean waters. This feat is achieved through a unique mutualistic relationship between coral hosts and their algal dinoflagellate symbionts ("zooxanthellae") of the genus *Symbiodinium* (Hoegh-Guldberg et al. 2004). Algal photosynthetic products partially support the metabolic needs of the coral host, including tissue growth, reproduction, and calcification, while coral excretory products provide carbon inputs required for algal photosynthesis (Hoegh-Guldberg et al. 2004).

Reef-building corals provide the structural framework for tropical reef ecosystems. Individual coral polyps secrete hard skeletons consisting of aragonite, a form of calcium carbonate ($CaCO_3$), according to the equation:

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O$$
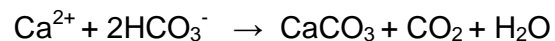
Most coral-based paleoenvironmental studies focus on the reef-building genus *Porites* due to its: long life span (typically 100 - 800 years) of the massive morphologies; widespread distribution; relative resilience to high-energy environments, temperature variations, turbidity and nutrient stress; and consistent annual growth banding patterns (Knutson et al. 1972, Buddemeier et al. 1974, Veron 2000). Massive coral species grow vertically by secreting carbonate deposits from their calcioblastic layer located between the polyp base and the underlying skeleton (Barnes 1970). During the warm summer months, increased coral calcification rates result in deposition of high density bands, while low density bands are formed during the winter months (Lough & Barnes 1990). Each density band couplet represents an annual increment of growth, allowing accurate dating of chronologies by counting bands from the surface tissue layer (Hudson et al. 1976).

Corals incorporate chemical records of their seawater environment within their aragonite skeleton by various mechanism, including: (1) substitution of trace elements for calcium or carbonate ions during skeletal deposition (Lea et al.

1989, Allison 1996, Greegor et al. 1997); (2) incorporation of external detrital matter that is trapped within skeletal pore spaces (Barnard et al. 1974, Budd et al. 1993, Marion et al. 2005); (3) systematic incorporation of coral proteins into the calcium carbonate skeleton (Cuif & Dauphin 2005); and (4) nitrogen uptake by endolithic algae living within the skeleton (Highsmith 1981). Thus, geochemical tracers can be measured from *Porites* skeleton over the duration of the colony's lifespan that vary consistently with environmental parameters and oceanographic processes, such as sea surface temperature, upwelling, sea surface salinity, and sediment and nutrient delivery to the nearshore from terrestrial runoff. In the following three chapters, we report how geochemical tracers within *Porites* skeletons collected from islands along a distance gradient from Mackay can be used to describe nutrient and sediment delivery from the Pioneer River catchment to the nearshore, and how nutrient and sediment loads from Pioneer River discharge have changed over time.

Study Sites

In April 2004, December 2004 and March 2006, cores were drilled from massive *Porites* colonies from three locations described below (Round Top, Keswick and Scawfell islands) at increasing distances from the Pioneer River mouth (Figure 1, Table 1). All cores were collected using SCUBA in water depths of 4 – 8 m using a pneumatic, hand-held underwater drill attached to a stainless steel coring barrel. The *Porites* specimens selected for coring exhibited regular hemispheric shapes, had intact tissue layers, and showed little or no visible evidence of bite marks, boring bivalves or sponges, algal growth or other forms of

Table 1. Coral core specifications, including distance from Pioneer River, species, start year, coral tissue thickness, skeletal extension rate, and depth at collection, for cores used for δ^{15}N and trace element analyses described in Chapters 5, 6, and 7.

Core	Location	Collection date	Lat (°S)	Lon (°E)	Km offshore	Coral species	Start Yr	Tissue (mm)	Ext. rate (mm/yr)	Depth (m)
RTC	Round Top I	04/04/2004	21.1755	149.2630	5	*P. australiensis*	1962	6.5	7.6	8.0
RTF	Round Top I	08/12/2004	21.1708	149.2644	5	*P. lutea*	1945	6.0	8.8	8.5
RTH	Round Top I	06/03/2006	21.1705	149.2650	5	*P. australiensis*	1824	5.5	7.8	6.0
KIA	Keswick I	01/04/2004	20.9177	149.4186	33	*P. lutea*	1950	7.0	16.1	5.0
KIC	Keswick I	01/04/2004	20.9177	149.4178	33	*P. lutea*	1968	5.5	15.9	6.0
SCC	Scawfell I	02/04/2004	20.8552	149.6021	50	*P. lutea*	1952	2.5	14.8	4.0
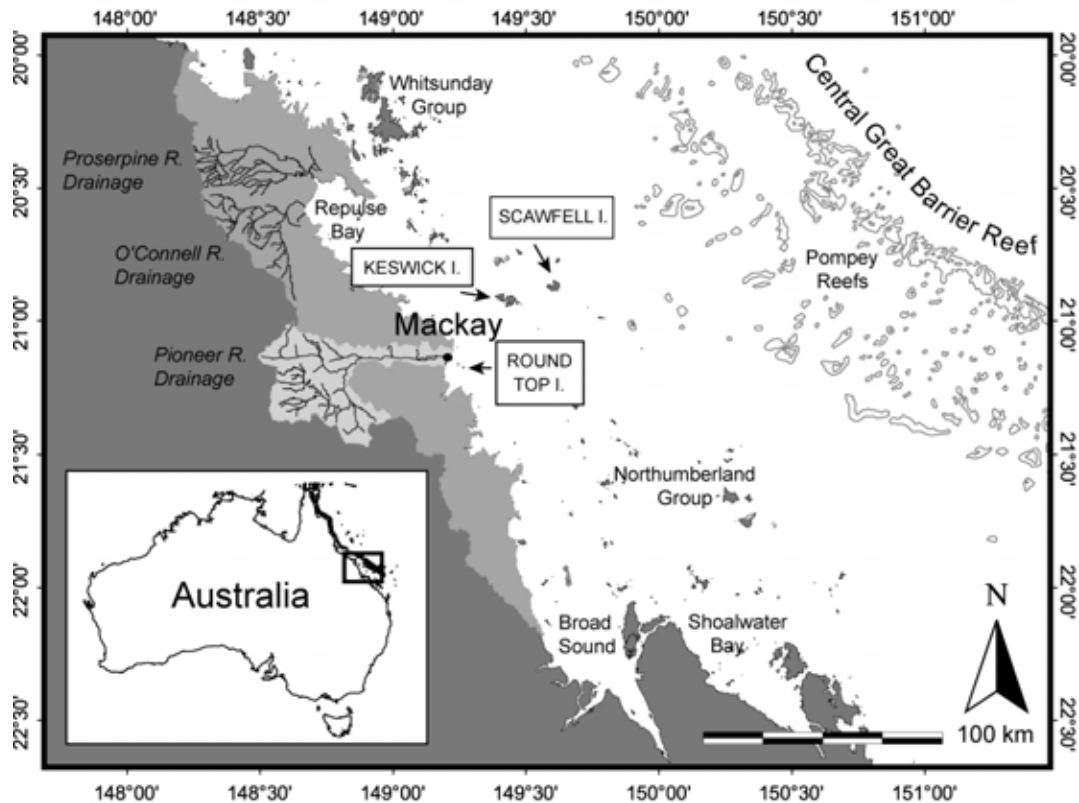
Figure 1. Coral core collection sites at Round Top Island, Keswick Island and Scawfell Island shown within the Mackay section of the Great Barrier Reef. The Pioneer catchment is shown in light grey within the darker grey Mackay Whitsunday management region.

bioerosion. Each core was slabbed, x-radiographed to reveal density band patterns, and photographed under ultraviolet light to visualise luminescent banding related to freshwater discharge and altered calcification (Hendy et al. 2003).

Round Top Island

Round Top Island is composed of continental granite, covering 24 ha, and is located 5 km from the Pioneer River mouth. It is therefore directly exposed to discharge from the Pioneer River, although the interaction of flood flows with complex tidal currents may result in distinct micro-environments (i.e. varying salinities and currents) around the island (QEPA 2004). The inshore coral community, defined as coral habitat "without appreciable framework or detrital accumulations" (van Woesik and Done 1997), at Round Top is dominated by rubble, pavement and sand, with higher densities of corals on the northwestern

side. A seagrass bed, located ~6 m below mean sea level off the northwestern side of Round Top Island, was first observed to contain *Halodule univervis* (Coles et al. 1987), and later found to also include *Halophila ovalis* (Rasheed et al. 2001), as confirmed by surveys in 2006.

Keswick and St. Bees Islands

Keswick Island (812 ha) and St. Bees Island (1329 ha) are located approximately 33 km from the Pioneer River mouth, separated from each other by a narrow channel < 1 km wide. The islands are part of the Cumberland Group, which are composed largely of Whitsunday volcanics that include ignimbrites, tuffs and rhyolitic flows (Ewart et al. 1990). Both Keswick and St. Bees are exposed to large flood plumes discharged by the Pioneer and other adjacent river systems. For example, Devlin et al. (2001) mapped the extent of the river plumes from Cyclone Justin in 1997 east of St. Bees Island, while recent satellite data from flood events in January 2005 (Chapter 6, Figure 4) and January-February 2007 show turbid waters surrounding the islands. Recent surveys (see Chapter 8) have documented fringing reefs within the channel and south-facing bays that were largely covered by brown macroalgae (Phaeophyta), particularly *Sargassum* spp. and *Podina* spp., over a carbonate framework, similar in nature to Calf Island and Pine Island reefs in the Whitsunday region surveyed by van Woesik et al. (1999).

Both Keswick and St. Bees islands have a long history of land modification. Aboriginal groups maintained island grassland communities by periodic burning, which provided fodder to grazers (e.g. goats, merino sheep) that were introduced to St. Bees in the first decade of the 20th century (Berck 1995). Koalas were introduced to St. Bees in 1938 and the island is now maintained as a national park. Keswick also has national park status, although there is a small airstrip and resort, and plans have been drawn for future residential and marina development.

Scawfell Island

Scawfell Island covers 1441 ha of national park lands and is also a member of the Cumberland Island Group. It is located approximately 51 km from the Pioneer River mouth and receives floodwaters only during extreme events.
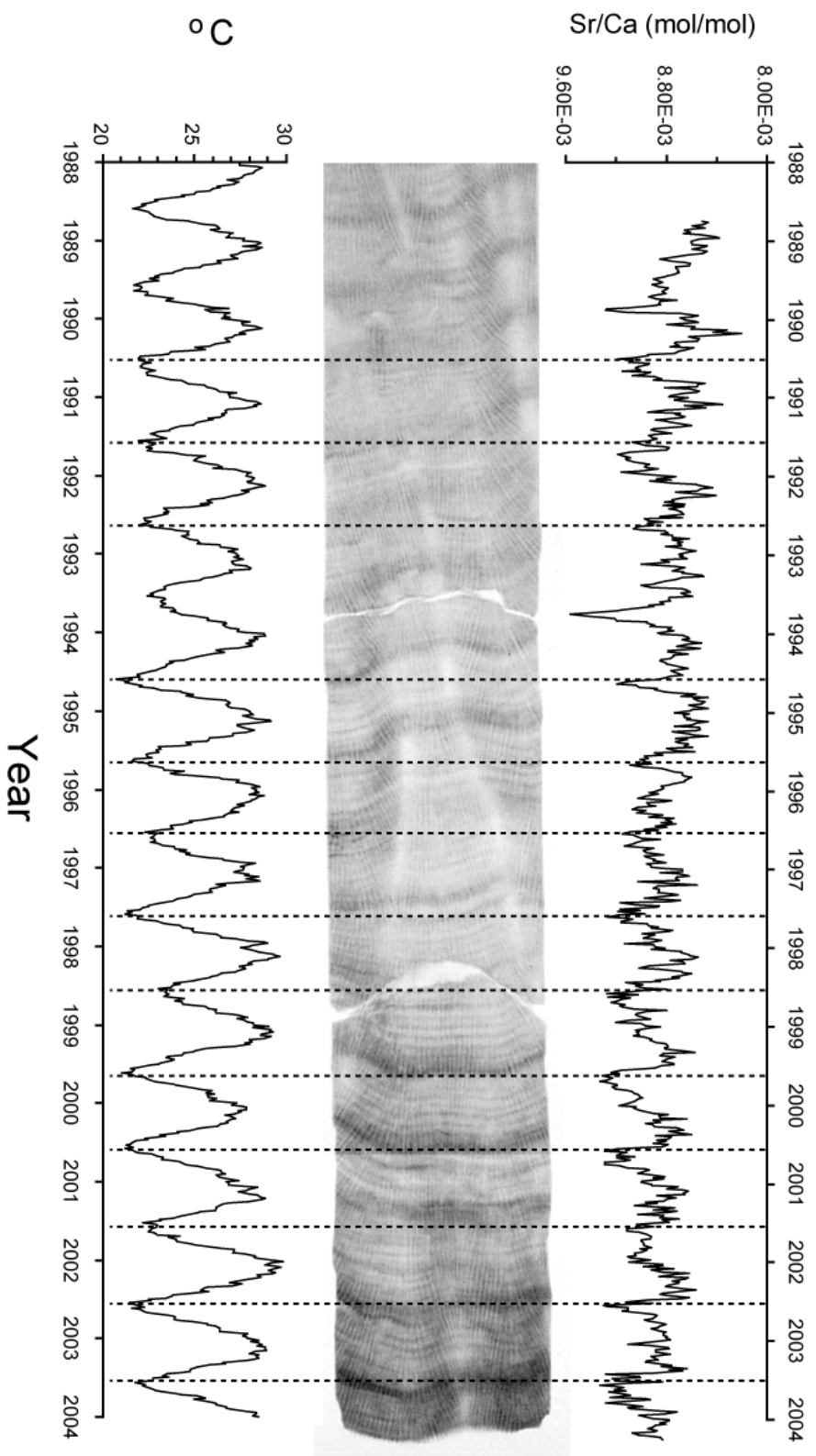
Figure 2. Example of chronology construction for Scawfell Island core (SCC). Dashed lines show alignment between: winter maxima of weekly Sr/Ca (above); seasonal density bands (middle); and winter SST minima (bottom)

While narrow fringing reef surrounds the island, the most extensive reef development occurs in Refuge Bay where the reef flat can extend up to 0.6 km (Kleypas & Hopley 1992). Reefs within Refuge Bay have diverse coral fauna, with an average coral cover of 26.9% in surveys by van Woesik and Done (1997).

Coral Chronology Assignment

Coral core chronologies were established by using a combination of tools, including: alternating patterns of annual high and low density bands; bright luminescence bands corresponding to known years of high discharge from the Pioneer River; and seasonal cycles of trace element to calcium (Ca) ratios for elements such as strontium (Sr), boron (B) and uranium (U) known to vary inversely with sea surface temperature (SST). High resolution (~weekly) Sr/Ca, B/Ca and U/Ca records measured by laser ablation inductively coupled mass spectrometry (LA-ICPMS) were compared with weekly SST from 1º gridded data composed of ship, buoy and satellite measurements (Reynolds & Smith 1994)[1]. For each year from 1981 (earliest instrumental SST records), maximum trace element ratios were assigned dates from the winter week with the minimum SST and minimum trace element ratios were assigned dates from the summer week with the maximum SST (Figure 2). For years before 1981, the average week of winter minimum temperatures and summer maximum temperatures were assigned to trace element peaks and troughs, respectively. These chronologies were verified independently by ensuring that the number of seasonal trace element cycles matched the counts of annual density bands, which were drilled in bulk samples for coral $\delta^{15}N$ measurements.

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Divers prepare to drill a coral core from a massive *Porites* colony at Keswick Island, 1 April 2004.

<div align="right">Chapter Five</div>

Anthropogenic and River Flood Signals in Massive Coral Skeleton: I. Nitrogen Isotopes

Introduction

Anthropogenic nitrogen inputs into the biosphere now exceed natural sources, threatening the health and dynamics of marine communities worldwide (Matson et al. 1997, Fabricius & De'Ath 2004, Foley et al. 2005). In 2000, an estimated 80.9 x 10^{6} megatons (MT) of N fertilisers were applied to agricultural lands adjacent to coastal marine ecosystems, a figure that is predicted to rise to 187 x 10^{6} MT by 2050, representing 27% of the global N fertiliser use (Vitousek et al. 1997, Beman et al. 2005). Coastal ecosystems such as coral reefs are thought to be highly sensitive to enhanced nutrient concentrations arising from agricultural activity. In the case of the Great Barrier Reef (GBR), coastal reefs border its large catchment area (422,000km[2]) of which ~76% is under agriculture (GBRMPA 2001, Neil et al. 2002). Studies estimate that the total nutrient load

delivered into the GBR Lagoon has increased 2 to 4-fold since European arrival in 1860 (Furnas 2003, Brodie et al. 2004), and represents 30% of the annual N input into the Lagoon at present (Devlin et al. 2001). Marine ecosystems that inhabit land-sea margins, however, are naturally exposed to elevated inputs from runoff and upwelling at shelf margins, resulting in uncertainty over the timing and extent of anthropogenic N-enrichment of coastal environments (Paerl 1997, Larcombe & Woolfe 1999, Fabricius et al. 2005). Historical data on baseline variability of N sources and dynamics in turbid coastal regions are thus critical for linking the health of marine communities with gradients of exposure to anthropogenic inputs.

Nitrogen isotopic analysis ($\delta^{15}N$) of benthic producers, such as reef-building (Scleractinian) corals (Sammarco et al. 1999, Heikoop et al. 2000b, Risk & Erdmann 2000, Risk et al. 2001) and macrophytes (McClelland & Valiela 1998, Costanzo et al. 2001, Umezawa et al. 2002, Yamamuro et al. 2003, Lapointe et al. 2005), when combined with extensive characterisation of end-member inputs from land-derived sources (Chapter 3), represent a direct means of tracing anthropogenic N sources into freshwater and marine communities. Biological processes alter $\delta^{15}N$ values (the relative abundance of ^{15}N to ^{14}N in a sample compared to the ratio in air) via a kinetic affinity for transformations involving the ^{14}N isotope. This produces traceable signatures of specific N sources and transformations (Mariotti et al. 1984, Owens 1987, Cifuentes et al. 1989, McClelland & Valiela 1998, Middelburg & Nieuwenhuize 2000). However the tissues of corals, macrophytes, and other primary producers only record brief intervals of seawater $\delta^{15}N$ values (2-9 months in corals), limiting their usefulness for historical studies.

Nitrogen partitioned into reef-building coral skeletons is well preserved over centennial to million year timescales (Ingalls et al. 2003, Muscatine et al. 2005), and compositionally reflects the source of dissolved (Allemand et al. 1998, Hoegh-Guldberg et al. 2004) and particulate N species (Marion et al. 2005) assimilated from the water column. Scleractinian coral skeleton is a three-phase composite structure composed of mineral aragonite permeated by a glycoprotein-rich organic matrix (Johnston 1980, Allemand et al. 2004, Cuif & Dauphin 2005), and infilled with mostly allochthonous interstitial materials partitioned from the ambient environment (Barnard et al. 1974, Cortes & Risk 1985, Edinger et al.

2000). The insoluble nitrogen (functionally defined here as the residual organic fraction captured by filtration through a 0.7 um^{-1} pore size glass fibre filter) represents 51% of total skeletal N and compositionally is closely related to sources and transformations of N in the water column (Chapter 3, Marion et al. 2005). Composed primarily from deposited sedimentary organic matter incorporated from the water column (Barnard et al. 1974, Cortes & Risk 1985, Edinger et al. 2000), organic matrix elements, and siphonaceous euendolithic algae primarily of the genus *Ostreobium* (Highsmith 1981, Le Campion-Alsumard et al. 1995, Fine et al. 2004), δ^{15}N values are identical in *Porites* tissue and underlying insoluble skeletal N (Marion et al. 2005). This supports observations that organic ^{15}N composition is not altered during assimilation of skeletal carbonate (Hoegh-Guldberg et al. 2004, Muscatine et al. 2005).

Marion et al. (2005) analysed insoluble δ^{15}N values preserved within nearshore *Porites* skeletal cores from Bali, Indonesia. In a reef coral exposed to elevated dissolved inorganic nitrogen (DIN) inputs from a nearby agricultural drainage point (1/2 km away), δ^{15}N values declined from 9.9‰ in 1970 to 3.5‰ in 2000. This was interpreted as a reflection of increasing inputs of fertiliser-derived DIN in runoff (δ^{15}N = -0.8‰). Using a different approach, Hoegh-Guldberg et al. (2004) analysed the intracrystalline organic matrix proteins isolated from *Pocillopora damicornis* corals. Organic matrix δ^{15}N values were significantly depleted (0.2 ± 0.3‰) in specimens treated with daily NH_4Cl additions (δ^{15}N = 0‰) over a two year period relative to controls (1.3 ± 0.3‰), supporting findings that dissolved N is rapidly assimilated from the water column into skeletal proteins (Allemand et al. 1998).

Here we examine sources of annual to decadal δ^{15}N variability in 60-year long δ^{15}N time series developed from insoluble fractions of N in massive *Porites* coral skeletons. The cores were collected from nearshore to midshelf reefs (5-50 km offshore) on the southern GBR (see Figure 1 in Chapter 4). The adjacent city of Mackay represents an epicentre of agricultural activity, producing 1/3 of Queensland's annual sugarcane harvest (EPA 2004). A comprehensive isotopic study of end-member inputs in the catchment (Chapter 3) revealed distinctively enriched particulate δ^{15}N values in the lower river (up to 9.5‰) relative to those measured in the coastal waters (4.9 – 5.1‰). We hypothesized that: (1) coral tissue and skeletal δ^{15}N values would exhibit a cross-shelf decline reflective of

decreasing exposure to enriched anthropogenic sources of N in runoff; (2) δ^{15}N values in nearshore coral skeletons would exhibit increased variability (enrichment) during major Pioneer River flood years; and (3) substantial increases in N fertilisation rates and land clearing for agricultural cultivation since the early 1940s would be reflected by a long-term rise of δ^{15}N values in nearshore coral skeletons.

Coral Collection and Analysis

Massive *Porites sp.* colonies were cored from a cross-shelf transect of reefs (Round Top Island, Keswick Island and Scawfell Island) ranging from 5 – 50 km offshore of Mackay as described in Chapter 4 (see Table 1). All cores were rinsed with freshwater, air-dried, packaged in casings made from PVC piping, and returned for preparation. Seven-mm thick slabs were sliced from the five cores at the Australian National University using a water cooled, diamond blade rotary saw (Kearney & Trecker 3HP-No2 Model E) mounted to an automatic feeder tray (12.5 cm min^{-1} feed rate). Slabs were cleaned in RO water, air dried for five days and stored. Digitally captured X-radiographs (Kodak CR500, 35x43cm phosphor cassettes, 6s exposure time) revealed clear bands of alternating high and low density skeleton in all cores (Fig. 2). Each density band couplet represents an annual increment of growth (Knutson et al. 1972, Buddemeier et al. 1974), providing an accurate means of backdating from the surface tissue layer (=collection year). Slabs were illuminated by UV light and photographed using a yellow/orange filter on black and white film (Hendy et al. 2003) in order to visualise luminescent band stratigraphy (Figure 1, bottom image).

Prior to sample preparation, an ultra-fine (<1mm thick) layer was cut from the entire slab to remove superficial contamination. Annual density bands were mapped from x-radiographs onto core slices, and overlap between adjacent years of growth was minimized by illuminating the slabs under UV light and cutting around fine-variations in luminescent bands. Annual coral carbonate subsamples, ranging from 1.5 – 2.8g, were ground to a powder, decalcified in 1M H_3PO_4, and the acid-insoluble organic fraction filtered (Whatman GF/F, 0.7 um^{-1} pore size), dried for 24 hr at 60^{0}C, and loaded in 9x10mm tin capsules into a 31-run multi-sampler carousel. In the Keswick Island coral, seasonally-deposited

high and low density bands (two yr^{-1}) were analysed separately (yielding 2 samples per year). This specimen was selected for its high growth rate (semi-annual samples weighed from 1.2 – 2.2g), and clear, perpendicular banding stratigraphy. Samples were analysed using a Carlo Erba NA1500 elemental analyser (EA) coupled to a Finnigan MAT Delta+ mass spectrometer via a ConFlo II open split interface (Stanford University Stable Isotope Laboratory). Six isotopic (IAEA-N1, USGS-24) and seven elemental (acetanilide) standards were analysed with each set of 40 C/N samples, yielding instrumental standard deviations of 0.07‰ (δ^{15}N) and 0.35‰ (δ^{13}C). Isotopic values are reported using standard delta notion (described here for nitrogen):

$$\delta^{15}N\ (‰) = \frac{^{15}N\ /\ ^{14}N_{sample} - ^{15}N\ /\ ^{14}N_{atm.}}{^{15}N\ /\ ^{14}N_{atm}}\ x\ 1000$$

as the permil variation (‰) of the sample relative to the isotopic ratio of N in air.

Chronologies were initially set by counting the annual density bands from the surface tissue layer and backdating from the collection date. To clarify banding stratigraphy through obscured growth regions, we established an independent age model using density and luminescent time series overlaid on digital x-ray and UV images (Figure 1). Chronologies were assigned using the density profiles (Figure 1, top image), with annual maximums corresponding to calcification during the peak seasonal temperatures in February (Lough & Barnes 2000). The location of each annual density peak (in mm from core top) was transposed onto UV photographs and compared with luminescent banding patterns (Figure 1, bottom image). Skeletal areas with clear luminescent bands typically coincide with obscured density bands and vice versa (i.e. 1988 to 1992, Figure 1). Intense "marker" bands reflective of major floods were visible in all cores in 1974, 1989, 1991, 2000, providing a useful reference for validating age models.

A 3-core composite time series spanning the years 1944 - 2005 was developed for the inshore Round Top Island site by averaging the three δ^{15}N
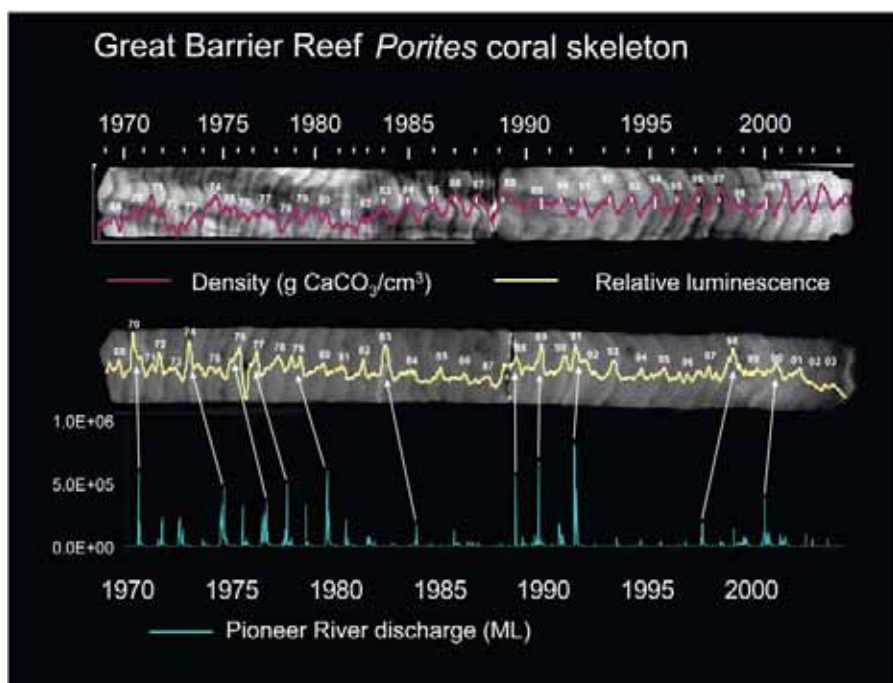
Figure 1. High resolution density (purple graph, top) and luminescence data (yellow graph, bottom) were measured in this core slab from Keswick I., GBR, at 0.25mm increments using a gamma densitometer (Chalker & Barnes, 1990). Plots are overlaid on an x-radiograph (top) and image of a Porites slab illuminated under UV light (bottom). The stratigraphy of annual density and luminescent bands in these Porites sp. coral slabs was used to verify chronologies assigned to δ^{15}N time series.

values associated with each year of growth from cores RTC, RTF, and RTH (reported as ± 1 standard deviation). RTC spanned the years 1963 – 2004, while RTF and RTH covered the entire 60 year record. Linear regression analysis was used to assess correlation coefficients between δ^{15}N time series. Single series Fourier (spectral) analysis was used to identify seasonality in the composite inshore δ^{15}N record, after first subtracting means and removing linear trends. Observations were padded to the nearest factor of 2 (n=128). All analysis was performed using the StatSoft package Statistica 6.0.

Spatial Variability in Coral δ^{15}N Values

Significant variability in the δ^{15}N time series data originates from both exogenous and endogenous factors, including: (1) climate, anthropogenic, and ecological processes that influence the isotopic composition and concentration of the N source; (2) conservative (physical) and non-conservative (biological) processes that determine the fate of δ^{15}N ratios in the coastal marine

environment; and (3) isotopic change associated with the incorporation of N species into the skeleton. In order to understand each, we first examine processes that may account for the decrease in *Porites* tissue and skeletal $\delta^{15}N$ values across the inshore to midshelf transect of the southern Great Barrier Reef offshore of Mackay. We then examine environmental and coral factors that explain the trends and seasonality in $\delta^{15}N$ data between 1944 and 2005.

Cross-GBR shelf trends

   Porites tissue $\delta^{15}N$ values decreased significantly (by 3.9‰) between the 3 inshore and midshelf reef sites (Figure 2). Potential sources of inter-site variability in coral tissue $\delta^{15}N$ values include expression of light-related symbiotic dinoflagellate fractionation in turbid inshore waters (Muscatine & Kaplan 1994, Heikoop et al. 1998) or exposure to anthropogenic sources of N from land-based inputs (Heikoop et al. 2000a, Heikoop et al. 2000b).
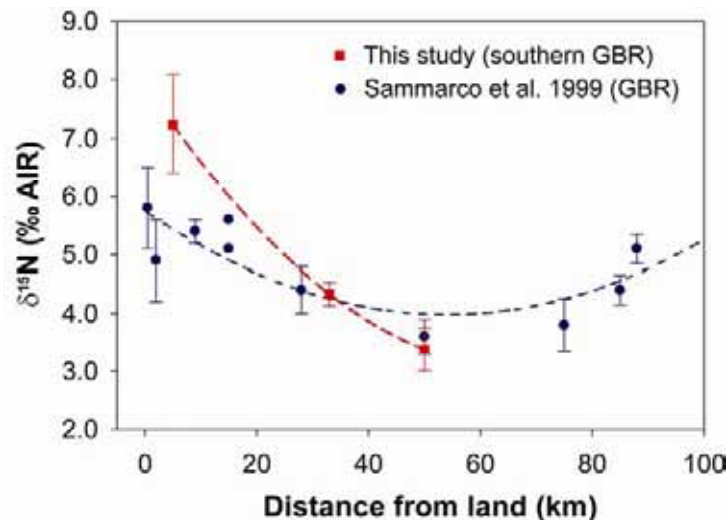
Figure 2. Comparison of average *Porites sp.* coral tissue $\delta^{15}N$ values from inshore and midshelf reefs of the Great Barrier Reef in this study (red squares), and between inshore and offshore reefs from the central GBR (blue circles) reported by Sammarco et al (1999). Error bars represent mean ± 1 standard error (SE).

   Light- Light is an influencing factor on tissue $\delta^{15}N$ values in coral species containing symbiotic dinoflagellates (Muscatine & Kaplan 1994, Heikoop et al. 1998). In low light scenarios characterised by reduced rates of symbiont photosynthesis, coral and symbiotic dinoflagellates cells in the gastrodermis (cell layer that lines the gastrovascular cavity) selectively assimilate ^{14}N from internal

DIN pools, fractionating (lowering) average tissue $\delta^{15}N$ values (Muscatine & Kaplan 1994, Heikoop et al. 1998). If expression of light-related fractionation was a primary influencing factor across the Mackay transect, we would expect to observe low $\delta^{15}N$ values in the turbid coral reefs surrounding Round Top Island. The opposite occurred with our data, where $\delta^{15}N$ values from the inshore coral tissues were 1.5‰ higher than from the midshelf corals (all specimens were collected from depths of 4.0-8.5m), suggesting that light is a secondary or inconsequential source of variability.

Anthropogenic N in terrestrial runoff- The most probable explanation for the decline in *Porites* tissue $\delta^{15}N$ values between the inshore and midshelf reefs is differential exposure to anthropogenic sources of N in river runoff. Presently, total N exports from the Pioneer River are estimated at 1224 T N yr^{-1} (McKergow et al. 2005), representing the 8th highest rate of DIN export of the 35 major GBR river catchments (Furnas 2003). Mackay's secondary-sewage treatment facility at Mt. Bassett delivers 211.5 T N yr^{-1} in effluent into the estuary (concentrations = 30 mg N L^{-1}), representing 17% of the total river N load during average flow conditions (unpublished report). If we assume that fertiliser-derived N from the upstream sugarcane land accounts for the balance of the river's N load, and use end-member $\delta^{15}N$ values measured in Chapter 3 from downstream sugarcane-bordering river waters (8.99%, 1012 T N yr^{-1}) and from the sewage outfall (2.95‰, 211 T yr^{-1}), then an annual $\delta^{15}N$ input value of 7.96‰ is calculated for the Pioneer. The assumption that agricultural inputs account for the balance of the river N-load is reasonable given that land used for sugarcane cultivation covers 71.1% of the lower Pioneer alluvial flood plane (Jupiter & Marion 2007), with grazed land, forest preserves and the Mackay urban centre (serviced by Mt. Bassett sewage treatment plant) accounting for the remainder (Chapter 2). The calculated value exceeds the estuarine $\delta^{15}N$ end-member (6.06 ± 0.40‰) measured during non-flood conditions in March 2006 (Chapter 4), but is similar to the average inshore *Porites* coral tissue (7.24 ± 1.69‰) and skeletal (7.84 ± 0.24‰) values. Given that the range of marine particulate $\delta^{15}N$ values are isotopically depleted in comparison (4.9 – 5.1‰), this suggests that coral $\delta^{15}N$ values are reflecting chronic enrichment from river N inputs over the 6-month integration time represented in these coral tissue layers.

Comparison with the Burdekin Region

Sammarco et al. (1999) studied values of $\delta^{15}N$ from *Porites lobata* tissue on reefs collected along a 120km-wide tract of the central GBR off Townsville, 320km north of Mackay. The authors observed a curvilinear cross-shelf $\delta^{15}N$ decline, which was interpreted as a reflection of enriched anthropogenic and natural N inputs into the inshore waters, N fixation in the midshelf, and upwelling at the shelf edge. The tissue values from the midshelf reefs located 40-50km offshore (3.8‰) matched results presented here (midshelf tissue $\delta^{15}N$ = 3.4 – 4.3‰, Figure 2). Inshore Mackay coral tissue $\delta^{15}N$ values, however, were 1.5 – 2‰ higher than nearshore Townsville corals (Sammarco et al. 1999). This is interesting given that 97% of total land in the Burdekin-Haughton region (including Townsville) is dedicated to cattle grazing and 1% to cropping, compared to 67% and 13% respectively in the Pioneer-O'Connell region (Devlin et al. 2001). The average annual discharge from the Burdekin River (10.29 km^3 yr^{-1}) is 8.6-times that of the Pioneer, while the pool of biologically-available DIN exported is 8.3-times higher in the Pioneer (when standardized by land area) (Furnas 2003). The enriched $\delta^{15}N$ values observed both in Pioneer river particulate matter (Chapter 3), and in the nearshore coral tissues, suggest that a concentrated DIN dose is funnelled into nearshore Mackay coral reef waters, resulting in frequent phytoplankton blooms (Furnas et al. 1997).

Temporal Variability in Inshore Coral $\delta^{15}N$ Values: 1945 - 2005

Coral $\delta^{15}N$ data revealed three distinctive patterns between 1945 and 2005: (1) between the years 1944 and 1979, annual $\delta^{15}N$ values rose by 2.5‰ along a relatively consistent trajectory (Figure 3a); (2) after 1980, isotopic variability increased by 2 to 7-fold (Figure 3b); and (3) $\delta^{15}N$ signals of Pioneer River flood events increased by 3‰ between 1946 and 2000. Although $\delta^{15}N$ values are correlated to Pioneer River discharge, particularly when data is binned into 3-yr averages ($r^2 = 0.42$, $p < 0.001$), river discharge patterns did not exhibit long-term trends and thus cannot alone account for the 60 yr enrichment evident in the coral record.
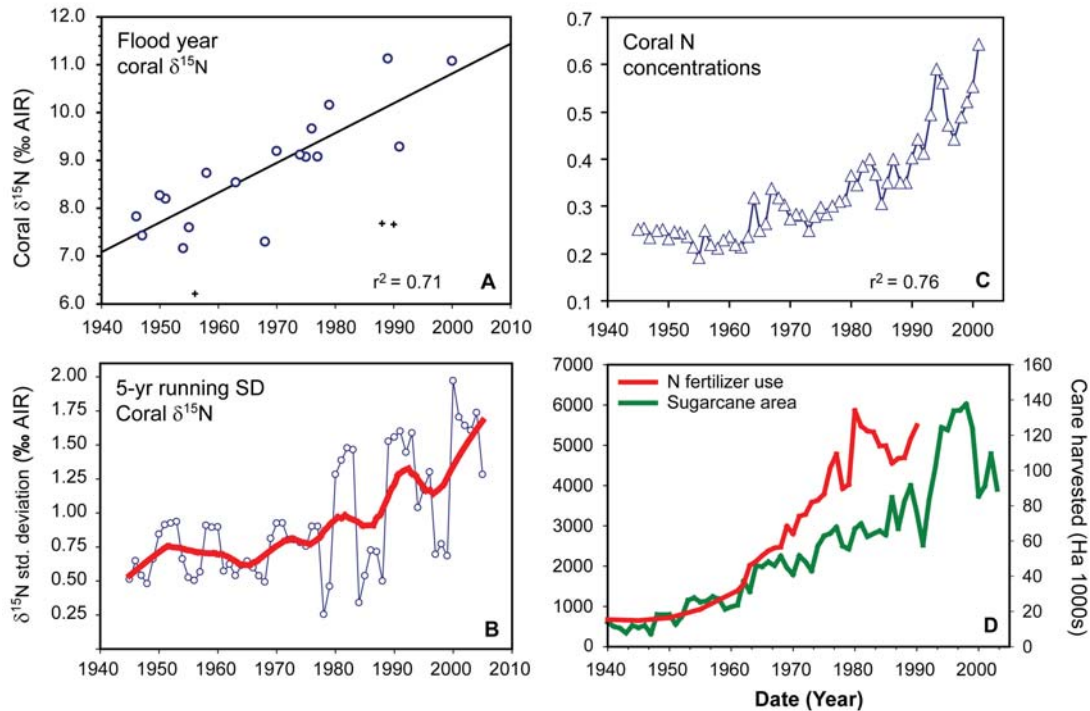
Figure 3. Coral evidence of long-term nitrogen loading of inshore Great Barrier Reef (GBR) coral communities between 1940 and 2005. Elevated $\delta^{15}N$ values represent anthropogenic N sources. Coral $\delta^{15}N$ values are becoming progressively more enriched during flood years (a), as well as more variable (b). These observations reflect increased concentrations of dissolved inorganic nitrogen in river discharge which fuel regular plankton blooms characteristic of this region of the southern GBR (Furnas et al. 1997). Coincident with rising signatures of human-derived N is a long-term increase in the amount of nitrogen accumulating in coral skeletons in nearshore reefs (c). These 3 coral-based indicators reflect the rising rates of N fertiliser use and land area under cultivation (d) in the Pioneer Valley of Mackay since 1940. Fertiliser data are from Pulsford (1996).

Linear increase in coral $\delta^{15}N$ values between 1944 and 1979

One explanation for the rise in baseline and flood-associated $\delta^{15}N$ values between 1944 and 1979 is that the amount of N export required to express detectable $\delta^{15}N$ signals in coral skeletons surpassed a critical threshold over that time period. Between 1944 and 1979, the rise in coral $\delta^{15}N$ data is consistent with rapid agricultural development and increasing anthropogenic N inputs from the Pioneer catchment (Figure 3a-d). Coral $\delta^{15}N$ values are significantly correlated to the 6-fold increase of N fertiliser use in the Pioneer Valley between 1944 and 1980 ($r^2 = 0.54$, n = 37, $p < 0.001$). Nitrate leaches strongly from soluble N fertilisers (primarily urea and ammonium nitrate in Queensland sugarcane farming; Rasiah et al. 2003), which is lost to surface water runoff (10% of applied N) and to groundwater discharge (5%), totalling runoff rates of 25kg ha^{-1} yr^{-1} in the Pioneer Catchment (J. Brodie, pers. comm.). River nitrate concentrations are

highly variable through time, ranging from 1.2 - 7.8 µM during ambient flow scenarios (Chapter 3) and extending up to 138.4 µM in sugarcane-bordering waterways (Plane Creek) during flood conditions (Rhode et al. 2005). As a comparison, in the Johnstone River catchment of Northern Queensland, 23 to 81kg N ha^{-1} (or 27 – 73% of the applied 180 kg ha^{-1}) is leached to groundwater in the crop root-zone <0.75m deep, of which large quantities enter the GBR Lagoon (Rasiah & Armour 2001, Rasiah et al. 2003). Over the same period, the land area cultivated for sugarcane harvesting in the Pioneer catchment increased by a factor of 5 to 109,410 ha in 2002 (Figure 3d), while between 1972 and 2004, 56.4 km^2 of riparian vegetation along the banks of the Pioneer was cleared, representing a 32% loss of the lower Pioneer's total vegetative buffer zone (Jupiter & Marion 2007).

McClelland et al. (1997) reported that the δ^{15}N values of eelgrass and macrophyte tissues in Cape Cod, MA were significantly enriched after N loading (total N applications) reached 90 kg ha^{-1} yr^{-1}. The authors suggested a threshold exists between 0 and 90 kg ha^{-1} yr^{-1} where δ^{15}N signatures delivered in groundwater to estuaries become evident in producer tissues. In the Pioneer Catchment, N-loading from agriculture alone increased from 35.3 – 87.7 kg ha^{-1} yr between 1940 and 1980, calculated from fertiliser consumption data (Simpson et al. 2001) and land use records for the region. By 1999, this figure reached 175 kg N ha^{-1} yr^{-1} for the broader Mackay region (Brodie 2004). The first consecutive pair of flood-associated δ^{15}N values to differ significantly coincided with annual N fertiliser loading rates of 43 and 56 kg N ha^{-1} in 1958 and 1989 respectively. These rates do not account for N inputs from human sewage, urban runoff, or groundwater seepage, for which historical data is not available. However given that between 1958 and 1989 the rise in human population (13,486 to 51,591, or 280% increase) and N fertiliser use in Pioneer Valley (1160 to 5160 T yr^{-1}, or 340%) was proportionally similar, and that total N discharge from Mackay's wastewater treatment facility accounts for an estimated 17% of annual N exports presently, the N loads calculated from fertiliser data alone likely to account for 80 – 90% of total annual N export. Incorporating the N contribution from human wastewater, a critical threshold of 47 – 67 kg N ha^{-1} is estimated to be sufficient to generate distinctive δ^{15}N signals in nearshore coral skeletons exposed to

Pioneer River discharge, which is consistent with the threshold estimated by McClelland et al. (1997).

Concomitant with the long-term enrichment of coral $\delta^{15}N$ values was a significant 2 - 4 fold increase ($r^2 = 0.76$, $p < 0.001$) in N concentrations in all three inshore cores (Figure 3c), which occurred primarily between 1975 and 2005. Two possible explanations exist for the observed change in N concentrations: (1) increasing loads of deposited particulate matter discharged from the Pioneer River and/or from sinking phytoplankton biomass have accumulated in *Porites* coral skeletons; or (2) the insoluble N content has been degraded by euendolithic organisms, including microborers such as bacteria, fungi, and algae (Disalvo 1969, Le Campion-Alsumard et al. 1995, Priess et al. 2000, Vogel et al. 2000). Importantly, the increasing N concentrations were observed in all 3 inshore cores, and were absent in both midshelf specimens (although midshelf coral N concentrations were more variable), suggesting that the long-term increases are more reflective of rising N inputs rather than degradation.

Climate-related $\delta^{15}N$ variability from 1980 - 2005

The second prominent feature evident in the composite inshore $\delta^{15}N$ time series is the period of high isotopic variability that extends from 1980 to 2004 (Figure 3b). This variability is linked to climate-related cycles in annual river flow. The drought decades of the 1980s and 1990s exhibited $\delta^{15}N$ values that were 2-5‰ lower than those observed during the wet 1970s (mean $\delta^{15}N$ = 9.4‰) or during the flood years of 1989 – 1991 and 2000. Peak $\delta^{15}N$ values observed over the 60 yr record coincided with cyclone-related floods, specifically with cyclones "Kerry" (1979, 13.9‰ in core RTC), "Aivu" (1989, 12.8‰ in core RTF), "Joy" (1991, 11.0‰ in core RTF), and with the 2000 Pioneer River flood (16.9‰, core RTH). Each of these floods was manifested by narrow, intense luminescent bands, which in the GBR correlate closely with the magnitude and timing of river floods (Isdale 1984, Lough et al. 2002).

The coral $\delta^{15}N$ data also reveals strong inter-annual to decadal seasonality from 1945 to 2004, with significant periods of 3.0, 3.7, 10.0 and 12.8 years (Figure 4). The 3.0 to 3.7 year $\delta^{15}N$ cycle is synchronous with El Niño Southern Oscillation (ENSO)-related SST cycles, which have periods normally falling within the 3-5 year band (Tudhope et al. 2001). The GBR typically experiences reduced

summer monsoon rainfall during El Niño years, resulting in higher surface radiation due to reduced cloud cover, coupled with warmer sea surface temperature (SST) anomalies in late summer (Lough 1991, 1994). The opposite scenario occurs during La Niña years: summer monsoon circulation is stronger, seasonal temperatures are low, and precipitation and elevated river discharge patterns are elevated, resulting in higher turbidity of nearshore coastal GBR waters (Lough 1991, 1994). The Pacific Decadal Oscillation (PDO) modulates the strength of teleconnections between ENSO and rainfall in Eastern Australia (Gedalof & Mantua 2002, Mantua & Hare 2002). During negative (cool) PDO phases, there is greater spatial coherence of NE Australian precipitation anomalies, producing stronger and more predictable rainfall and ENSO events (particularly during La Niña phases) and greater interannual variability (Lough 1994, Power et al. 1999, Lough in-press). The 10 – 12.8 yr frequency band detected in the $\delta^{15}N$ time series supports that coral $\delta^{15}N$ values are strongly related to river discharge patterns, which in turn are governed by the regional climate patterns that influence eastern Australian precipitation. Global warming due to the greenhouse effect is predicted to increase the variability and/or magnitude of extreme events (i.e. cyclones, floods) in the coming century (Power et al. 1999, Verdon & Wyatt 2004), posing dangerous synergistic threats to inshore GBR marine communities already stressed by enhanced nutrient and sediment delivery during baseline river flow conditions (Van Woesik et al. 1999, Fabricius et al. 2005).
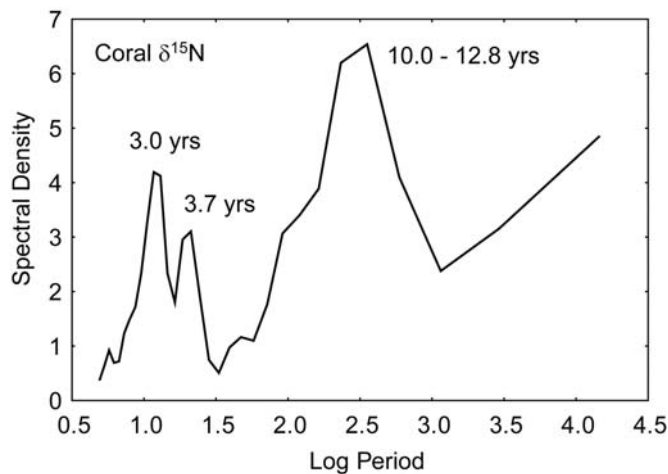
Figure 4. Fourier transform of inshore coral $\delta^{15}N$ values, 1945 – 2005. Coral $\delta^{15}N$ cycles in the inshore composite coral record occur every 3.0 – 3.7, and every 10 – 12.8 years. These are synchronized with ENSO and PDO-related sea surface temperature cycles, which normally fall within the 3-5 year band (see text for discussion).

Another potential cause of post-1980 isotopic variability is linked to changes in the hydrology and composition of N species in the Pioneer River (Chapter 3). The construction of two semi-rigid weir dams between 1982 and 1998 (16km and 32km upstream) (Brizga 2001), combined with other water storages resulted in a total holding capacity of 226,000ML, or 25% of the unregulated mean annual flow (Brodie 2004). The sharp rise of particulate δ^{15}N values (+6‰) observed through this river section are consistent with extensive microbial fractionation of elevated DIN concentrations, primarily through denitrification in the anoxic bottom (hypolimnion) layers in the stagnant reservoir waters (Chapter 3).

High δ^{15}N values following Pioneer River floods

Coral δ^{15}N values associated with flood events increased by 3‰ between 1944 and 2005 (Figure 3a). Table 1, however, shows that the number of flood-bearing years and the average volume of freshwater reaching the inshore reef corals (inferred from mean coral luminescence intensities) has not changed over the past 6 decades. One explanation for this long-term increase is that total N loads transported by Pioneer River floods have increased over this 50 yr period. Flooding in the GBR catchment typically occurs between December and April and accounts for ~90% of total annual freshwater inputs (Wolanski 1994, Furnas 2003, Devlin & Brodie 2005). In the Mackay region, a relatively minor 125,900ML Pioneer River flood pulse in 2005 (representing 14% of the average annual

Table 1. Decadal changes in flood events, inshore coral δ^{15}N values, luminescence intensities (a proxy for river discharge in nearshore coral skeletons), and agricultural activity in the Mackay Region, southern Great Barrier Reef. See text for discussion.

Decade	Flood years	Mean annual discharge (ML)	δ^{15}N (‰ AIR)	Lumin intensity	Sugarcane area (ha)	N fertilizer use (T)
2000	1	1,893,591	11.1	0.695	85,428	-
1990	2	2,353,540	8.5	0.663	66,889	5,490
1980	2	1,422,057	9.4	0.737	86,926	4,928
1970	6	1,632,138	9.4	0.819	58,038	3,913
1960	2	1,164,501	7.9	0.734	41,291	2,245
1950	6	2,316,683	7.7	-	22,802	911
1940	2	1,269,066	7.6	-	9,671	671

discharge volume over a 3 day period) produced nitrate and ammonium concentrations that reached 7.4 µM and 1.6 µM respectively at the inshore Round Top I. site (Rhode et al. 2005). These values were well above typical DIN concentrations observed in coastal GBR waters (0.05 – 0.1 µM; Furnas et al. 2005), and exceeded threshold concentrations (1.0 µM) sufficient to sustain macroalgal blooms on Caribbean reefs (Lapointe 1997).

Secondly, McCulloch et al. (2003) reported that barium to calcium ratios (a proxy for suspended sediment concentrations in the nearshore GBR) measured in *Porites* skeletons from offshore of the Burdekin River in the central GBR approximately doubled during drought-breaking floods relative to typical river discharge loads. In Mackay, the highest flood-related δ^{15}N values observed in the inshore *Porites* cores (12.0 - 16.8‰) exceeded measured Pioneer river end-member values by 3-7‰, suggesting that enhanced erosion and topsoil loss during major river floods mobilises highly-fractionated N into nearshore waters (McCulloch et al. 2003, Sinclair & McCulloch 2004). Approximately half (55%) of the 243 T of nitrogen discharged during the 2002 Pioneer flood pulse was sediment-bound (Rhode et al. 2005), most likely in the form of organic detrital matter or inorganic complexes with mineral components (Fallon et al. 2002, Alibert et al. 2003, Sinclair 2005). Sedimentary and particulate organic matter discharged from large river catchments can contain extreme δ^{15}N values. Kendall et al. (2001) observed that particulate organic matter (POM) in large river systems in the U.S. included inputs with outlier δ^{15}N values (-15‰ to + 14‰) that were well beyond normal isotopic ranges characteristic of terrestrial materials (-2 to +7‰). Similarly, in the Johnston River catchment of tropical northern Queensland, Udy and Bunn (2001) measured δ^{15}N values of up to 12.15 ± 0.56‰ in primary producers (macrophytes- *Vallisneria sp.*) from waters adjacent to lands variably cleared (41-100% cleared) for sugarcane farming.

A third explanation for the long-term increase in flood-associated δ^{15}N values is related to the extensive and frequent phytoplankton blooms that characterise the inshore Mackay Whitsunday region of the inner GBR lagoon (Furnas et al. 1997). Phytoplankton blooms can exert a major control on the δ^{15}N values of particulate matter (Wada & Hattori 1976, McCarthy et al. 1990, Altabet 2006) and nitrate and ammonium (Pennock et al. 1996, Waser et al. 1998) delivered into the coastal ocean. Average chlorophyll-a (chl-a) concentrations (a

proxy for phytoplankton biomass) in the GBR Lagoon range from 0.2 and 0.8 µg L^{-1}, while the tract of the central GBR distributed between 18.5^0 and 22^{0}S, which includes the inshore Mackay sector, generally exceeds 0.5 µg L^{-1} (Furnas et al. 1997). These are among the highest chl-a concentrations measured in the GBR Lagoon (Furnas et al. 2005). Values of up to 2300 µg L^{-1} were observed 20km offshore of the O'Connell River, 75km north of Mackay following a 2005 flood (J. Brodie, pers. comm.).

The δ^{15}N values observed in both the composite and individual coral records are enriched by 1 - 7‰ relative to the fluvial source of N. This enrichment may occur through two mechanisms. First, preferential algal uptake of $^{14}NO_3^-$ and $^{14}NH_4^+$ advected in river flood plumes produces a residual DIN pool that is isotopically enriched by +3 to +9‰ (Cifuentes et al. 1989, McCarthy et al. 1990, Pennock et al. 1996, Waser et al. 1998). Vertical mixing of the DIN pool (>9‰) to colonies living 6.0 – 8.0m deep at Round Top Island allows assimilation and deposition of the enriched δ^{15}N signal. Secondly, downward-fluxing senescent plankton detritus is enriched due to extensive microbial remineralisation and biological processing (Wada & Hattori 1976, Saino & Hattori 1980, Wainwright & Fry 1994, Waser et al. 1998). The rate of coral heterotrophic ingestion of senescent plankton detritus will vary between individual colonies and species in terms of feeding preferences and morphology, and is likely to be accountable for the variability of annual δ^{15}N data between inshore cores. The highly lobed forms of most massive *Porites australiensis* increases the potential for suspended particulate matter to become trapped within the complex surface cavities, impairing the colony's ability to selectively slough particulate matter from the surface (Mills et al. 2004). Alternatively, core RTF was collected from a smooth-surfaced *P. lutea* coral, which is physically better adapted to selective, consistent modes of feeding (Anthony 1999, Anthony & Fabricius 2000, Mills & Sebens 2004). Overall the time series developed from the *P. lutea* specimen (RTF) produced the "cleanest" record of the 3 inshore cores, indicated by significant correlations to river discharge, steady increase in N concentrations (Figure 3c), and consistent C:N ratios (Figure 5). Future studies should emphasize collection of identical species with consistent smooth external surfaces.

Isotopic Variability in Midshelf Coral Cores

Nitrogen isotopic data from the two midshelf *Porites lutea* corals spanned the years 1969 – 2004 in the Keswick I. core and 1953 – 2004 in the Scawfell core. Both were isotopically depleted and more variable than the inshore corals (Figure 5), and neither reef is exposed to the threshold N-loading rate of 47 – 67 kg N ha^{-1} calculated for the inshore reefs. Sources of variability in these midshelf corals include incorporation of senescent cyanobacterial plankton including *Trichodesmium*, intermittent exposure to terrestrially derived N at Keswick I., or degradation of insoluble N within the coral carbonate.
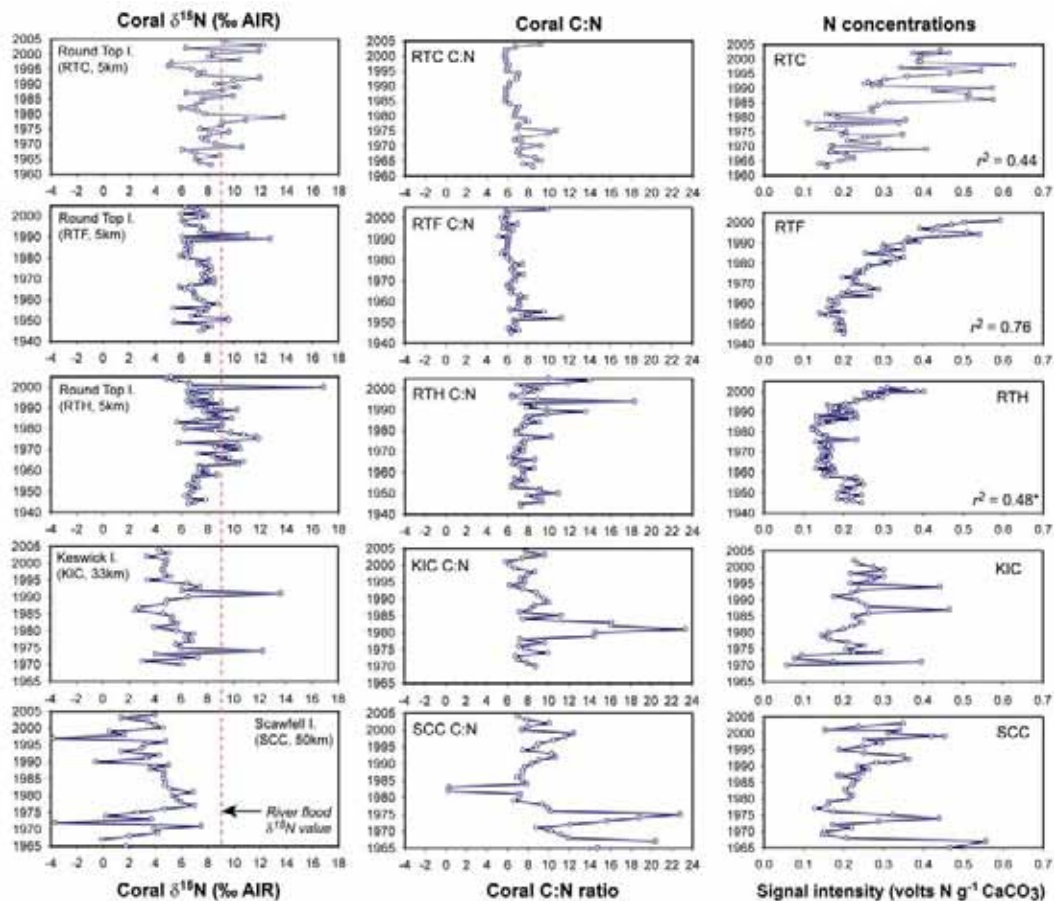
Figure 5. δ^{15}N (left column), C:N (center column) and N concentration (right column) time series developed from the five Great Barrier Reef *Porites sp.* coral cores. The first three rows of graphs are from three inshore coral colonies from a coral community located 5km offshore of the region's main river mouth. The fourth row are data from a reef located in the midshelf (33km offshore), and the fifth from a healthy midshelf coral reef located further offshore (50 km). Particulate matter measured in the river exhibited max. δ^{15}N of 9.0‰ (red line).

N-fixation and cyanobacterial N-fixing blooms

Nitrogen-fixation accounts for an estimated 38% of N inputs into the GBR Lagoon (Furnas et al. 1997), and is largely attributable to the widespread distribution of the pelagic N-fixing (diazotrophic) cyanobacteria *Trichodesmium* (Jones et al. 1986, Capone et al. 1997, Sinclair 2005). Being N_2-fixers, *Trichodesmium* are at an ecological advantage in the N-depleted waters characterised by low rates of primary productivity by marine photoautotrophs (Capone et al. 1997), such as the midshelf GBR, and typically bloom (forming "red tides", red due to their reddish phycobiliproteins that are involved in light harvesting) during calm, warm, high insolation, high salinity conditions (Altabet 2006). On the GBR, this typically occurs during the transition between dry and wet seasons (Jones et al. 1986, Sinclair 2005). $\delta^{15}N$ fractionation associated with N_2 fixation varies between 2 – 3‰, and given that dissolved N_2 has an isotopic composition of ~0.7‰, typical $\delta^{15}N$ values of *Trichodesmium* and other pelagic diazotrophs range from -1 to -2.5‰ (Wada & Hattori 1976, Montoya et al. 2002, McClelland et al. 2003). While the lowest $\delta^{15}N$ values observed in the midshelf coral records was -3.82‰ (Scawfell I.), $\delta^{15}N$ values dropped below 0.5‰ 10 times between 1955 and 2004 but only once in the Keswick I. core. This supports the notion that N-fixation rates are more consistent and productive in oligotrophic ocean environments (Altabet 2006).

Variable exposure to terrestrial N inputs at Keswick I. (33km)

In the Keswick core, low $\delta^{15}N$ values generally occurred in the low density (winter) bands, while $\delta^{15}N$ values from the high density bands were positively correlated to Pioneer River discharge ($r^2 = 0.40$, $n = 37$, $p < 0.001$). The Keswick Is. coral exhibited highly enriched values in 1974 (12.24‰), 1977 (17.99‰), and 1991 (13.62‰). This is significant for two reasons. First, all three values coincide with the timing of large floods. The 1974 and 1991 $\delta^{15}N$ peaks were measured in high density (summer) bands, which is consistent with the timing of each between December and February (2.83 and 2.53 million ML, 1st and 2nd largest floods by volume between 1968 and 2004). Alternatively, the 1977 peak was measured in the low-density (winter) band, and follows a 4-month period of elevated river discharge (>10 times the monthly mean) between January to April. The exact timing of density band formation is not fully understood but is likely to include a 3

- 6 month integration period associated with calcification through the tissue layer (5.5mm thick in KIC) (Lough & Barnes 1990, Lough et al. 2002), which would be consistent with preservation of the later summer isotopic flood signal in the low-density skeleton .

Secondly, the 1974, 1977, and 1991 peak $\delta^{15}N$ values coincide with intense luminescent bands (6th, 10th, and 1st highest peak luminescence intensities over the 36 yr record respectively; see luminescence graph in Figure a), providing an independent means of verifying linkages between isotopic enrichment in coral skeleton and exposure to freshwater flood plume. Lough et al. (2002) measured luminescence intensities by eye in 232 similarly-sized *Porites* coral colonies from 30 reefs distributed between the inner (0km) and outer (176km) GBR and reported that coastal reefs (up to 20km offshore) are impacted by freshwater flood plumes every year, while they reach the midshelf GBR (up to 56km offshore) every 2-3 years. Less is known, however, about the frequency and extent to which river flood plumes can transport land-derived sources of N into the midshelf GBR. Furnas et al. (2005) emphasized that the conversion of terrestrial DIN inputs into fixed organic forms (phytoplankton biomass), which persist for 2-3 weeks and are advected in tidal and wind-influenced flood plumes, are the primary mechanism by which anthropogenic sources of N may be distributed throughout the oligotrophic midshelf environment. This data supports that the reef located 33km offshore of the Pioneer R. was clearly exposed to enriched land-derived nitrogen sources at least 3 times between 1968 and 2004.

Conclusions

The data presented in this chapter suggests that the 60-year rise in $\delta^{15}N$ values and variability in the inshore *Porites* coral cores reflects a shift in the provenance and dynamics of nitrogen in Mackay coastal waters. The 3‰ increase occurred in two phases: between 1945 and 1979 $\delta^{15}N$ values increased linearly, as did fertiliser usage and sugarcane land area (by 6 and 5-fold respectively) in the Pioneer Valley. Annual $\delta^{15}N$ values were significantly correlated to Pioneer R. discharge. Secondly, between 1980 and 2005, coral $\delta^{15}N$ data variability increased by 2 – 7 fold, which is most likely related to the consecutive drought decades of 1980 – 1987 and 1992 – 1999, punctuated by major floods in the early 1990s and in 2000. End-member $\delta^{15}N$ values in the

Pioneer Catchment are isotopically enriched ($\delta^{15}N$ = 9.0‰) relative to background $\delta^{15}N$ variability in coastal Mackay waters (4.9 – 5.1‰) (Chapter 3). Peak $\delta^{15}N$ values recorded in the inshore and midshelf (Keswick Is.) coral records coincide with flood years and are 1 - 7‰ higher than maximum end-member input values determined for the river catchment (Chapter 3) during ambient flow scenarios. Potential causes for this enrichment include the mobilisation of N sources with $\delta^{15}N$ values that exceeded those measured in Chapter 3 (for example fractionated detrital N bound to subsurface soils), phytoplankton blooms and senescence, or coral stress responses. Between 1970 and 2004, there was only strong evidence terrestrially-derived N reached the reefs of the midshelf Keswick Is. twice (during the floods of 1974 and 1991). Fourier transforms of coral $\delta^{15}N$ data revealed strong inter-annual to decadal variability with significant periods of 3.0, 3.7, 10.0, and 12.8 years, which is in-synch with El Nino Southern Oscillation (ENSO)-related (and possibly Pacific Decadal Oscillation, PDO-related) temperature and precipitation cycles in the GBR.

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Core drilled from coral carbonate skeleton at Keswick Island, 33km offshore of Mackay.

Chapter Six

Anthropogenic and River Flood Signals in Massive Coral Skeletons: II. Trace and Rare Earth Elements

Introduction

Human activity on land has increased global sediment loss by an order of magnitude over natural weathering rates (Wilkinson 2005). A substantial proportion of this material is stored in adjacent downslope regions such as floodplains, reservoirs and estuaries (Vorosmarty et al. 2003). Yet despite this catchment retention, sediment supply models for northeastern Australia suggest that sediment delivery loads into the Great Barrier Reef (GBR) World Heritage Area have increased approximately two to eightfold above estimated values before European land clearing (~1850) for grazing and crops (Table 1) (Hacker 1988, Moss et al. 1992, Neil & Yu 1996, Neil et al. 2002, Prosser et al. 2002,

McKergow et al. 2005). These models are based largely on predictions of sediment loss (due to land use, vegetation cover, rainfall intensity, slope, and soil weathering) and sediment transport capacity (which varies with river geomorphology, sediment type and hydrological modifications such as dams), therefore the outcomes are sensitive to the quality of data for each input variable (Neil et al. 2002, McKergow et al. 2005).

A different type of approach to determine how sediment delivery to the nearshore has changed is to measure long-term records of trace and rare earth elements from coral skeletal records (Fallon et al. 2002, McCulloch et al. 2003). The ratios of trace elements to calcium within coral aragonite ($CaCO_3$) skeletons are usually in equilibrium with seawater composition, and are good natural tracers of fluvial or pollutant inputs to seawater (Livingston & Thompson 1971). Several elements, including barium (Ba) and the rare earth elements and yttrium (REY), have been related to suspended sediment delivery. River discharge is the main source of both Ba and REY to the coast (Hanor & Chan 1977, Byrne & Sholkovitz 1996). Since river waters are usually enriched in barium and yttrium and depleted in calcium (Ca), relative to nearshore marine waters, pulses of floodwater to the nearshore will increase the ratios of Ba/Ca and REY/Ca that are deposited in skeletons of massive *Porites* corals (Sinclair 1999). As land use intensification increases the available catchment sediment supply, the prediction is that the magnitude and frequency of flood-associated Ba/Ca and REY/Ca peaks will increase. Indeed, using a coral record from the Burdekin River region, McCulloch et al. (2003) found both an ~30% increase in baseline Ba/Ca values timed during the rapid expansion of cattle stocking rates (~1870) and a resulting

Table 1. Modelled and estimated increases in rates of sediment delivery to the Great Barrier Reef lagoon relative to pre-clearing conditions (~1850).

Study	Sediment delivery increase over natural rates	Study Region
Hacker 1988	2.2 - 4.0	Pioneer Catchment
Moss et al. 1992	3.0 - 5.0	Total GBR Catchment
Neil and Yu 1996	3.8	Total GBR Catchment
Neil et al. 2002	1.5 - 4.0	Range of all GBR Catchments
Prosser et al. 2002	6.0	Burdekin River Catchment
McKergow et al. 2005a	8.0	Total GBR Catchment

five to tenfold increase in sediment delivery rates to the nearshore since that time.

Sediment yield to the coast is largely determined by vegetation cover, precipitation and river transport capacity, but once fine particles are discharged into the ocean, their fate is determined mainly by electrostatic forces, gravity and flood plume dynamics (Douglas 1967, Larcombe & Woolfe 1999, Devlin & Brodie 2005). Within low salinity, freshwater-seawater mixing zones, fine particles aggregate and sink, resulting in deposition of most terrestrial material within a few kilometres of shore (Sholkovitz 1976, Gibbs 1985). Ba and REY, however, dissociate from the fine particles within the estuarine mixing zone, remain in solution, and are transported out to sea with the river plumes. As described in Chapters 2 and 5, the dispersal of plumes in the GBR lagoon is governed by wind, tides and the Coriolis effect, which typically act in concert to force the plumes to the north within 20 km of the coast (Figure 1a) (King et al. 2001, Devlin & Brodie 2005). However, when wind stress from very strong winds exceeds the Coriolis effect, or when northerly winds oppose the direction of Coriolis forcing, river plumes may spread south and east across the shelf (Figure 1b) (Chao 1988, Wolanski 1994, Devlin & Brodie 2005). Although most fine suspended sediment remains within an inshore wedge, plumes dispersing across the shelf may contain dissolved nutrients and other pollutants that may affect coral reefs systems (Hutchings & Haynes 2000).

Within this chapter, we report on spatial and temporal variation in sediment delivery from the Pioneer River between 1946 and 2003, estimated from geochemical measurements of barium, yttrium and rare earth elements in the same *Porites* coral skeletons discussed in Chapter 6. We investigate correlations of high resolution records of coral Ba/Ca and Y/Ca with fluvial discharge and wind to evaluate their utility as proxies of terrestrial runoff. We additionally discuss spatial differences in total coral REY content and assess whether there have been changes over time. To assess whether differences in our results are attributable to land use activities specific to the intensively cultivated Mackay region, we compare our data with those from other inshore coral records along the Queensland coast.
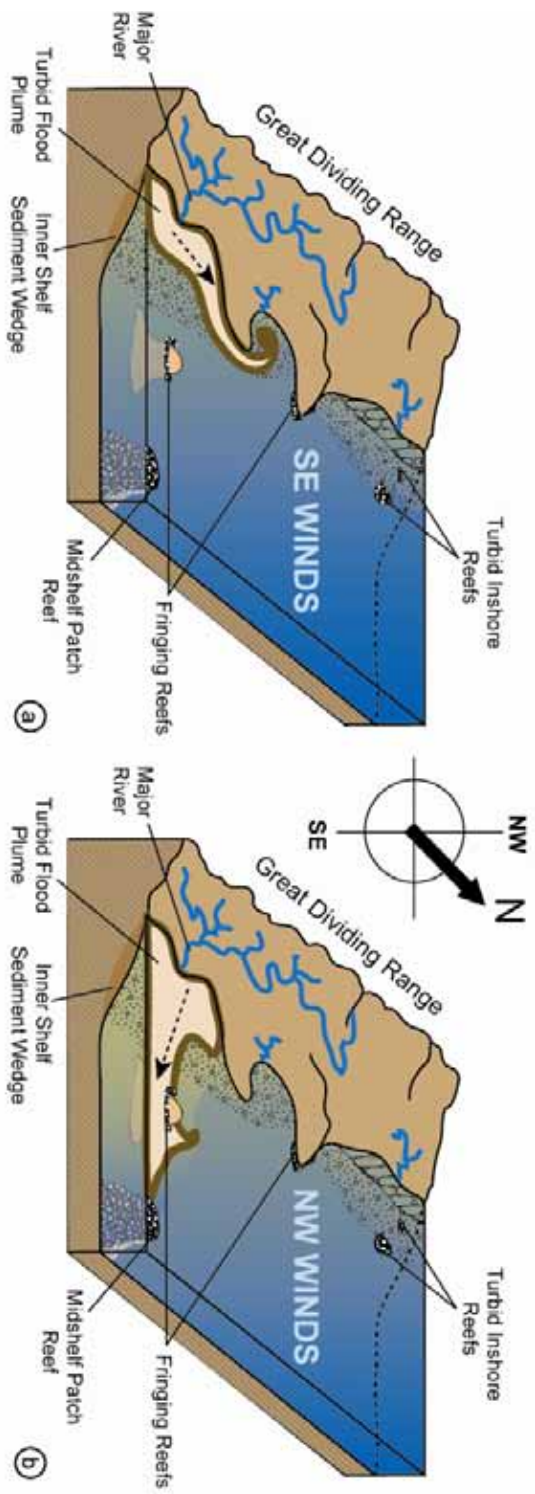
Figure 1. Schematic of flood plume behaviour along the central Queensland coast during (a) prevailing south-easterly trade winds; and (b) northwesterly winds. Dashed arrows show net movement of flood plumes. (modified from Larcombe and Woolfe 1999).

Correlations of Ba/Ca and Y/Ca with River Discharge

Correlations were calculated between weekly Pioneer River discharge and high resolution (weekly) records of Ba/Ca and Y/Ca measured using laser ablation inductively coupled mass spectrometry (LA-ICPMS) at the Research School of Earth Sciences, The Australian National University, on four of the same coral cores analysed for δ^{15}N: RTC (Feb 1962-May 2003); RTF (Aug 1959-May 2003); KIC (Jan 1991-May 2003); and SCC (Jan 1989-May 2003). To assess the impacts of flood events and wind on correlation strength, separate sets of correlations were repeated with data restricted to: all flood weeks; flood weeks with northwesterly wind stress $(\tau)^2$ (where alongshore $\tau < 0$); and weeks with strong winds. Flood weeks were defined as those that exceeded the weekly mean recorded between 1916 and 2003 (16,060 Ml), and weeks with strong winds as those with wind stress $\geq$ mean + 1 SD ($\geq$ 21.73 dynes/cm^2). Full specifications for the instrumentation used to measure trace element concentrations can be found in (Eggins et al. 1998) and (Sinclair et al. 1998), while details on coral preparation, data reduction and coral chronology assignment are described in (Jupiter 2006).

Replicate cores (RTC, RTF) from Round Top Island had very similar qualitative patterns of Ba and Y throughout the time series (1962-2003; Figure 2). Ba/Ca and Y/Ca were most different between 1975 and 1982, although the seasonal and longer-term fluctuations remained largely consistent between cores. Baseline winter values were elevated for both elemental ratios during wetter periods (1968-1980, 1988-1991 and, to a lesser extent, 1998-2002), but were most noticeable in the Ba/Ca records (Figure 2e). Inshore Ba/Ca ratios had strong annual peaks (Figure 2e), but had low correlations with Pioneer River discharge when all weeks were compared (RTC: r = 0.271, RTF: r = 0.272; Table 2a). Annual peaks of Y/Ca from Round Top Island were less obvious (Figure 2f), and both Round Top cores had low correlations of Y/Ca with discharge when all weeks were compared (RTC = 0.282, RTF = 0.244; Table 2b). Correlations of inshore Ba/Ca and Y/Ca with discharge were substantially higher when the

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[2] Wind stress was calculated using an equation adapted from Large and Pond (1981):
$\tau = \frac{1}{2} \rho C_d V^2$, where ρ is mean air density, C_d is the drag coefficient, and V is wind velocity. Alongshore wind stress was also calculated using the velocity vectors oriented along a NW-SE axis, approximately parallel to the Mackay coastline.
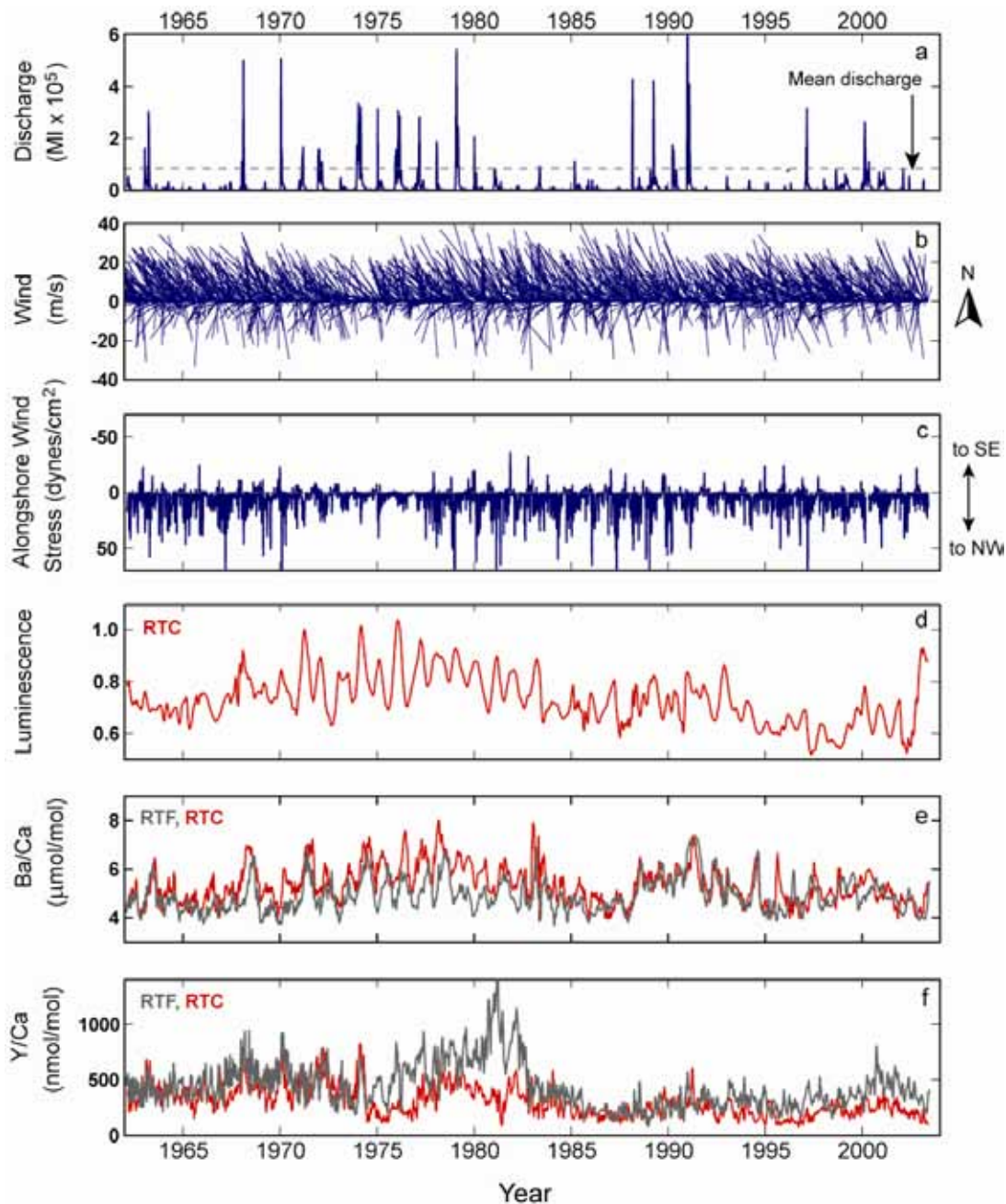
Figure 2. Fluvial, anemometer (wind), and inshore coral records from the Pioneer region, 1959-2003. (a) Pioneer River discharge. Weeks > mean (dashed line) were considered flood weeks. (b) Weekly wind vectors indicating magnitude and direction. (c) Alongshore wind stress (τ with positive values denoting winds to the northwest. (d) Luminescence from Round Top core RTC. (e) Ba/Ca ratios from two Round Top cores (RTF = grey; RTC = red). (f) Y/Ca ratios measured from the same two cores.

analyses were restricted to flood weeks only; they rose further when restricted to flood weeks that coincided with northwest wind stress (Table 3a,b). Both proxies also had higher correlations with discharge during periods of strong wind stress from any direction (Table 3c).

Table 2. Correlation coefficients (r) of weekly Ba/Ca and Y/Ca ratios with discharge for the entire record from each core. n = number of weeks.

Core	# years	r	lag (wks)	n	p <
A. Ba/Ca					
RTC	44	0.271	13	2147	0.010
RTF	41	0.272	14	2272	0.010
KIC	12	0.168	4	646	0.100
SCC	13	0.213	0	747	0.050
B. Y/Ca					
RTC	44	0.282	3	2147	0.010
RTF	41	0.244	0	2272	0.020
KIC	12	0.210	0	646	0.050
SCC	13	0.215	3	747	0.050

Strong correlations of Ba/Ca and Y/Ca with river discharge have been reported for other inshore reefs of the GBR (Sinclair 1999, Alibert et al. 2003, McCulloch et al. 2003, Sinclair & McCulloch 2004), but no previous study from the region has addressed the effects of wind stress on these ratios. In *Porites* from Shirigai Bay, Japan, peak values of Ba/Ca coincided with wind-forced upwelling of cold, nutrient-rich water (Fallon et al. 1999). While large upwelling events occur during summer months along the GBR, these events typically occur on the seaward margin of the outermost reefs, and the subsequent diffusion and spread of this water across the continental shelf rarely reaches inshore islands, within the 40 m depth contour (Andrews & Furnas 1986, Furnas & Mitchell 1986, Sinclair 2005). Elevated Ba/Ca related to wind in Mackay corals probably reflect north-northwesterly winds coinciding with discharge events, which tend to blow plumes offshore (Furnas 2003, Devlin & Brodie 2005); and strong wind periods which generate waves that resuspend previously deposited, shallow sediment that may be remobilised and carried offshore (Orpin et al. 1999, Neil et al. 2002).

As early as 1918, wind direction was noted as the reason for a low salinity plume over the Whitsunday reefs after an extreme cyclone hit Mackay (Rainford 1925, Devlin et al. 2001). More recently observations showed that the Burdekin River plume associated with Cyclone Justin was influenced by alongshore wind stress in March 1997: it moved southeast to merge with the plumes from the Mackay-Whitsunday rivers, including the Pioneer (Devlin & Brodie 2005). During that event, the edge of the plume was between Keswick and Scawfell Islands

Table 3. Correlation coefficients (r) of weekly Ba/Ca and Y/Ca ratios with Pioneer River discharge restricted to: (A) flood weeks (> mean discharge) only; (B) flood weeks coincident with northwest wind stress; and (C) strong wind weeks (> mean + 1 $\underline{S}$D τ) only. n = number of weeks.

Core	# years	A. Flood Weeks			B. Flood Weeks + NW winds			C. Strong Winds		
		r	n	p <	r	n	p <	r	n	p <
Ba/Ca										
RTC	44	0.578	275	0.001	0.610	44	0.001	0.615	52	0.001
RTF	41	0.590	288	0.001	0.631	47	0.001	0.607	56	0.001
KIC	12	0.495	78	0.001	0.630	8	0.100	0.657	19	0.010
SCC	13	0.503	105	0.001	0.600	11	0.100	0.700	23	0.001
Y/Ca										
RTC	44	0.545	275	0.001	0.630	44	0.001	0.595	52	0.001
RTF	41	0.522	288	0.001	0.597	47	0.001	0.570	56	0.001
KIC	12	0.565	78	0.001	0.632	8	0.100	0.616	19	0.010
SCC	13	0.452	105	0.001	0.540	11	0.100	0.716	23	0.001

(Devlin & Brodie 2005). Correspondingly, the Ba/Ca and Y/Ca records from all cores in this study had higher correlations with Pioneer River discharge during flood weeks coinciding with northwest wind stress (which is often associated with cyclonic activity; Sinclair 1999).

Since floods are episodic and infrequent, corals and other reef organisms may be more likely to experience high levels of turbidity-induced stress from resuspension of previously deposited sediment, driven by strong winds (Larcombe et al. 1995, Orpin et al. 1999, Larcombe et al. 2001, Brinkman et al. 2002, Furnas 2003). Strong onshore surface winds are capable of causing downwelling currents that may carry sediment offshore during periods of high inshore sediment resuspension caused by wind waves (Orpin et al. 1999). In the Mackay cores, Ba/Ca and Y/Ca were strongly correlated with discharge during strong wind weeks, particularly at the midshelf sites. While some of the inshore sediment may be mobilised offshore by downwelling currents, Keswick and Scawfell Islands may additionally be influenced by their own pools of sediment from weathering and land use activities on the islands, especially since Keswick and St. Bees have been grazed since ~1909 (Berck 1995).

Ba/Ca Patterns and Lags

Corals collected from other inshore GBR corals, such as King Reef near the Tully River, and Havannah and Pandora reefs within the trajectory of Burdekin River flood plumes, have Ba/Ca spikes that are in phase with luminescence, Y/Ca and La/Ca (a rare earth element to calcium ratio) and time precisely with river discharge events (Sinclair 1999, Alibert et al. 2003, McCulloch et al. 2003, Sinclair & McCulloch 2004, Sinclair 2005). Unlike these corals, the inshore coral Ba/Ca ratios from Round Top Island rise slowly to peak values, remain elevated for up to several months, and drop to baseline values by midwinter (Figure 3). The initial rise of Ba/Ca occurs, on average, ~6-7 weeks after floods, and the best correlation between maximum annual Ba/Ca values and Pioneer discharge occurs when Ba/Ca lags discharge by ~13-14 weeks (Table 3). These patterns were not observed in the cores from the midshelf sites at Keswick and Scawfell islands, suggesting that the lags are likely to be related to terrestrial influence. Furthermore, the differences in Ba/Ca patterns between the Pioneer, Tully and Burdekin corals are likely to be related to differences in land
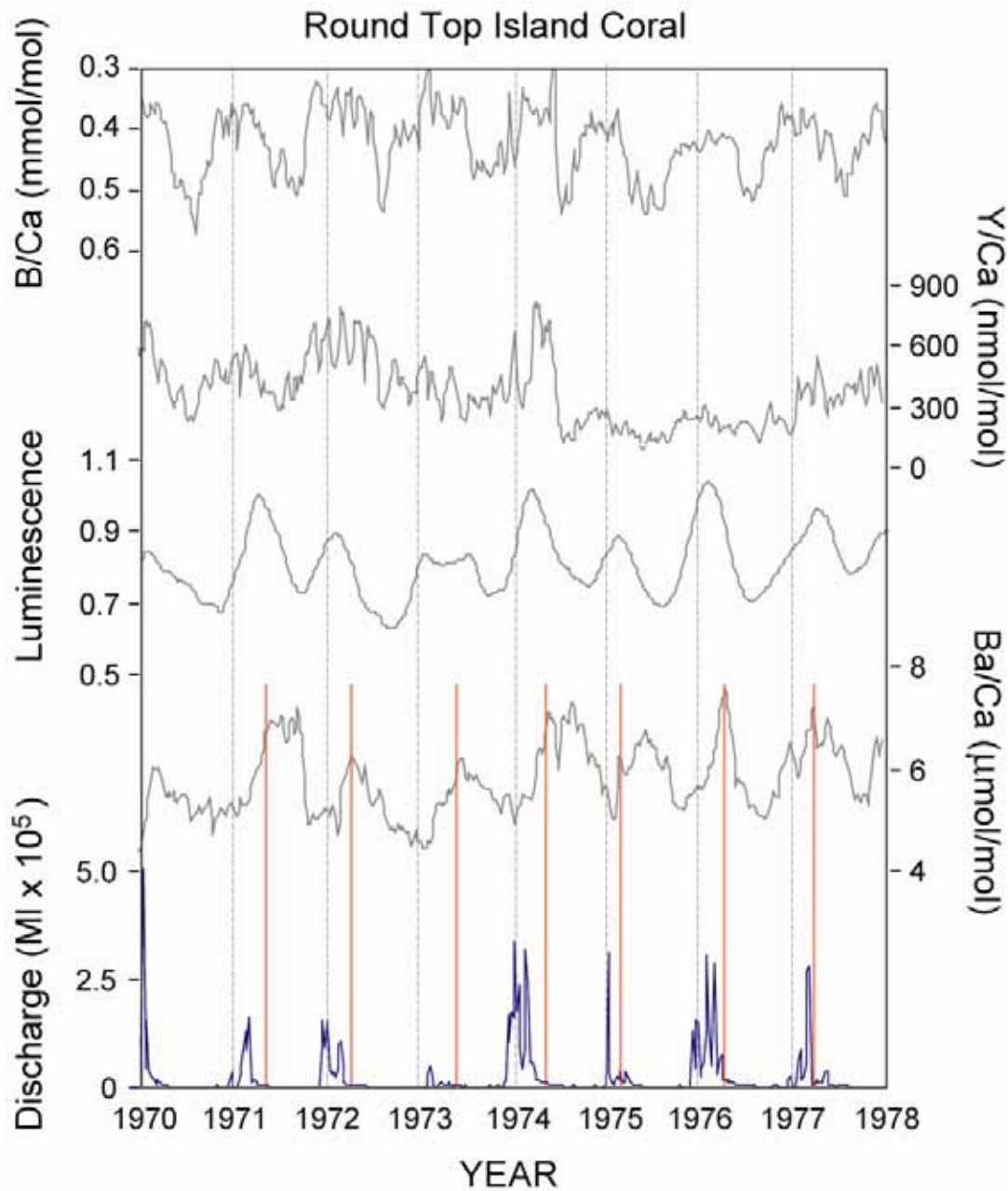
Figure 3. Profiles of four tracers (grey) in Round Top core (RTC) during wet years from 1970 to 1978. Vertical dashed lines are at the beginning of each year. B/Ca indicates seasonality, with peaks (minimum values) coinciding with warm summer SSTs. Luminescence and Y/Ca peaks largely coincide with discharge peaks (in blue at bottom). Ba/Ca peaks lag behind discharge by ~13 weeks, with the initial rise occurring ~6-7 weeks (on average) following maximum discharge each year (examples highlighted in red).

use activity and climate between the catchments.

The Tully River drains a catchment of similar size (1683 km^2) to the Pioneer, but with approximately three times the annual runoff, due to much higher annual rainfall and multiple floods per year (Furnas 2003, Devlin & Brodie 2005).

The upper part of the Tully catchment is predominantly wet tropical forest with only 10% cleared for agriculture and grazing (Haynes et al. 2001). Meanwhile, the Burdekin River system is the second largest catchment (130,126 km^2) draining into the GBR Lagoon, with a drier, more seasonal wet-dry climate, and episodic flooding at 4-10 year intervals (Furnas 2003, Devlin & Brodie 2005). Grazing now occupies 95% of Burdekin catchment lands, and coral Ba/Ca increases coincided with increases in cattle stock (McCulloch et al. 2003). By contrast, in the Pioneer catchment, sugarcane cropping is the dominant land use, and the Mackay region has one of the highest rates per unit area of total N and total P additions from fertiliser application (Pulsford 1996).

As described in the previous chapter, pulses of nutrient enriched waters from floods stimulate phytoplankton blooms (Furnas et al. 2005). Biological recycling, whereby Ba is removed from estuarine and coastal waters in association with phytoplankton blooms and released upon their senescence, is a likely hypothesis to explain the Ba lags from the inshore Mackay corals. (Stecher & Kogut 1999) documented >90% removal of dissolved barium from a Delaware estuary in mid-May, followed by 80% recovery by early June. They proposed that barite precipitates within sulphate-rich detrital assemblages of senescing blooms and becomes released as the particles disaggregate upon sinking. (Nozaki et al. 2000, Nozaki et al. 2001) observed a similar phenomenon in the Chao Praya Estuary, Thailand, where significant removal of barium occurred in January during a red tide bloom that was absent in either July or November when barium followed typical conservative mixing curves for mid-salinities and higher.

Biological recycling has been previously proposed to explain anomalous Ba/Ca peaks in *Porites* corals. Tudhope et al. (1996) suggested that anomalously high Ba/Ca peaks in a *Porites* core from Oman were due to incorporation of barium from organically-bound barite released following phytoplankton blooms. Sinclair (2005) suggested local enrichment of dissolved barium from senescent *Trichodesmium* blooms in the Whitsunday region could explain the uncharacteristic timing of spring Ba/Ca peaks observed in a *Porites* core from Cow and Calf Island, near the Proserpine and O'Connell River drainages. *Trichodesmium* spp. are nitrogen-fixing cyanobacteria that often bloom along the GBR coast, particularly near river outlets with elevated phosphate levels (Bell 1992, Fu et al. 2005). In January 2005, a plume covering the entire Mackay-

Whitsunday region (Figure 4) contained large quantities of *Trichodesmium* (Rohde et al. 2006). The plume appears on a MODIS satellite image as a dark green slick, which is distinctly different from the light brown, sediment-laden plume emerging from the Burdekin River to the north (Figure 4). Depending on regional wind conditions, plume waters from single, large events may persist for several weeks (King et al. 2001), and these periods can be extended by successive flood flows, as in 1958 and 1991, when there were 5-6 week intervals between Pioneer River flood pulses.
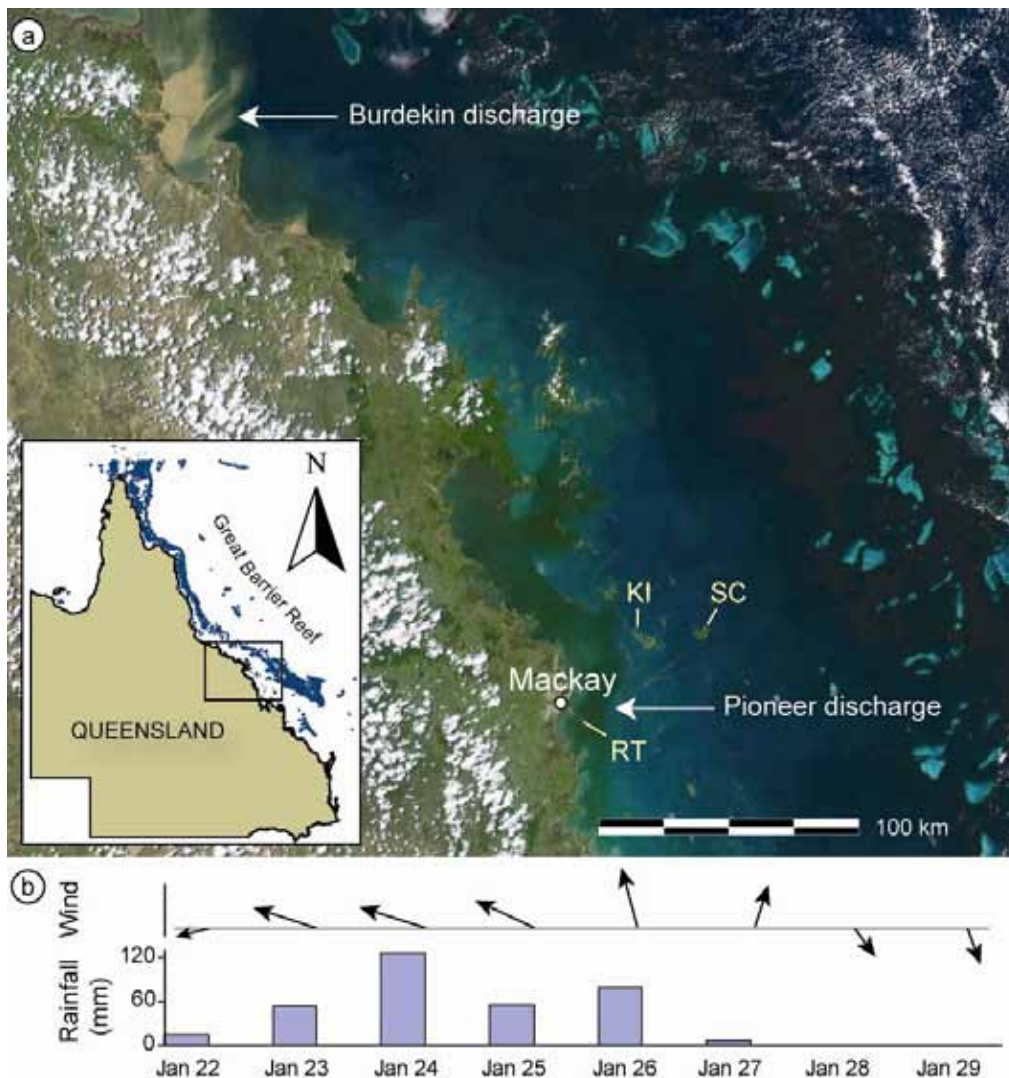
Figure 4. (a) MODIS satellite image of January 2005 flood (captured 29 Jan) showing distinctions between brown sediment-laden discharge from the Burdekin River and dark green plumes along the Mackay-Whitsunday coast. Lower inset shows location along Queensland coast. (b) Magnitude of rainfall and wind vectors for duration of flood to date of image capture.

Enrichment of dissolved barium from senescing blooms seems a reasonable hypothesis for the nutrient-enriched coastal region near Mackay, but direct links between decaying phytoplankton and elevated dissolved barium still need to be demonstrated in this region and the timing relative to discharge needs to be quantified. Several other ideas have been proposed to explain persistence of high values. (Carroll et al. 1993) suggested that barium continues to desorb from terrestrial sediments buried in the nearshore following floods, and this process increases with strong wind stress that generates sediment resuspension. Similarly, sediments deposited within the mangroves may be slowly flushed from the estuary (Alibert et al. 2003, McCulloch et al. 2003), especially in places like Mackay that have large (up to 6.4 m) tidal ranges. Groundwater additions may also be a source of elevated barium in nearshore waters (Moore 1997, Shaw et al. 1998, Swarzenski et al. 2001), but because groundwater aquifers in the Pioneer catchment are heavily used for sugarcane irrigation and town drinking water, and because coastal aquifers are being monitored for saltwater intrusion rather than freshwater export (Baskaran et al. 2001), coastal groundwater flux seems unlikely to be a major source of barium in this region.

Spatial Trends in Rare Earth Elements and Yttrium

Concentrations of rare earth elements and yttrium (REY) in coastal corals are good geochemical tracers of freshwater runoff and/or chemical weathering of continental crust because they are incorporated into coral lattices in close proportion to ambient seawater concentrations, and are fractionated differentially in rocks, river water and seawater (Elderfield et al. 1990, Sholkovitz & Shen 1995, Byrne & Sholkovitz 1996). For identifying potential terrestrial sources in marine REY, the data are typically normalised to a sediment or sedimentary rock (e.g. shale) composite to remove the natural "saw-tooth" distribution of absolute abundances and to describe the pattern relative to a continental source (Byrne & Sholkovitz 1996). Elemental deviations from the much smoother, normalised pattern can be used as "fingerprints" of biological and physical processes and/or provenance features.

To investigate the magnitude of coastal enrichment in REY and differences in REY patterns among sites, REY data were compared from bulk annual samples drilled from an inshore (RTF) and a midshelf (KIA) *Porites* core

analysed by solution mass spectrometry at the University of Queensland's ACQUIRE facility. Coral core details are outlined in Chapter 4, Table 1. Sample preparation is described in (Jupiter 2006), while instrument specifications can be found in (Lawrence & Kamber 2006). To compare coral REY patterns with those from seawater, river water and sediment, we performed a principal components analysis using REY data from: RTF and KIA corals; a composite of Queensland mud (MUQ); and water samples collected from the Pioneer River mouth and estuary, the Coral Sea, and streams draining different regions of the Pioneer catchment (Table 4). Because river water, estuarine water, marine water and corals have greatly different magnitudes of total REY, all REY values were scaled to the same value of samarium (Sm), for which anomalies are not expected.

When the scaled REY data were ordinated along the first two principal components, which explained 67.9% and 20.8% of the total variance respectively, the data from RTF clustered tightly with water samples from the Pioneer River mouth and estuary, suggesting that the inshore coral REY pattern reflects a local source (Figure 5). Coastal seawater, the inshore (RTF) coral and terrestrial sediment (MUQ) all had high positive values along principal component 2, which are largely explained by differences in scaled light rare earth element (LREE) abundances. LREE enrichment in the inshore coral probably relates to greater terrestrial influence, as LREEs may be more readily mobilised by weathering than HREEs (Nesbitt et al. 1990). By contrast, the midshelf coral

Table 4. Sources of REY samples (coral, water, sediment) used as inputs for principal components analysis.

Sample #	Sample Name (Code)	Type	Lat °S	Lon °E	Source
1	Inshore coral (RTF)	Coral	21.171	149.264	This study
2	Midshelf Coral (KIA)	Coral	20.918	149.419	This study
3	Coral Sea (St.SA7, 0 m)	Seawater	14.256	154.334	Zhang and Nozaki 1996
4	Pioneer River mouth	Seawater	21.147	149.220	M. Lawrence, unpublished data
5	Pioneer River estuary	Seawater	21.129	149.196	M. Lawrence, unpublished data
6	Lower Pioneer River (S31)	Freshwater	21.142	149.026	Lawrence et al. 2006
7	Blacks Creek (S26)	Freshwater	21.310	148.836	Lawrence et al. 2006
8	Owens Creek (S19)	Freshwater	21.113	148.727	Lawrence et al. 2006
9	Finch Hatton Creek (S10)	Freshwater	21.068	148.637	Lawrence et al. 2006
10	Upper Cattle Creek (S4)	Freshwater	21.141	148.540	Lawrence et al. 2006
11	Mud of Queensland (MUQ)	Sediment	various		Kamber et al. 2005
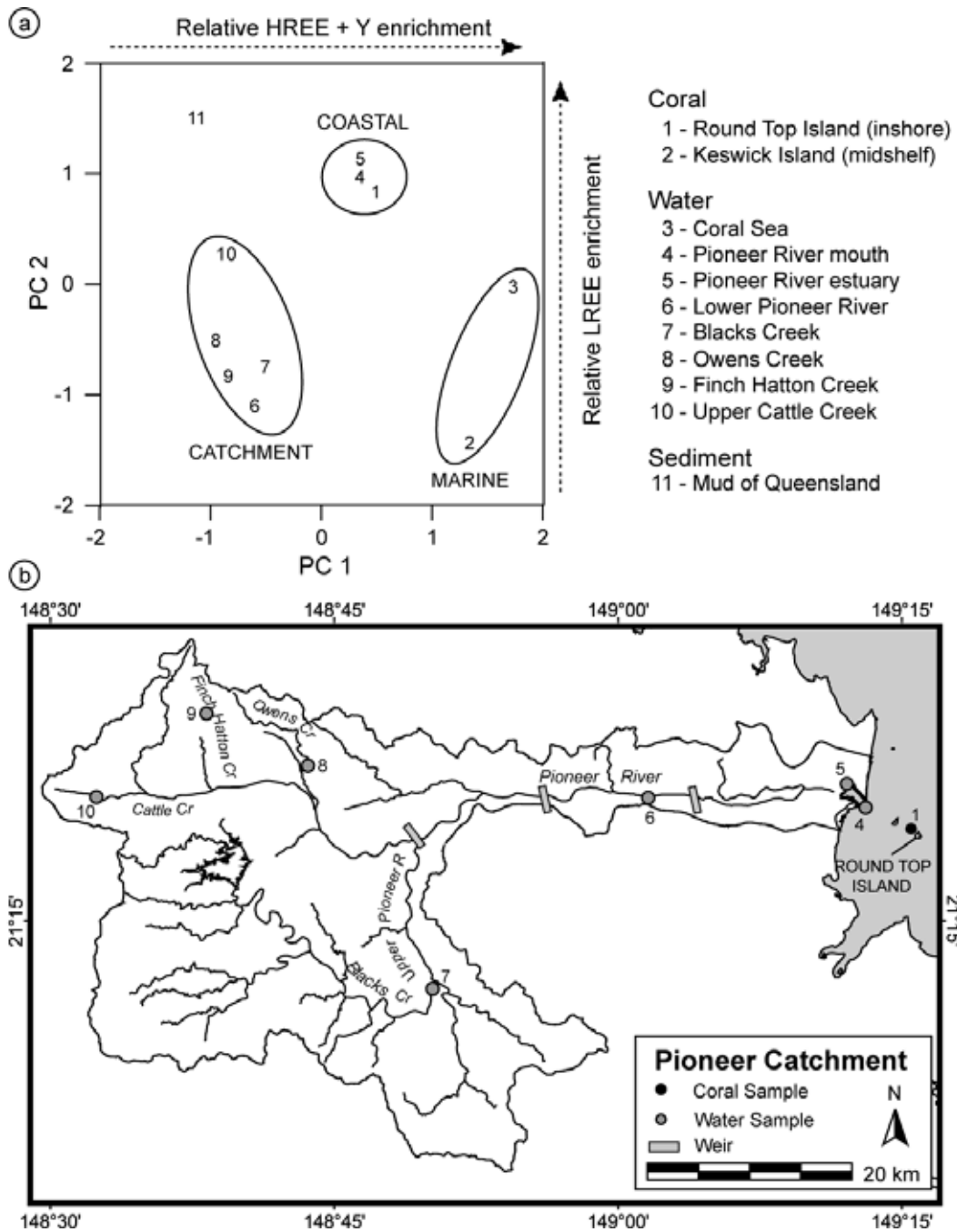
Figure 5. (a) Scaled REY data from coral, water and sediment samples plotted against principal components PC1 and PC2. Dashed arrows indicate directional enrichments of different groups of elements. The clusters have signatures reflective of catchment, coastal and offshore marine sources. (b) Locations of sampling sites in and adjacent to the Pioneer catchment.

(KIA) and the offshore seawater sample from the Coral Sea, had high positive values along principal component 1, which is largely explained by differences in scaled middle rare earth element (MREE) and heavy rare earth element (HREE)

abundances (Figure 5). While HREE enrichments are typical features of normalised oceanic seawater patterns, relative HREE depletions in coastal waters probably result from fluvial discharge, biological activity or a combination of the two (Goldstein & Jacobsen 1988, Wyndham et al. 2004). The large differences in scaled Y abundances also contribute to principle component 2, with scaled abundances of Y strongly mirroring a gradient of terrestrial influence (MUQ < Pioneer catchment streams < Pioneer River mouth < RTF < KIA < Coral Sea). The differences in position among Pioneer stream samples along principal component 1 also reflect relative enrichments of HREE and Y from Blacks Creek and the Lower Pioneer River: this may be due to leaching from fertiliser since the REY patterns in typical fertilisers that resemble natural phosphorites are nearly indistinguishable from the marine REY pattern (Martin & McCulloch 1999, Otero et al. 2005, Lawrence et al. 2006).

In every decade from 1950 to 2002, REY abundances from the inshore Round Top Island core (RTF) were approximately two to five times higher than REY abundances from the midshelf Keswick Island core (KIA) (Figure 6). In general, the inshore Round Top Island core had MUQ-normalised REY patterns and magnitudes that were in strong agreement with other inshore GBR corals (Wyndham et al. 2004). By contrast, the midshelf Keswick Island core had lower
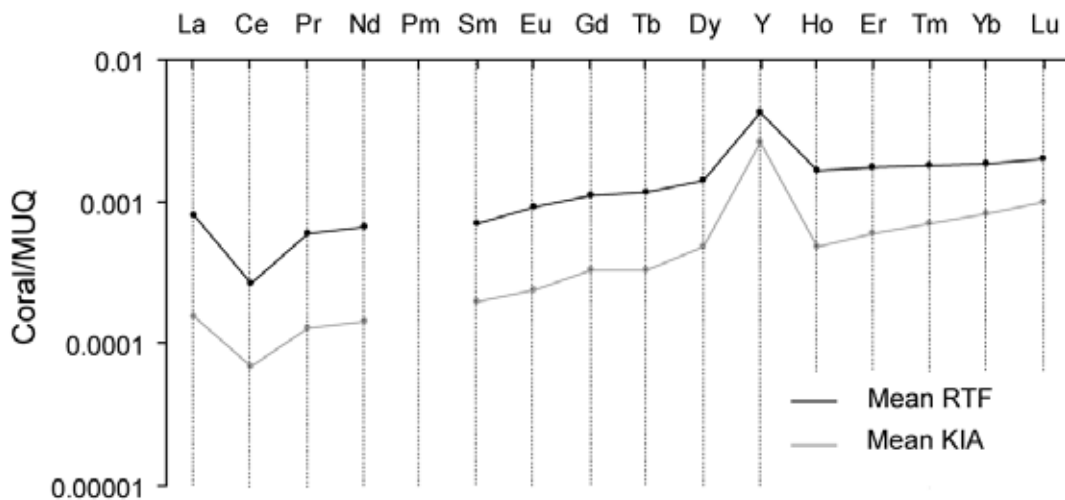
Figure 6. Inshore (RTF: black) and midshelf (KIA: grey) coral REY normalised to Mud of Queensland (MUQ).

MUQ-normalised magnitudes that were similar to values from an offshore GBR reef (Wyndham et al. 2004) and values from a *Porites astreoides* collected from Bermuda (Sholkovitz & Shen 1995), suggesting reduced terrestrial influences at these sites. Similarly, in the high-resolution LA-ICPMS data, there was a 3-4 fold enrichment of Y/Ca at Round Top Island compared with the midshelf Keswick and Scawfell Island sites. These results are consistent with those of Alibert et al. (2003) who found approximately five-fold enrichment of Y/Ca from coastal *Porites* corals relative to those from the midshelf off of the Burdekin River.

Temporal Trends in Trace and Rare Earth Elements

Coral REY concentration increased over time in both the RTF and KIA corals between 1950 and 2002. The rate of increase in total REY abundance was approximately three times greater in RTF than in KIA (Figure 7), and multiple regression analysis showed significant relationships to both year and Pioneer River discharge: when combined they explained 49% and 46% of the total variance at the inshore and midshelf sites, respectively. While the statistical significance of the change in the total inshore coral REY load was more affected by river discharge at Round Top Island (partial r^2 = 0.365, p < 0.002) than at Keswick Island (partial r^2 = 0.134, p < 0.025), most of the higher KIA REY values
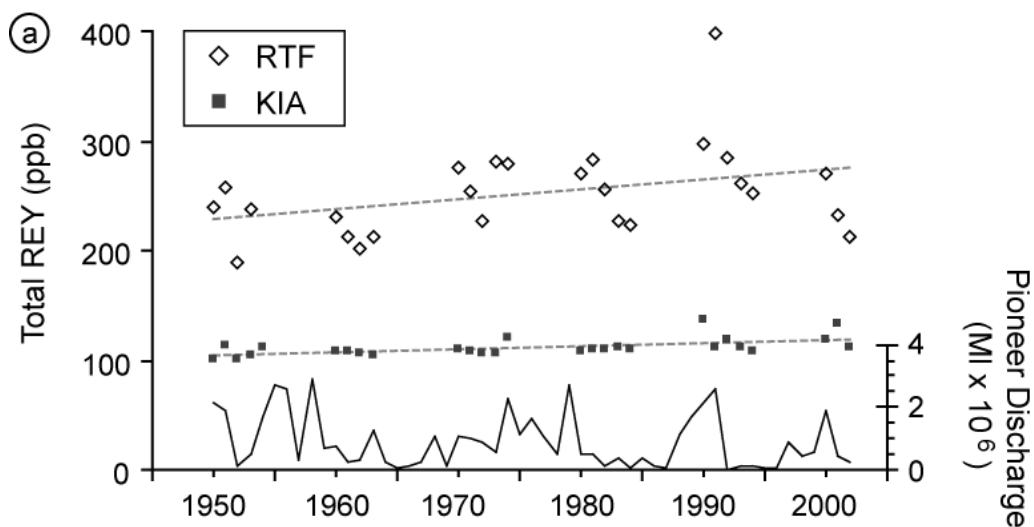
Figure 7. Temporal trends in total REY concentration for RTF core between 1950 and 2002. Annual Pioneer River discharge (in megalitres) is displayed below.

were associated with years of high annual rainfall and strong floods (1951, 1974, 1990, and 2001) whose plumes probably reached the vicinity of Keswick Island. The underlying steady but small increase over time at both sites suggests diffuse inputs of REY, possibly from greater catchment erosion coincident with agricultural expansion and riparian zone loss.

By contrast, there was no net increase in Ba/Ca or Y/Ca over time in a high-resolution LA-ICPMS Round Top Island record (RTF) between 1946 and 2003. Instead, periods of elevated Ba/Ca and Y/Ca were highly tied to regional climate cycles (Figure 8). The periodicity of climatic cycles in northeastern Australia strongly influences the frequency and magnitudes of floods and high winds associated with cyclones along the GBR (Lough 1994). When strong

Round Top Island Ba/Ca and Y/Ca, 1946-2004
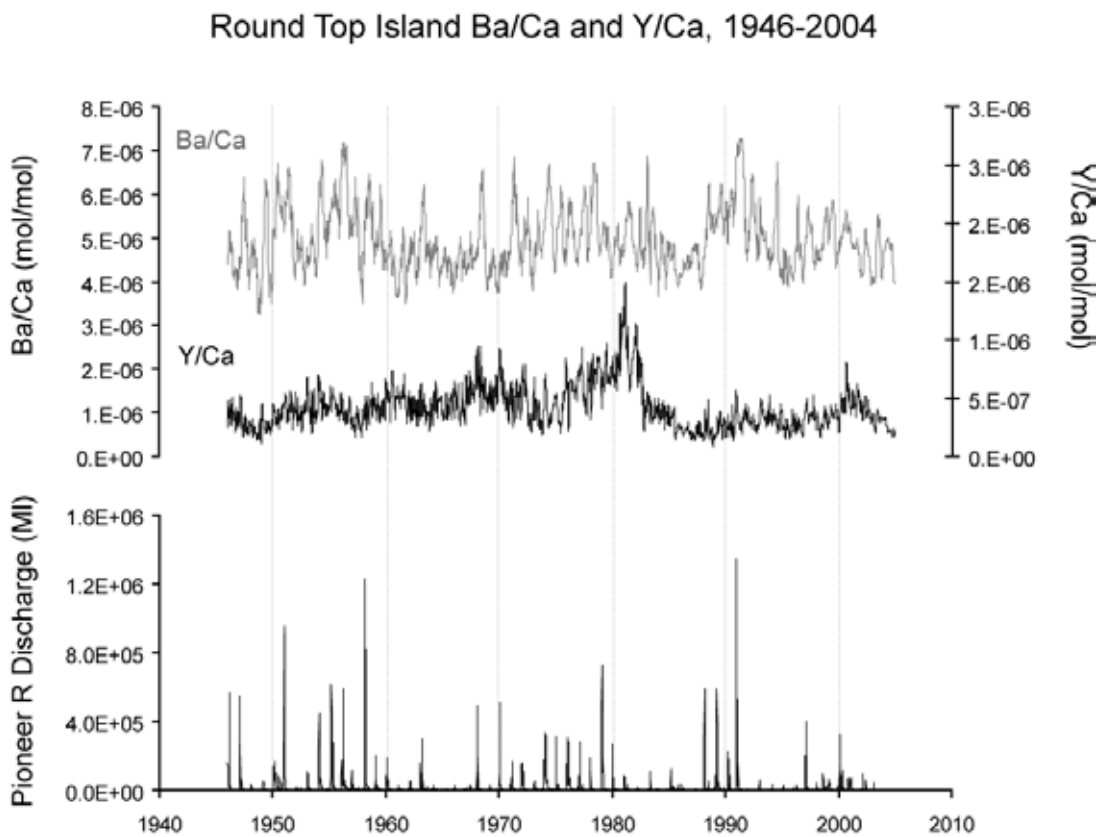
Figure 8. Weekly coral Ba/Ca and Y/Ca ratios measured with LA-ICPMS from an inshore Round Top Island coral (RTF) between 1946 and late 2004. The Ba/Ca record had substantially elevated baseline values during wet periods in the 1950s, 1970s, and late 1980s-early 1990s, and a strong ~20 year cycle likely related to regional climate activity. The Y/Ca record had elevated baseline in ~10 year cycles possibly related to cycles of the Southern Oscillation Index. Pioneer River discharge (in megalitres) is displayed below to show wet vs. dry periods in Mackay.

positive Southern Oscillation Index (SOI) cycles (a measure of El Niño-Southern Oscillation strength) coincided with strong negative Interdecadal Pacific Oscillation (IPO) cycles in the 1950s and 1970s, they produced very wet decades and high runoff from Queensland rivers (Power et al. 2005). The dominance of these climatic signals probably generated the strong ~19.5 year cycle observed in the RTF Ba/Ca data, which had elevated baseline Ba/Ca values during both of those wet decades. The ~19.5 year cycle was absent in the Y/Ca record, which instead had strong cycling of approximately decadal intervals. This cycle seems to coincide with the decadal mode identified from long-term dendroclimatic records of the SOI (Lough and Fritts 1985; Brassington 1997), but because this mode has not been identified in most twentieth century reconstructions of the SOI (Brassington 1997), the coral may have responded to some other decadal environmental signal.

Conclusions

Ba/Ca, Y/Ca and total REY in *Porites* coral skeletons are proxies for river discharge from inshore corals in the Mackay region. Because the correlations of Ba/Ca and Y/Ca with discharge are influenced by wind direction and magnitude, the behaviour of these tracers may also be used to characterise the spatial extent of past flood plumes. Results from trace element data are consistent with coral $\delta^{15}N$ data that suggest that Keswick and Scawfell Island reefs are less frequently affected by discharge from the Pioneer River, though longer records from these sites are needed to understand temporal variations in trace element concentrations on the midshelf. The observed time lags in Ba/Ca following discharge events indicate that regional differences in land use dynamics (between the Mackay Whitsunday, Burdekin and Wet Tropics regions) likely affect trace element incorporation, with large pulses of nutrients from the Pioneer and adjacent rivers stimulating phytoplankton blooms that can initially take up and recycle available barium. While there has been a slight but significant increases in both inshore and midshelf total REY measured at annual resolution since ~1950, which may reflect limited increases of soil erosion from agricultural intensification, inshore Ba/Ca and Y/Ca records were more influenced by climate fluctuations over the same period.

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Large stands of brown macroalgae (*Sargassum* spp) that dominated the fringing reefs of Keswick Island (33 km from the Pioneer River mouth) in March 2006.

Chapter Seven

Post-European Baseline Shifts in Nutrient Accumulation in the Nearshore GBR Lagoon

Introduction

Human transformation of coastal lands that border vulnerable areas of the world's oceans is linked to globally-observed declines of nearshore marine ecosystems (Vitousek et al. 1997, Fabricius and De'Ath 2004, Beman et al. 2005, Foley et al. 2005). Coral reef ecosystems, which mostly thrive in clear, nutrient-poor (oligotrophic) waters, are particularly threatened by enhanced nutrient and sediment delivery in runoff from highly modified coastal lands. Recent evidence shows that coral reefs were substantially degraded pre-1900, and that "even the reefs of the Great Barrier Reef (GBR), which are some of the best protected

worldwide, are still considered far from pristine and are vulnerable to phase shifts from coral to algal dominated communities" (Pandolfi et al. 2003). Land-derived pollution, as well as overfishing, is considered the only plausible explanation for the early and pervasive decline of coral reef species (Pandolfi et al. 2003).

The effects of anthropogenic land use change on GBR water quality and marine community health is a longstanding and controversial issue (Bell 1991, Furnas and Mitchell 1996, Larcombe and Woolfe 1999, McCook 1999). European settlement of the Queensland coastline in ~1850 led to the rapid expansion of agriculture, urban and port development, and coastal reclamation (Duke and Wolanski 2001, Johnson et al. 2001, Furnas 2003). Over half of Queensland's 117 million hectares of woody vegetation has been cleared since European arrival (QEPA 1999), and nearly 80% of the 422,000km^2 GBR catchment is dedicated to agriculture, primarily cattle grazing for beef production (77% of land area), and cultivation for sugarcane cropping (1%) (Devlin and Brodie 2005, Furnas et al. 2005). Grazing and tilling of agricultural lands reduces surface water infiltration, leading to increased erosion and runoff (Pimentel et al. 1993), while fertilisers and pesticides leach into surface and ground waters (Matson et al. 1997, Vitousek et al. 1997, Prasertsak et al. 2002, Rasiah et al. 2003).

Consequently, the delivery of terrigenous sediments and anthropogenic nutrients (mostly from N fertiliser leachate) to the nearshore GBR lagoon is directly linked to the proportion of land use dedicated to intensive sugarcane cropping (Brodie and Mitchell 2005, McKergow et al. 2005, Wooldrige et al. 2006). This varies considerably in total area occupied by the 35 major Queensland river catchments that drain into the GBR lagoon (Devlin et al. 2001, Furnas 2003), with sugarcane accounting for a high proportion of land area within the lower alluvial floodplains that line the waterways (Brodie and Mitchell 2005, Jupiter and Marion 2007). The 5-fold expansion of agricultural areas within the GBR catchment has also led to the loss of a large percentage of riparian vegetation (the vegetation at the interface between terrestrial and aquatic systems) over the past 50 years (Chapter 2, Johnson et al. 2001, Brodie and Mitchell 2005, Jupiter and Marion 2007). Riparian zones act as nutrient sinks, buffering dissolved and particulate loads from surrounding agroecosystems by direct vegetative uptake and indirectly through microbial cycling (Lowrance et al. 1984, Lowrance et al. 1997, Arthington et al. 2000). Riparian vegetation also

helps control the flow of sediments by dampening water velocity and shear, reducing scour, and increasing particle settlement (Norris 1993, McKergow et al. 2003, McKergow et al. 2004a,b). Taken together, the northeast region of Australia is a coastline of extremes: the immense ecological complexity that characterises the Great Barrier Reef is deeply interconnected with the globally significant scale of agricultural activity that dominates the catchment lands.

Historical Change in Great Barrier Reef Water Quality

Predicting how complex ecological systems will respond to human modification of the land, ocean, and atmosphere requires understanding how such systems have varied in the past. Thus the debate on the sources and extent of water quality change in the GBR Lagoon has been exasperated by the scant availability of long-term water quality data (Fabricius et al. 2005), and more specifically, by incomplete understanding of how nutrients and sediments delivered in runoff accumulates in sensitive areas of the inner GBR lagoon (Larcombe and Woolfe 1999, McKergow et al. 2005, Wooldrige et al. 2006). Present day nutrient delivery into the GBR lagoon is estimated to have increased by 2 – 5 fold relative to natural, pre-impacted rates (Moss et al. 1992, Neil and Yu 1996, Furnas 2003, Brodie and Mitchell 2005, McKergow et al. 2005, Wooldrige et al. 2006), and sediment delivery by a factor of 5-10 (McCulloch et al. 2003).

However, the largest continuing impact of nutrient delivery is associated with its ultimate fate, namely senescent phytoplankton biomass, terrigenous sediment particles, and particulate organic matter that deposits on the shallow shelf benthos (Fabricius and Wolanski 2000, Fabricius et al. 2005, Wooldrige et al. 2006). Impacts to coral reefs occur via direct smothering (Fabricius and Wolanski 2000), increases in turbidity that reduce the photosynthetic rates of the symbiotic dinoflagellates (Anthony 2000, Anthony and Fabricius 2000), and by the cascading effects of microbial remineralisation and reuptake by competitive macroalgae, phytoplankton, and cyanobacteria (McCook 2001, Alongi and McKinnon 2005, Fabricius et al. 2005, Furnas et al. 2005). Coral proxies are advantageous as they offer direct insights into the fate and burial of terrigenous pollutants in benthic reef skeletons (Fallon et al. 2002, Alibert et al. 2003, McCulloch et al. 2003, Wyndham et al. 2004, Sinclair 2005). This chapter focuses on the environmentally relevant issue of understanding how the sources and fate

of land-based nutrients and sediments delivered into the southern GBR lagoon have varied between pre-European and modern time periods. Key findings from the catchment end-member characterisation study (Chapter 3) emphasise the need to understand both the sources and transformations of fluvial N species delivered into the GBR Lagoon in order for an accurate interpretation of coral $\delta^{15}N$ records. A $\delta^{15}N$ and Ba/Ca time series is presented from an inshore core described in Chapters 5 and 6 that spans the years 1824 – 2005. This record provides a baseline period that precedes the intensive land clearing experienced shortly after European settlement of Mackay in 1862 and provides the first account of the historical context within which modern coral $\delta^{15}N$ records need to be interpreted. Coral-based measures of long-term N accumulation rates are determined from $\delta^{15}N$ systematics, and general comparisons are drawn with proxy data of sediment delivery into the GBR over the same time periods from analysis of skeletal barium to calcium (Ba/Ca) ratios. Newly acquired knowledge of how long-term nitrogen accumulation is impacting GBR ecosystems is discussed within the context of the literature and global reef systems.

Coral $\delta^{15}N$ reconstruction from 1824 - 2005

Chapter 5 illustrated that inshore coral $\delta^{15}N$ values have a significant positive correlation with Pioneer River discharge, and that a highly coherent relationship (r^2 = 0.71) is obtained by plotting $\delta^{15}N$ values from major flood years against time. Between 1944 and 2005, flood-associated $\delta^{15}N$ rose by 0.62‰ per decade, and correlated strongly with the 6-fold increase in the amount of N fertilisers applied to sugarcane paddocks in the Pioneer Valley (r^2 = 0.67). These observations provide evidence that intensified farming practices in the Mackay region have substantially increased the delivery to and accumulation of nutrients in coastal GBR coral communities since the mid-1950s (Chapter 5). Here we extend the record back to 1824 via continued down-core analysis of one of the inshore Mackay *Porites* cores ("RTH"- time series presented in Chapter 5).[3] By pre-dating the first sugarcane harvest in 1865 (Manning 1983), this record

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[3] The methods used to develop this $\delta^{15}N$ time series are identical to those described in Chapter 5. U-series dating techniques were used to verify the age of prominent bands in the distal portion of the skeleton, as this core (RTH) showed an approximately 45 yr hiatus in skeletal growth between ~1900 and 1945.

provides insights into how baseline $\delta^{15}N$ values, and therefore systematics associated with deposition of terrestrially-derived nitrogen in the inner GBR lagoon, varied prior to European-style clearing of Pioneer catchment lands. Nitrogen isotopic data was obtained for the years 1824 – 1875, after which period this colony exhibited anomalous $\delta^{15}N$ values associated with bioerosion of inner sections of the core after a 50 yr growth hiatus between 1900 and 1943.[4] Thus $\delta^{15}N$ results were not obtained for the early period of the 20th century. However, average $\delta^{15}N$, C:N and concentration data values were consistent between the late 1800s (end of the pre-coral mortality growth period) and the start of the latter portion of record in the 1940s.

Frequency and timing of coral $\delta^{15}N$ enrichment since 1824

The inshore Mackay coral $\delta^{15}N$ time series is shown in Figure 1, and spans the years 1824 – 2005, with a missing period from 1876 – 1943. Values that exceed the mean (7.41 ± 1.09‰, n = 120) are shaded in red, and those that are depleted are shaded in blue. There was a noticeable rise in the frequency with which $\delta^{15}N$ values exceeded the dataset average in the latter half of the record, particularly after 1958. Between 1824 and 1875, 64% of the annual $\delta^{15}N$ values fell below the dataset average, with values ranging from 4.61 – 8.90‰, while from 1944 - 2005, 60% of the annual $\delta^{15}N$ values were isotopically enriched (above the mean), and ranged from 5.19 to 11.13‰. In the early years of the record, interannual variability exhibits few coherent patterns, as was observed in the midshelf $\delta^{15}N$ records developed from the Keswick and Scawfell cores. This indicates that the ambient N concentrations were low at the time (Chapter 5). The range of $\delta^{15}N$ values observed in the inshore core during the pre-impacted years (1824 – 1875) is 1 - 3‰ higher than the modern range exhibited in the midshelf GBR cores (Chapters 5,6), suggesting that even in pre-impacted times, the coral reef assemblages of Round Top Island were naturally exposed to enhanced nutrient delivery from land-based runoff, as would be expected in this inner reef. Several high values >8.0‰ are observed in 1844 - 46, 1854 and 1869, which is consistent with the potential influence of minor phytoplankton blooms that

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[4] The bioerosion did not appear to significantly affect the coral Ba/Ca ratios during the period between 1875 and ~1900.
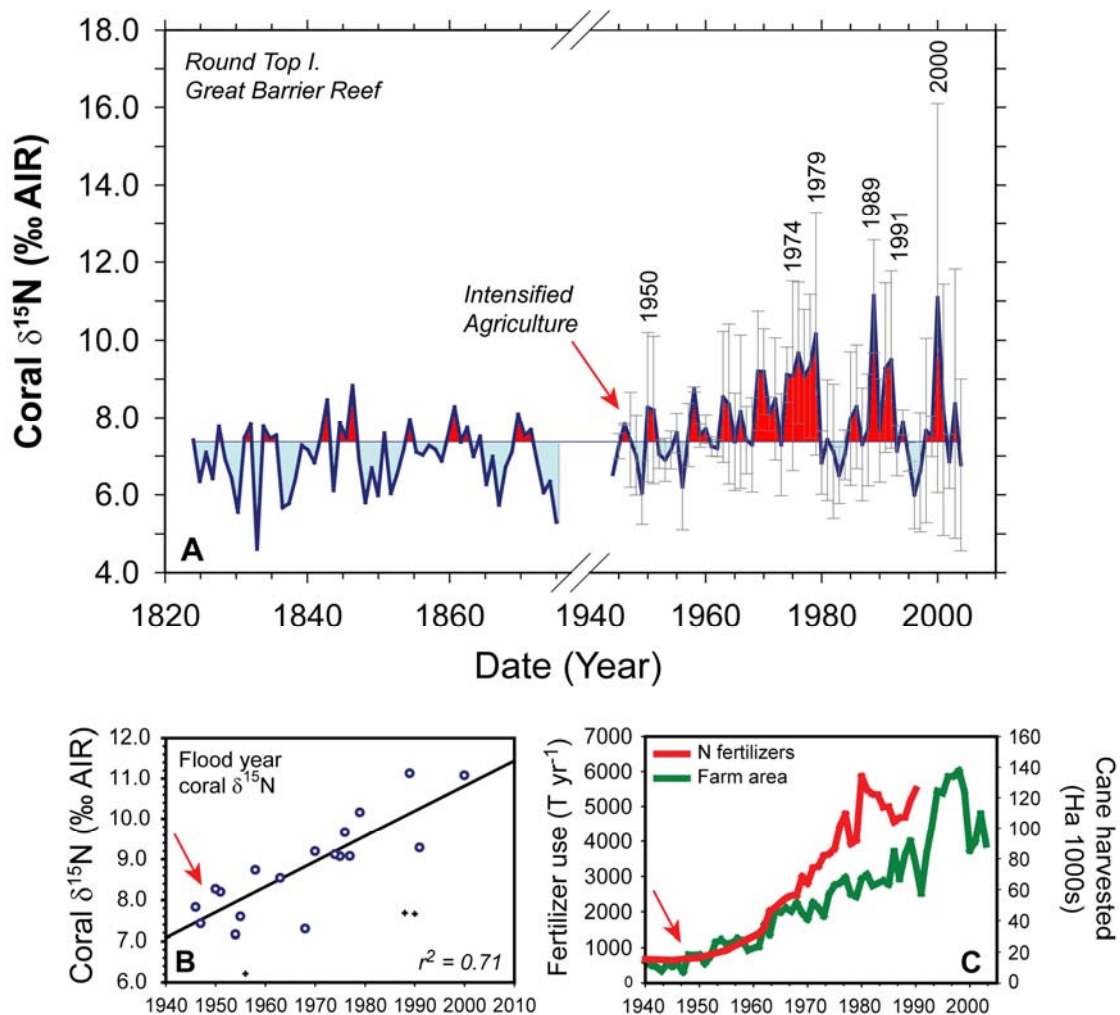
Figure 1. The coral δ^{15}N record (a) of anthropogenically-derived nitrogen loads delivered into the inner Great Barrier Reef lagoon since prior to the onset of European-style land clearing in approximately 1862. Between 1940 and 2005, (b) the isotopic composition of nitrogen preserved in coral associated with flood years has increased by 0.62% decade^{-1}. Mechanisation of farming processes allowing large areas of agricultural lands to be harvested, and the introduction of synthetic fertilisers (c) led to rapid growth of the sugarcane industry between 1940 and present.

possibly coincided with river floods, although of a lesser degree than is presently observed in the coastal Mackay region (Furnas et al. 1997, Mitchell et al. 2005, Rhode et al. 2005).

Interestingly, there was no consistent change in the frequency of positive or negative δ^{15}N excursions following European settlement, which occurred in 1862 in Mackay (Gourlay and Hacker 1986). This is likely related to the pattern of agricultural expansion that occurred in the region, which followed two distinct phases. First, after the first sugarcane plots were planted in 1865, agricultural activities grew rapidly, and by 1872, Mackay was Australia's leading sugarcane

producing region, accounting for 40% of Queensland's production (Kerr 1980, Gourlay and Hacker 1986). Pioneer Valley harvests reached 28,000 t yr^{-1} in 1894 (Manning 1983), and most of the land area available for sugarcane cultivation was already cleared by 1902 (Bolton 1963). However farming practices exerted relatively little impact, with tilling and harvesting operations performed manually and fertilisation occurring exclusively via organic manures and traditional methods (Gourlay and Hacker 1986). The end of WWII ushered the second phase of agricultural "intensification" in Queensland. The arrival of new equipment and a ready and able workforce of returned servicemen led to the mechanisation of planting, tilling, and harvesting operations, which in Mackay sustained a pervasive and long-term rise in sugarcane production (Rolleston 1987). Between 1945 and 2000, the area of sugarcane harvested increased by over 11 times (to a peak of approximately 124,000 ha in 1998) (Simpson et al. 2001, Brodie 2004), with present day harvests totaling 1.3 million t yr^{-1}, or approximately 1/3 of Queensland's total (Rolleston 1987, QEPA 2004). Substantial enrichment of δ^{15}N values are apparent in the coral record from the late 1950s, when critical N loading thresholds (47 – 67 kg N ha^{-1}) were surpassed (Chapter 5). Fertiliser applications in the Pioneer catchment remained low (under 1000 T yr^{-1}) until the late 1950s, after which period they increased rapidly from 1,000 t yr^{-1} in 1956 to 5,500 t yr^{-1} by 1990 (Pulsford 1996). Prior to the late 1950s-the wettest decade on record in Mackay- the range of coral δ^{15}N values were similar to those of the natural, pre-impacted years. This suggests that the extensive N delivery and resulting enhancement of algal growth that characterises the region's coastal waters today (Furnas et al. 1997, Mitchell et al. 2005, Rhode et al. 2005) is a 50 yr old phenomenon.

Another prominent feature in the coral δ^{15}N record is that absolute δ^{15}N values have increased by 2 - 4‰ over the last five decades, particularly between 1958 and 2005. These reflect the interactive effects of increased anthropogenic N supply (primarily from fertiliser leachate) and substantial biological fractionation during transport of N species through the catchment system and into the coastal waterways (Chapter 3). Alterations to the river hydrology by the construction of three large weir systems in 1952, 1982, and 1998, have increased the propensity for algal N uptake and denitrification of residual nitrate in the low oxygenated bottom layers of the monomictic (seasonally stratified) and permanently stratified

river weir reservoirs (Cifuentes et al. 1988, Middelburg and Nieuwenhuize 2000, 2001). Consequently, a latent pool of isotopically distinctive nitrogen ($\delta^{15}N \geq 9$‰) presently resides in the lower Pioneer stretch (Chapter 3). During flood pulses, large quantities of this ^{15}N-enriched load (i.e. 243 T during a 4 day event flow in 2002, or 315 T during a 2 day event in 2005) (Mitchell et al. 2005, Rhode et al. 2005) are discharged into the inner GBR Lagoon, where fractionation expressed during phytoplankton uptake and microbial remineralisation of senescent plankton detrital matter increases the signal by a further 1 – 7‰ (Chapter 5, Pennock et al. 1996, Waser et al. 1998). Thus the N isotopic systematics paint a picture of the non-conservative transformations acting on fluvial N species during transport, which are likely to occur in proportion to the input N concentrations delivered from anthropogenic sources (McClelland and Valiela 1998).

Baseline shift in coral $\delta^{15}N$ between pre-European and modern periods

The primary objective of this and any baseline study is to quantify the magnitude of change experienced between the natural, pre-impacted and the modern, impacted state of the system. Here this is achieved by first grouping the coral $\delta^{15}N$ data into three time and signal-dependent scenarios: "natural baseline" (1824 – 1875), "modern baseline" (1944 – 2005), and "modern flood" ($\delta^{15}N$ values from flood years between 1944 and 2005, n = 16). Because instrumental river discharge data only extends back to 1918 for the Pioneer, "natural flood" conditions are not quantifiable without high-resolution luminescence measurements and preparation of an accurate proxy record of river discharge (not completed in this study).

The modern baseline $\delta^{15}N$ value (7.83 ± 0.29‰) was 0.9‰ higher than the natural baseline (6.97 ± 0.22‰), while the modern flood-associated value was enriched by 2.4‰ (9.36 ± 0.64‰; Figure 2). Both represent significant upward shifts (Kruskal Wallis ANOVA, df = 2, 136, $p < 0.000$) that realistically can only be explained by the increased delivery and accumulation of total N in the inshore reef from high levels of fertiliser leachate transported through the Pioneer River system. This assertion is supported by: (1) the significant relationship shown for flood $\delta^{15}N$ values and fertiliser rates used ($r^2 = 0.67$; Figure 3); (2) the observation that baseline coral $\delta^{15}N$ values only rise above the range of natural $\delta^{15}N$ variability after N
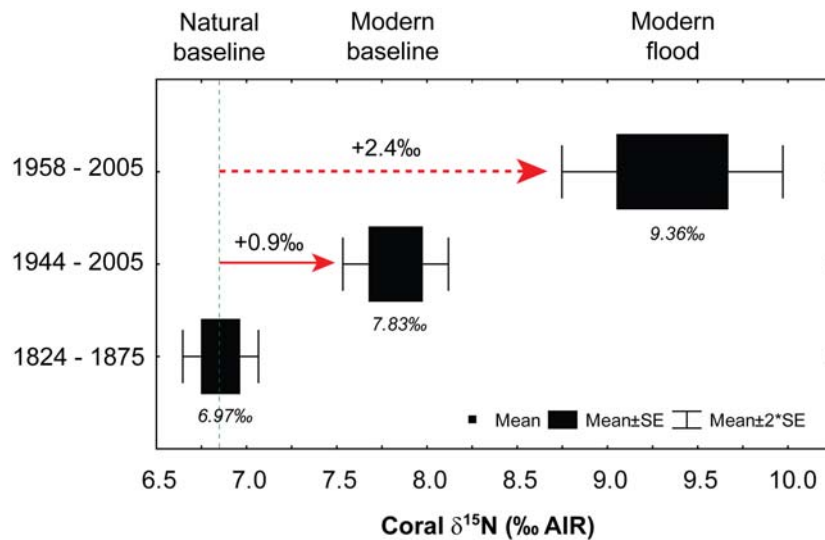
Figure 2. Long-term changes in ambient and flood-related coral $\delta^{15}N$ values were calculated by classifying annual coral samples into three groups: "natural baseline", which mostly includes years prior to European settlement of Mackay, "modern baseline" which includes all samples taken from 1944 – 2005, and "modern flood", which includes all coral $\delta^{15}N$ values that were measured in years of major Pioneer River floods. The boxes represent the mean $\delta^{15}N$ ± 1 std error (SE), and the error bars represent 2 SEs.

fertilisers were introduced to Mackay sugarcane farms in the late 1950s; and (3) the absence of high $\delta^{15}N$ values in the natural baseline period, despite the fact that these inshore corals appear to have been exposed to similar volumes of freshwater runoff (inferred from coral luminescent bands). The associated change in catchment

N application rates (t N yr^{-1}) associated with these shifts in baseline coral $\delta^{15}N$ values can be derived from the approximately linear relationship that is obtained between the modern coral $\delta^{15}N$ flood values and the corresponding fertiliser application rates (Pulsford 1996) in those flood years ($r^2 = 0.67$, n = 16, $p < 0.001$; Figure 3). We call this the "N accumulation rate", which is given by:

$$Kt \ N_{fertiliser} = 1.24 \ x \ \delta^{15}N_{coral} - 8.28$$

Substitution of the natural baseline $\delta^{15}N$ value established from the coral record (6.97‰) into the above equation shows that the pre-impacted, natural N application rate in the Pioneer catchment expected by the coral-fertiliser relationship is 0.35 kt N yr^{-1}. McKergow et al. (2005) estimated natural

background specific nitrogen export rates from the Pioneer River of 1.5 kg N ha^{-1}, which in the broader Mackay region (124,000 ha sugarcane) (Simpson et al. 2001, Brodie 2004) equates to 0.20 kt N yr^{-1}. This is within range of the empirically derived value reported here. Extending the relationship to the values of the modern baseline δ^{15}N, modern flood δ^{15}N, and δ^{15}N values from major Pioneer recent floods, we find that compared to the pre-impacted conditions, N accumulation rates have shown a:

- **4-fold increase**, to 1.4 kt N yr^{-1}, during the "modern baseline" years of 1944 – 2005,
- **10-fold increase,** to 3.3 kt N yr^{-1}, during Pioneer floods that occurred from 1958 – 2005,
- **16-fold increase,** to 3.2 – 5.5 kt N yr^{-1}, during the floods of 1989, 1991 and 2000.
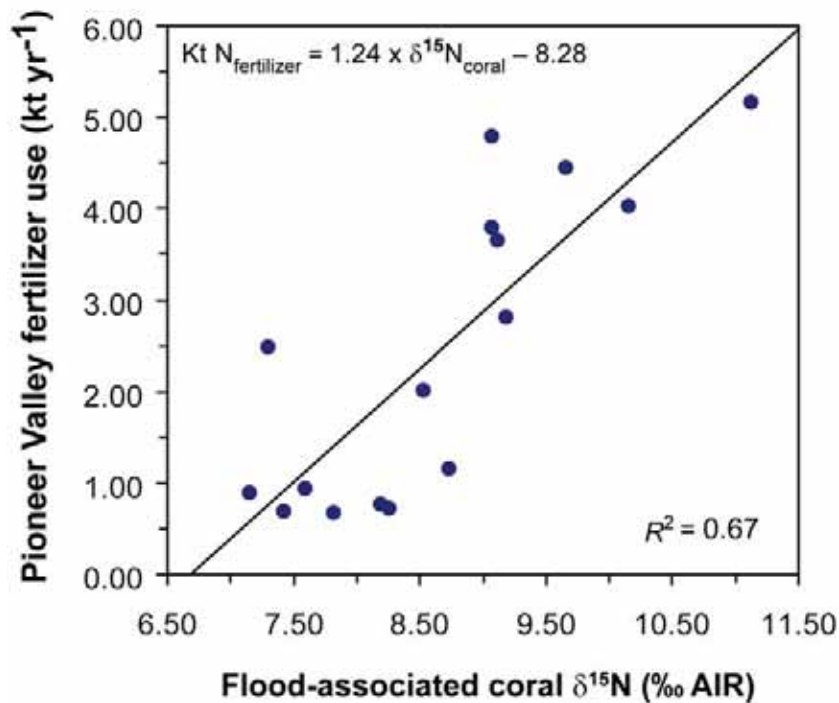
Figure 3. Linear regression of coral δ^{15}N values measured from years of major river floods ("flood-associated coral δ^{15}N values") against corresponding fertiliser use data for those same years. Fertiliser data sourced from Pulsford (1996).

These estimates (shown in Table 1) are considered to be conservative as they are based on aggregated $\delta^{15}N$ data from the three inshore cores into one common master series for the recent period only (Chapter 5). While development of a master series yields a more robust dataset which supports that several independent records show common features reflective of an overarching environmental influence (Fritts 1976, Hendy et al. 2003), the magnitude of individual events is diminished by the averaging effect (as indicated by the large standard deviations of major flood years of 1979, 1991, and 2000).

Table 1. Nitrogen accumulation rates in the inshore Great Barrier Reef lagoon were derived from the coral – fertiliser relationship plotted in Figure 3. "N" represents the coral-derived estimate of fertiliser application rates that produce result in the coral δ15N value. "Multiple increase" represents the factor by which N accumulation has increased in comparison to the natural, pre-impacted period (1824 – 1875).

Comparison period	Coral $\delta^{15}N$	N (kt yr^{-1})	Multiple increase
1824-1897	6.97	0.21	-
1944-2005	7.83	1.41	4
All floods post-1957	9.36	3.31	10
Floods of 1989, 2000	11.1	5.47	16

Recent modelling estimates of post-European N delivery rates

The 4-fold increase in the modern baseline N accumulation rates, and the 10 to 16-fold increase during large recent floods, relative to the "natural" period of 1824 – 1875, is within range of the most recent modelling estimates for the GBR lagoon (McKergow et al. 2005, Wooldrige et al. 2006). McKergow et al. (2005) used a hybrid modelling approach based on the nutrient ANNEX model of the *SedNet* (Sediment River Network Model) suite of programs (Prosser et al. 2001) to estimate that current N export rates from all GBR river catchments has increased from 14 to 63 kT yr^{-1} since the pre-European baseline, representing a 5-fold increase. Moreover, the authors noted that the biggest change in area specific N and P exports have occurred in the Mackay Whitsunday river systems (including the Pioneer), totalling an approximately 16-fold increase for N and 3 – 30 fold increase for phosphorus (McKergow et al. 2005). The ANNEX/SedNet model constructs budgets of particulate and dissolved nutrients through river

systems and accounts for both the rate of supply from erosion processes and land uses, and loss due to deposition and transformations during transport. Isotopic evidence of significant non-conservative biological transformations of fluvial N species presented here for the Pioneer River, and the similar estimates of long-term N delivery in the McKergow et al. (2005) study, highlight that the ANNEX/SedNet model captures a higher proportion of the variability in the system than do previous modelling estimates (i.e. Furnas 2003).

Wooldridge et al. (2006) used a spatial analysis technique (geographically weighted regression analysis) to test for spatial variance in a regression relationship that relates the runoff : seawater dilution ratio to measured GBR chl-a concentrations. The study reported a broad scale longitudinal gradient along the GBR, which showed that for equivalent runoff : seawater ratios, the relatively non-impacted far northern catchments of the GBR exhibited reduced levels of nutrient enrichment (manifested as chl-a concentrations) compared to the impacted catchments of the southern GBR. Substituting nutrient enrichment parameters of the impacted river systems with characteristics of the non-impacted northern rivers, the authors estimated a 10-fold increase in algal enhancement associated with river floods since pre-European periods, from which the authors extrapolated that inorganic nutrient (N+P) enrichment has increased by 10-20 fold (Wooldrige et al. 2006), impacting reefs 20 – 30km offshore. Chapter 5 showed that the midshelf coral δ^{15}N record from Keswick Island (33km offshore) registered two significant δ^{15}N peaks over a 35 yr period, corresponding with the historically significant floods of 1974 and 1991. This indicates that in the Mackay region, delivery and accumulation of terrestrially derived N reaches the midshelf during major flood events. Taken together, the maximum 10 – 20 fold increase in N delivery into the GBR lagoon relative to pre-impacted rates recently estimated (McKergow et al. 2005, Wooldrige et al. 2006) is well within the range of the baseline (4-fold) and flood-associated (10-16 fold) terrestrial nitrogen accumulation rates determined here.

Dual Tracer Comparisons of Changes to Sediment and Nutrient Delivery

High resolution trace metal analyses (see Chapter 6 and Jupiter (2006) for methods) were conducted on the same core over the years 1824 – 2005 in order to cross-examine how the frequency and intensity of suspended sediment loads
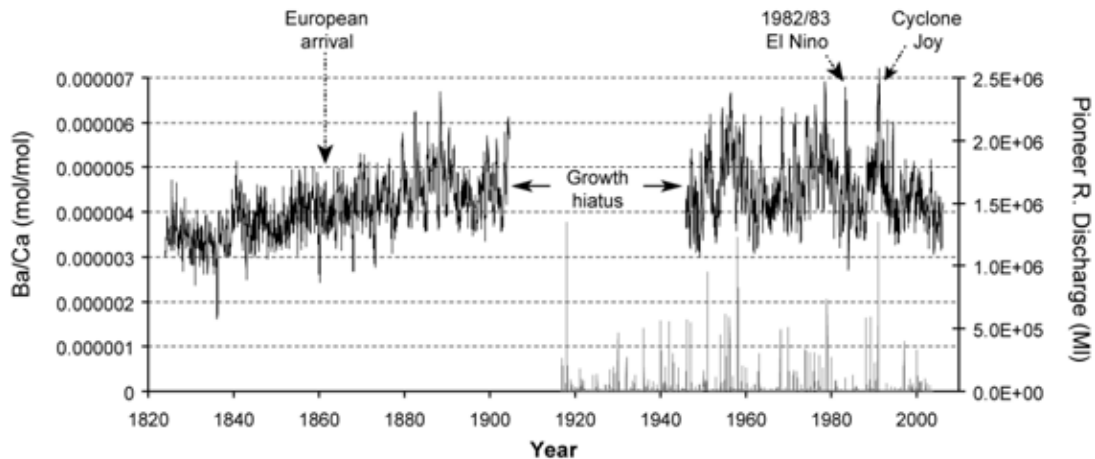
Figure 4. Long-term inshore coral Ba/Ca record (black) from a nearshore colony at Round Top Island. An increase in the baseline values occurs following European arrival to Mackay and land clearing for sugarcane production. Records since 1946 show strong decadal oscillations coinciding with wet and dry decades, with strong peaks during ENSO events and following major floods, such as after Cyclone Joy. Pioneer River discharge from gauge measurements shown below in grey.

contained within Pioneer River floods compared with terrestrial N accumulation rates. When the Ba/Ca record is extended back through time from the RTH coral record (1824-2005, with a growth hiatus between 1904-1946), there is a marked increase in baseline Ba/Ca levels that follow soon after European settlement of Mackay in 1862 (Figure 4). Ba/Ca concentrations increased from an approximate pre-European baseline of 3.5 x 10^{-6} between 1825 and 1855 to 4.8 x 10^{-6} by 1890, representing a 37% increase in Ba incorporation into the coral skeletons over a 50 yr period. While Ba/Ca to river discharge systematics required for the translation of the geochemical shifts into sediment accumulation rates have not yet been determined, McCulloch et al. (2003) similarly observed a 30% rise in baseline Ba/Ca concentrations in nearshore *Porites* corals collected from the Burdekin River region in central Queensland. The observed increase in sediment delivery occurred within 10 years of European arrival, over which period large numbers of cattle and sheep were introduced for grazing (approximately 180,000 sheep and 31,000 cattle in 1868 compared to 0 in 1862; Kerr 1980, McCulloch et al. 2003), and the authors used the Ba/Ca relationship to Burdekin River discharge to calculate a 5 – 10-fold increase in sediment delivery rates relative to pre-European conditions.

In the Pioneer catchment, where the estimated current average annual sediment export (0.05×10^6 tonnes yr^{-1}) is only ~1% of the estimated load for the Burdekin River (Furnas 2003), the rate of increase in sediment flux to the nearshore is expected to be lower. Hacker (1988) estimated two to four-fold increase in sediment delivery to the estuary since initial land clearing in the Pioneer catchment, of which the initial rise is likely to have occurred immediately following settlement of Mackay. The trajectory of the initial rise in Ba/Ca levels between 1862 and ~1880 mirrors the rapid early expansion of land clearing for sugarcane production in the region (Chapter 2). Large-scale catchment deforestation typically results in an immediate increase in streamflow, followed by an increase in sediment export once the root structures have degraded (Douglas 1967, Likens et al. 1970). Between 1890 and 1990, sediment delivery to the coast may have stabilised (no change in baseline Ba/Ca concentrations) as a result of considerable regrowth of vegetation on previously cleared catchment slopes and maintenance of crop cover through most of the year. Variability since 1946 has been dominated by strong cycles in Ba/Ca at ~19.5 year resolution that are likely related to climate fluctuations (Chapter 6, Jupiter 2006). This differs from the coral $\delta^{15}N$ time series, which shows a sustained rise and accumulation of agriculturally-derived nitrogen in the inner GBR lagoon starting in the late 1950s that stands out over and beyond influences of climate (Figure 5, and see also Chapter 5).

These results are consistent with hypotheses of how global water quality has varied since the rise of human civilisations (Lotze et al. 2006). Lotze et al. (2006) reconstructed historical baselines of change in 12 coastal ecosystems of Europe, North America, and Australia, dating from the onset of human settlement until present. During the "market colonial development" period, which encompassed periods of rapid human population growth and increasing demand, sediment loading strongly increased due to deforestation and associated mobilisation of sediments and nutrients. In Queensland, and Mackay specifically, this corresponds with rapid rates of vegetation and land clearing for agricultural activities that occurred between 1860 and 1900. During first of the "global market" periods (1900-1950), sedimentation of coastal environments stabilised; while the latter half of the century (1950-2000) led to strong increases in nitrogen and phosphorus delivery, resulting in enhanced primary productivity, eutrophic

plankton, oxygen depletion, and losses of epiphytic diatoms (Lotze et al. 2006). Here, the use of dual geochemical tracers (Ba/Ca and δ^{15}N) provide otherwise unavailable insights into the mechanisms by which European-style land clearing (starting in the 1860s) and agricultural intensification (fertilisation and mechanisation starting in the mid 20th century) exerted different environmental pressures on coastal GBR environments.
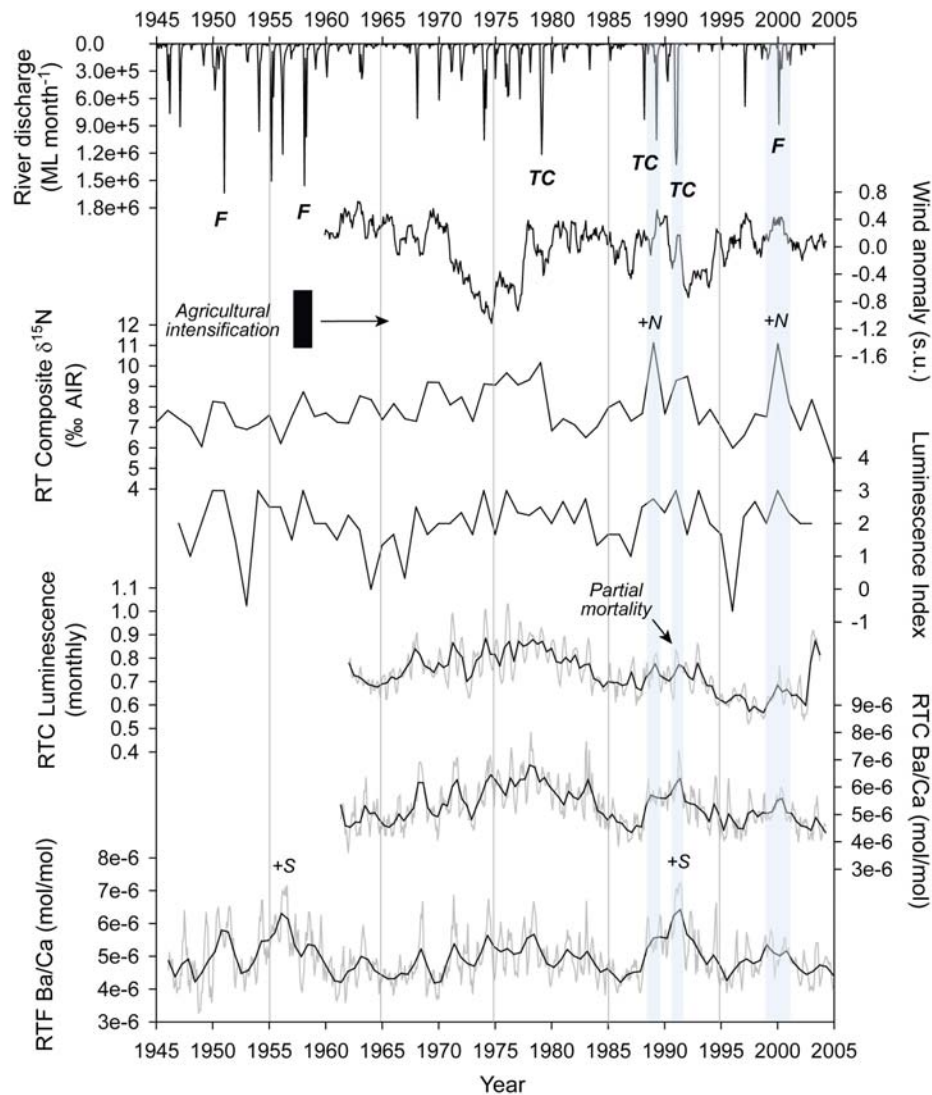
Figure 5. Alignment of Pioneer River discharge record, wind record, composite inshore coral δ^{15}N, luminescence index, instrumental luminescence intensity measured by gamma luminometry, Ba/Ca ratios from *Porite*s coral cores Round Top "C" (RTC) and Round Top "F" (RTF). TC= tropical cyclones, F = flood, +N = maximum d15N values. +S = maximum Ba/Ca values (proxy for suspended sediment load).

Since the mid-1990s, >90% of farmers have switched harvesting practices from paddock burning to green cane trash blanketing (GCTB). Following adoption of GCTB and minimum tillage, soil erosion rates on the paddock scale have dropped from 42 – 227 t ha^{-1} yr^{-1} (Sallaway 1979) to ~5 – 15 t ha^{-1} yr^{-1} (Rayment & Neil 1997, Mitchell et al. 2005). While there is a significant 16% reduction in mean Ba/Ca levels from 5.0 x 10^{-6} to 4.3 x 10^{-6} between the mid-1990s and early 2000s (two-sample t-test, $p < 0.001$), a longer observation period is required to determine whether this reduction is associated with new land management (GCTB) or with low natural sediment delivery as a consequence of drought conditions during the majority of years since 1991. By contrast, highly enriched inshore coral δ^{15}N values in flood years since the mid-1990s (particularly 2000) suggest that GCTB has had no diminishing effect on nutrient export rates into nearshore waters.

Conclusions

This study demonstrates the power of using multiple tracers from coral skeletons to understand the long-term changes to sediment and nutrient dynamics draining from a highly agricultural catchment of the Great Barrier Reef. While coral Ba/Ca records (a proxy for sediment delivery) showed a distinct 37% increase in baseline values following the onset of European land clearing in the mid-1860s, sediment delivery rates appeared to stabilise since ~1890. Meanwhile, large increases in fertiliser application since 1950 in the Pioneer catchment have substantially increased the delivery and accumulation of anthropogenic nitrogen loads to nearshore coral reef ecosystems. Inshore coral δ^{15}N records indicate that present day N accumulation rates associated with river floods in the Mackay region of the southern GBR have increased by at least 10 to 16-fold relative to natural baseline scenarios (1824 – 1875). A 4-fold increase occurred even under ambient non-flood conditions. The δ^{15}N systematics indicate that the corals incorporate recycled marine particulate nitrogen and senescent phytoplankton detritus, which in turn are stimulated by land-based sources of nutrients. Phytoplankton and organic loads suspended in low salinity flood plumes can traverse broad stretches of the GBR (Devlin et al. 2001, Devlin and Brodie 2005, Furnas et al. 2005, Wooldrige et al. 2006), and offshore of Mackay can disperse terrestrial N sources to midshelf reefs living 33km perpendicularly

away from land (Chapters 5 and 6). Recent modelling estimates of river systems flowing into the southern GBR estimate 10 – 20 fold increases of N delivery into the GBR lagoon relative to natural conditions (McKergow et al. 2005, Wooldrige et al. 2006), although total delivery rates vary substantially between catchments. Variability is related to the higher frequency with which rivers in the "Wet Tropics" in Northern Queensland flood (at least once per year) (Lough et al. 2002, Brodie and Mitchell 2005) and to the proportion of land use dedicated to intensive anthropogenic activities, primarily sugarcane cultivation and cattle grazing (Brodie and Mitchell 2005, Devlin and Brodie 2005, Wooldrige et al. 2006).

In the Pioneer catchment, 71% of the lower alluvial floodplain is currently cultivated for sugarcane production (Jupiter and Marion 2007), which uses fertilisers at average rates of 173 kg N ha^{-1} (Simpson et al. 2001, Brodie 2004). The region has experienced a 32% net decline in riparian vegetation since 1972 and a 22% net decline in mangrove cover since 1948 (Jupiter et al. 2006, Jupiter and Marion 2007), which are linked to clearing catchments for agriculture and/or to increased concentrations of herbicides leaching from surrounding sugarcane farms (Duke et al. 2005). Specific nitrogen exports from the Pioneer are currently estimated at 7.5 kg N ha^{-1} yr (McKergow et al. 2005), making it only the 7th largest N emitter of Queensland's 35 major river systems. N accumulation rates in nearshore GBR ecosystems are likely to be substantially higher in the Wet Tropics region (i.e. Russell-Mulgrave, Johnstone, and Tully rivers). These rivers exhibit export rates of 12 - 16 kg N ha^{-1} yr^{-1}, of which half to two thirds is in biologically available dissolved forms (Furnas et al. 2005, McKergow et al. 2005). The potential consequences of this recent enrichment of available nutrients to nearshore coral ecosystems will be discussed further in Chapter 9.

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Diverse mangrove communities of Bassett Basin within the Pioneer River estuary. 8 April 2003

Chapter Eight

Natural and Anthropogenic Changes to Pioneer Estuary Mangroves

Introduction

Globally, about one third of mangrove forests have been lost within the past 50 years (Alongi 2002). This has resulted in growing concern over the coincident decline of important mangrove ecosystem services, such as filtering river runoff, which are critical for maintaining ecological integrity in downstream ecosystems. While mangroves and tidal flats comprise only a small portion of catchment area, they trap and store disproportionate amounts of suspended particles, nutrient-rich organic matter, and associated pollutants from catchment runoff (Alongi & McKinnon 2005). Mangroves typically establish in areas of mud deposition where they accelerate sediment accretion rates by reducing water velocities (e.g. through creek meanders and root baffles), and by trapping

aggregates of suspended particles (Furukawa et al. 1997). Suspended particles in river runoff tend to aggregate after mixing with brackish estuarine water, either through salt flocculation caused by changes in the electrostatic stability of their coatings (Gibbs 1983), or through contact with abundant mucus produced by high bacterial populations in mangrove swamps (Alongi 1988). Activities affecting mangrove and wetland conditions change the flux of materials into and out of estuaries (Arthington et al. 1997); and changing estuarine water quality may ultimately impact downstream marine ecosystems (Duke & Wolanski 2001). Yet in order to assess potential impacts of mangrove loss on downstream ecosystems, it is first necessary to quantify the magnitude of anthropogenic change relative to natural changes as certain types of change are more likely to permanently alter mangrove ecosystem condition and therefore impact its ecosystem services.

In this chapter, we describe mangrove loss in the Pioneer River estuary and identify drivers of mangrove distribution change over the past 60 years to assess the magnitudes of both anthropogenic and natural losses and gains. We specifically focus on documenting changes to mangrove areas that are hydrologically connected to the Pioneer River flow which therefore have been affected by changes to catchment runoff and potentially act as sources of eroded sediments following mangrove loss.

Historical Changes to the Pioneer River Estuary

On geological time scales, the Pioneer estuary is relatively young: thin Holocene deposits and well-developed estuaries to the south with no direct river input today suggest that the Pioneer River mouth moved to its current position within the past 3000 years (Gourlay & Hacker 1986). Once the Pioneer River settled in its present location, deposition from successive floods caused the shoreline to prograde into extensive tidal flats, with outer beach ridges formed by sands accumulating under the actions of the large tidal range and prevailing south-east trade winds. Mangroves colonised the sheltered areas behind the outer beach ridges, where later floods deposited fine muds and silts (Gourlay & Hacker 1986). At least 17 different mangroves species are present within the Pioneer Estuary, with communities dominated by *Avicennia marina*, *Rhizophora stylosa* and *Ceriops australis* (Duke et al. 2001). Although data are not sufficient

to reconstruct historic mangrove distributions, it is likely that they fluctuated steadily in response to natural drivers of change similar to those at work in present times (e.g. shifting protection from wave exposure, sea level fluctuations, climate variations).

Since the beginning of European settlement in the region (1862), both natural changes and hydrological modifications to the Pioneer estuary have influenced mangrove distributions (Table 1, Figure 1). For example, training wall construction (1887-1927) on the north bank of the Pioneer River stabilised and deepened the main Pioneer River channel, but also increased mangrove area in Bassett Basin by restricting its tidal circulation and accelerating sediment deposition on muddy banks (Gourlay & Hacker 1986). Major floods have also altered channel bank morphology through erosion and deposition: e.g. in 1898, the Pioneer River broke through East Point to create a new mouth.
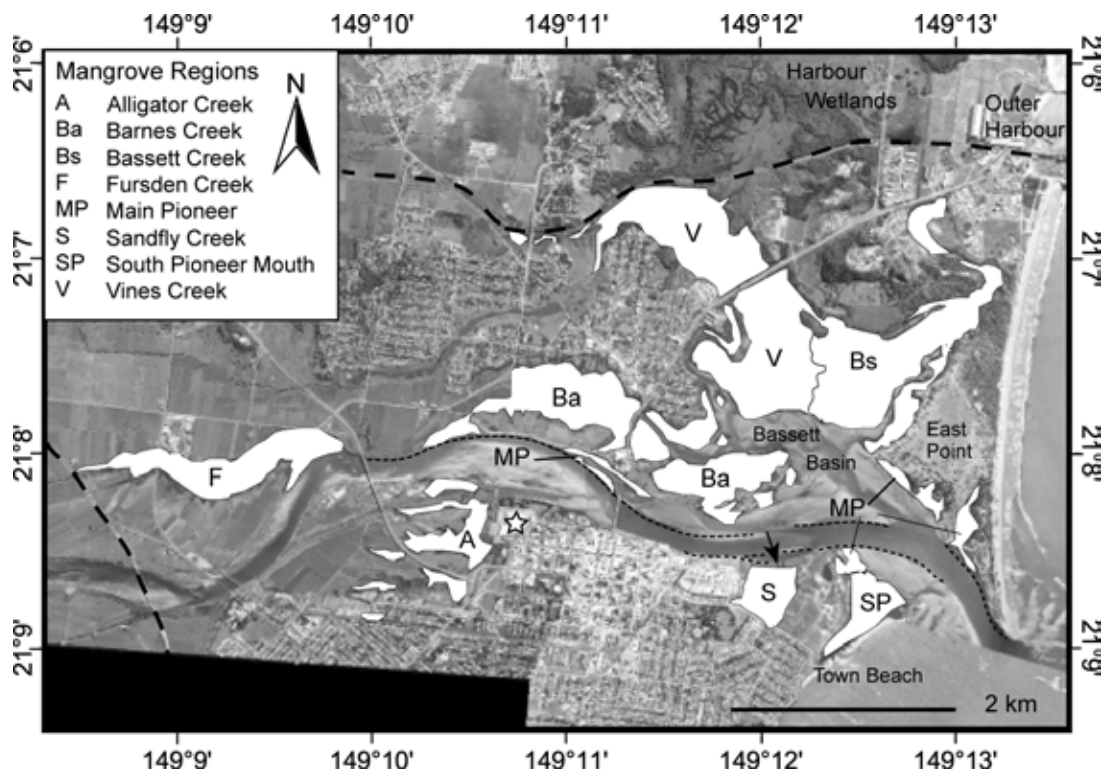

Figure 1. Mangrove sub-regions (white) within the Pioneer estuary. Major urban features include: railway (thick dashed line), Caneland Central Shopping Centre (star), tidal gates (arrow), and training walls (thin dashed line) along the north and south banks of the Pioneer River.

Table 1. History of modifications to the Pioneer estuary with potential or known impacts on mangrove distributions (1862-present).

Year	Modification to Pioneer Estuary	Effect on mangrove distribution
1862	City of Mackay established; harbor facilities begun along River Street (south bank of Pioneer)	Unknown[a]
1872-1885	Construction of (old) training wall along estuarine margin of East Point (to deepen and stabilize Pioneer River channel)	Silting of Bassett Basin with reduced tidal circulation and accelerated accretion[a]
1898	Catastrophic flood; sea broke through East Point creating new river mouth	Possible mangrove loss along inside of East Point[a]
1899	Old north wall raised and extended by 305 m	Increased silting in Bassett Basin[a]
1905	Construction of south wall and wall across entrance to Bassett Basin	Prevention of northward channel migration and mangrove colonization along south bank; decrease in size of Bassett Basin; deposition of sediments and mangrove colonization on Mangrove Island[a]
1920-1927	Construction of director wall downstream from Forgan Bridge to Bassett Basin (to deepen and stabilize Pioneer River channel)	Prevention of northward channel migration and mangrove colonization along north bank[a]
1958	Catastrophic flood	Mangroves cleared around Alligator Creek to reduce flood levels during next event[a]
from 1960	Construction of industrial zone near harbor facilities at northern end of Bassett Creek	Clearing of mangroves and isolation of remnant patches[b]
1978	Construction of Canelands Shopping Centre and southern approach to Ron Camm bridge	Substantial clearing of mangroves; large proportion of Alligator Creek infilled[a]
1978-1981	Construction of railway across northern end of Vines Creek	Isolation of remnant mangrove patches[b]
1986-1990	Proposed development in Sandfly Creek region	Clearing of mangroves in Sandfly Creek in preparation for development (which has not taken place)[c]
1993	Construction of culvert and levee across entrance to Sandfly Creek	Severe restriction of tidal flow entering Sandfly Creek[c]
1994	Construction of tidal gates at Sandfly Creek	Complete restriction of tidal flow until gates opened in 1996; substantial mangrove loss[c]

[a] Gourlay and Hacker (1986)
[b] Norman (1989)
[c] B. Discher, personal communication

Mangrove Change Since 1948

Changes to mangrove distributions within the Pioneer River estuary were mapped at approximately decadal intervals from black and white and colour aerial photographs borrowed from Queensland Department of Natural Resources and Water (QDNRW) and the Marine Botany Group at the University of Queensland. Specific mapping methods are described in detail in Jupiter (2006) and Jupiter et al. (2007). From 1948 to 2002, the total area of tidally-flushed mangroves[5] within the Pioneer estuary decreased by 22% from 634 to 497 ha, principally from such anthropogenic activities as clearing, filling and altering the natural hydrodynamic structure of the estuary (Figure 2). The total loss of tidal mangroves (274 ha) was partially offset by 137 ha of new growth. The proportions of mangrove changes attributed to clearing/natural loss, tidal isolation from hydrological manipulations and new growth are summarised in Table 2.
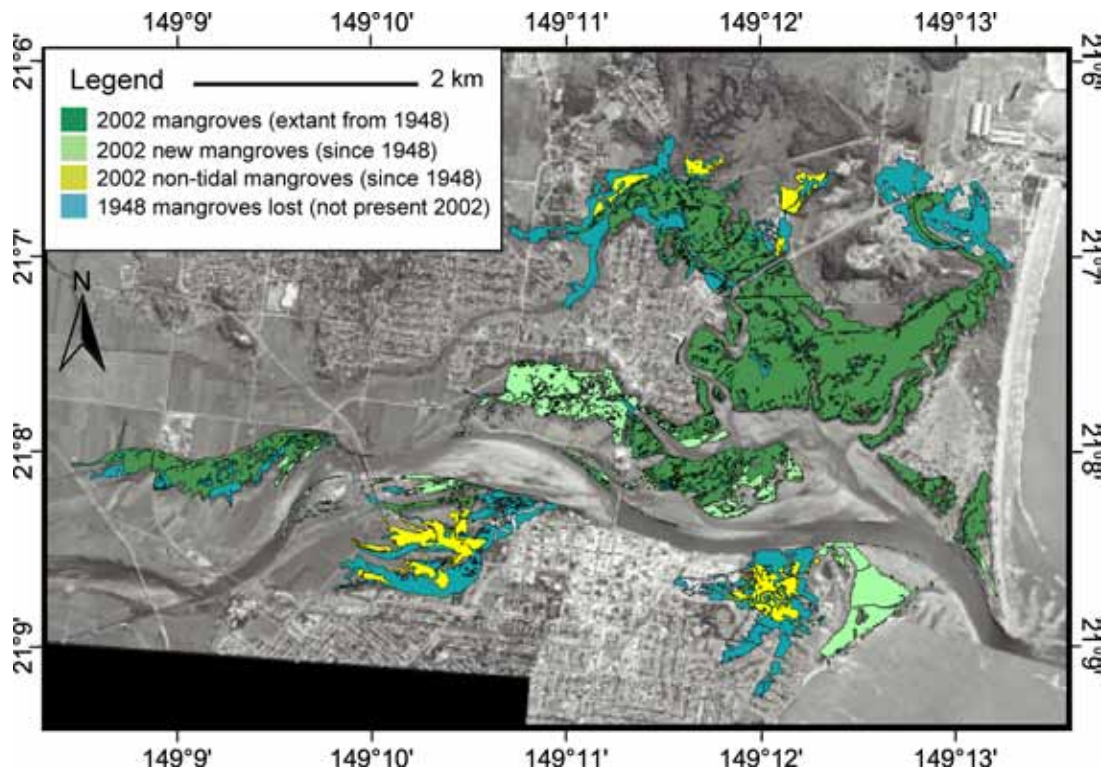

Figure 2. Net changes to mangrove distributions between 1948 and 2002.

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[5] Mangrove regions connected hydrologically to the Pioneer River and its tributaries were considered tidally-flushed, while regions cut off from the main tidal flow as a result of hydrological modifications to the estuary were categorized as non-tidal.

Table 2. Changes in mangrove areas (to nearest ha) in the Pioneer estuary digitised from aerial photographs between 1948 and 2002. Values for non-tidal, cleared or lost, and net change are reported relative to the previous time interval.

	TOTAL	CHANGE			
Year	Tidally flushed (ha)	Non-tidal (ha)	Cleared/Lost (ha)	New growth (ha)	Net Change (ha)
1948	634				
1962	625	0	66	57	-9
1972	658	5	25	63	+33
1982	567	35	66	10	-91
1991	522	3	44	2	-45
2002	497	10	20	5	-25
Net change	-137	-53	-221	+137	-137

Different, dominant processes can be ascribed to four distinct periods of change in the distributions of Pioneer Estuary mangroves in the past sixty years (Figure 3). During the first period (1948-1962), large-scale clearing in Alligator Creek (in response to an extreme flood in 1958) and Bassett Creek (for harbour expansion) was effectively matched by rapid mangrove expansion to yield little net change. Two mechanisms drove mangrove expansion during this period: wetter climate and newly deposited substrate on which to colonise. Natural rates of mangrove expansion and contraction are highly sensitive to climatic variation. For example, the proportion of mangroves relative to saltpans in unaltered estuaries can be reliably predicted from the mean annual rainfall alone (Bucher & Saenger 1994). Indeed, the rapid growth of mangroves during the 1950's in Barnes Creek corresponded with a period of increased rainfall that may have reduced salinity and facilitated colonisation (Gourlay & Hacker 1986) (Figure 3). Similarly, just as rainfall enabled mangrove colonisation onto previously uninhabitable substrate, new deposits of fine muds and silts along river bends following major floods facilitated rapid mangrove settlement of pioneer species onto previously unavailable substrate, particularly along the south bank of the Pioneer River mouth where mangroves expanded north-eastward from Town Beach. Although mangroves prograded rapidly, by 1991, net mangrove gain was reduced by losses from increased exposure to wave action as protective sand banks shifted to the north (Figure 4).
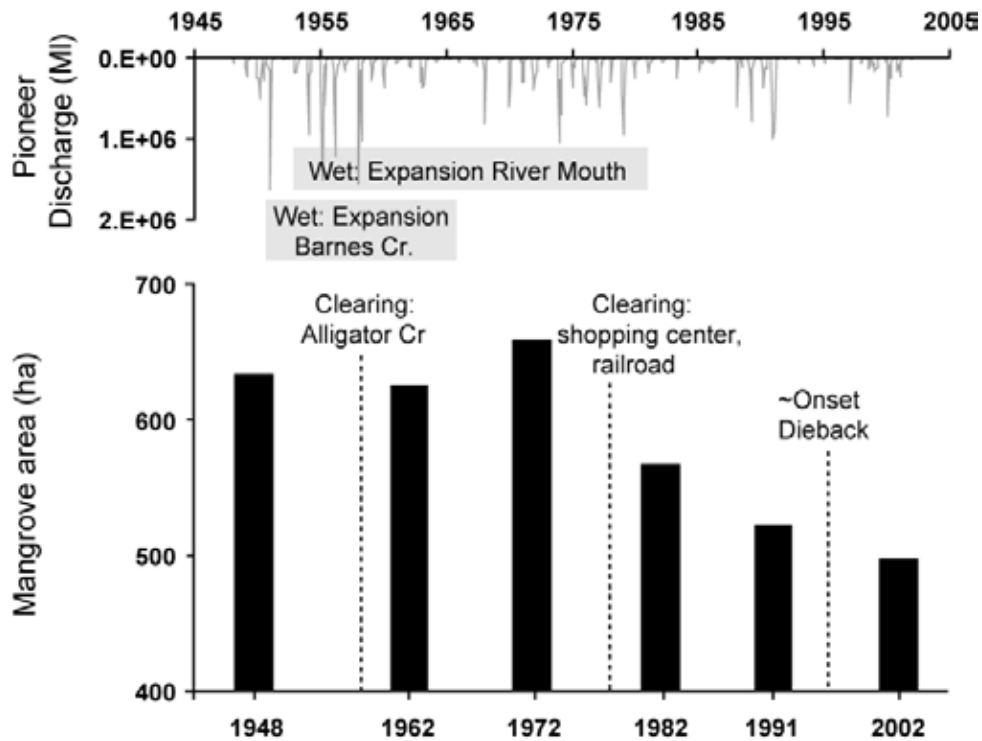
Figure 3. Time series of changes in Pioneer estuary mangrove area (black bars below) plotted with Pioneer River discharge (grey lines above). Dashed lines denote approximate timing of major mangrove losses. Horizontal grey bars cover periods of major mangrove expansion.

During the second period (1962-1972), mangrove expansion outpaced clearing activities. Even though there was less rainfall, mangroves expanded in Barnes Creek, where established trees probably provided shade and encouraged new growth by limiting evaporation (Gourlay & Hacker 1986). Additionally, mangroves colonised areas along newly deposited sediments, predominantly in Barnes Creek and at river bends (by Fursden Creek, the southwest bank of Bassett Basin, and the south bank near the Pioneer River mouth), where decreased velocity facilitated recent sediment deposition. Mangroves also recolonised some previously cleared areas, such as along Alligator Creek. While these new mangroves may have provided additional filtration of catchment runoff, the accelerated rate of mangrove expansion may itself be symptomatic of changes in upstream land use. Rapid mangrove expansion is indicative of a number of factors, including processes leading to increased sediment and nutrient concentrations in estuarine waters (Gourlay & Hacker 1986, Duke & Wolanski 2001); thus, the new growth in the Pioneer Estuary may be a response

to the estimated two to four-fold increase in sediment delivery to the estuary since initial land clearing (Hacker 1988).
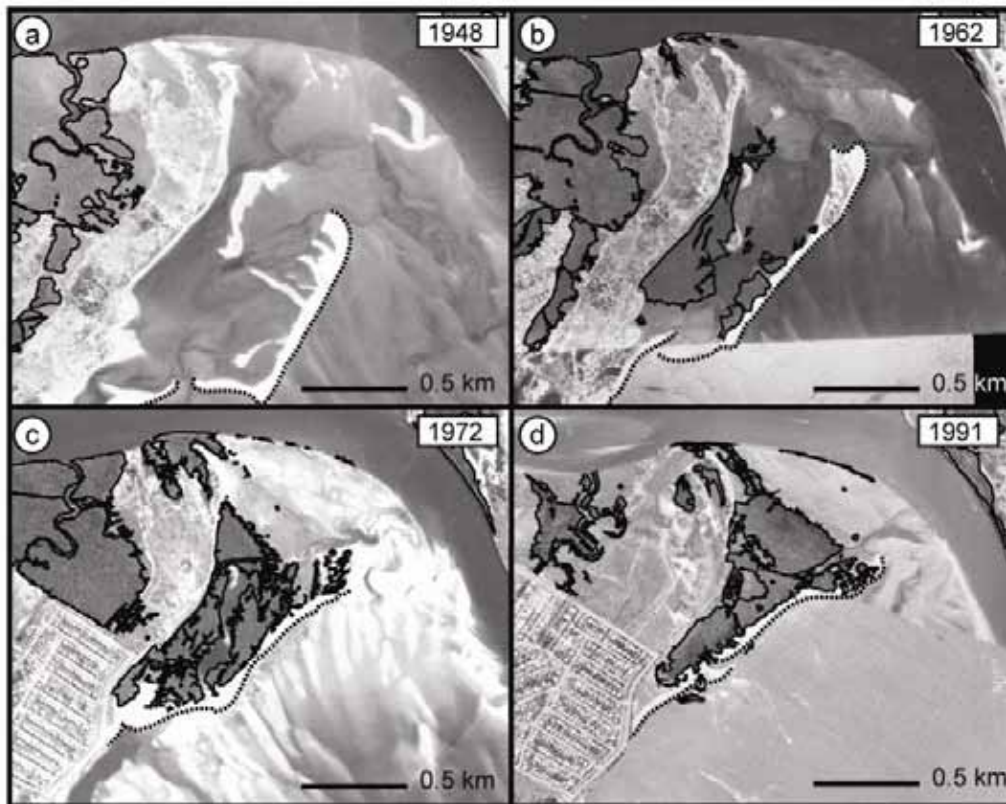
Figure 4. Northward shift of sand banks on the south bank of the Pioneer River mouth. (a) 1948. (b) 1962. (c) 1972. (d) 1991. Black dashed lines indicate eastern, exposed side of sand banks. Solid black lines delineate mangrove areas. Scale of photographs = 1:28,000.

Mangrove expansion decelerated through the third period (1972-1991), which was characterised instead by large-scale infilling of the estuary, preventing any future recovery of mangroves within these regions. There was little new expansion to replace losses from the major development activities of the 1970s and 1980s (e.g. railway, shopping centre, port expansion) that claimed 110 ha of mangroves and isolated another 38 ha from regular tidal flushing. This mangrove loss substantially reduced (by 21%) the mangrove area available to function as sediment and nutrient sinks and to provide refuge habitat for juvenile fish.

The fourth period of mangrove change (1991-2002) was dominated by the onset of the mangrove dieback. Local citizens first expressed concerns about mangrove dieback in the Pioneer estuary in the early 1990s when dieback became obvious (N. Whitehead, personal communication). The dieback

predominantly affected the grey mangrove, *Avicennia marina*, known for its broad latitudinal and salinity tolerances and high resilience to physical damage (Tomlinson 1986). As of 2002, moderate to severe dieback of *A. marina* affected 58% of mangrove area in the region, including the Pioneer estuary (Duke et al. 2005). While Duke et al. (2005) suggest that *A. marina* dieback was correlated with elevated herbicide concentrations in mangrove sediments and core waters, additional testing is warranted to confirm these preliminary data. However, in support of this idea, no dieback was observed in Sandfly Creek, where tidal gates built in 1993-94 remain closed during flood events and therefore prevent delivery of agrichemicals contained in pulses of catchment runoff.

Although the proportion of mangroves lost during this period is less than in 1972-1991, the consequences of dieback may be magnified in severity by the location of large *Avicennia marina* trees mainly along creek margins and tidal banks: within large gaps, previously deposited sediments are remobilised and actively eroded. Exposed cable roots of *A. marina* trees suggest that sediments eroded following decomposition of live fibrous roots (Figure 5), which may lose 30-52% of original mass after 154 days following death (Albright 1976). There is clear visual evidence of bank destabilisation in regions of severe dieback and sediment loss associated with uprooted trees (Figure 5), but the fate of this material and its contribution to nearshore water quality has not yet been quantified.

Mangrove Change in the GBR Catchment

Over the past 60 years, there have been no consistent trends in mangrove distribution change across catchments of the Great Barrier Reef (GBR) lagoon. In the Johnstone River estuary, net mangrove area increased by 14.8% between 1951 and 1992 (Russell & Hales 1994), yet as in the Pioneer, the new mangrove area is likely an indicator of rapid sedimentation at the river mouth from increased catchment erosion (Duke & Wolanski 2001). In other GBR estuaries, such as the Trinity Inlet surrounding the city of Cairns (19.5% loss between 1952 and 1998, Wolanski & Duke 2002) and Port Curtis surrounding the industrial city of Gladstone (30.4% loss between 1941 and 1989, QDEH 1994), mangrove losses are common from urbanisation and industry expansion.
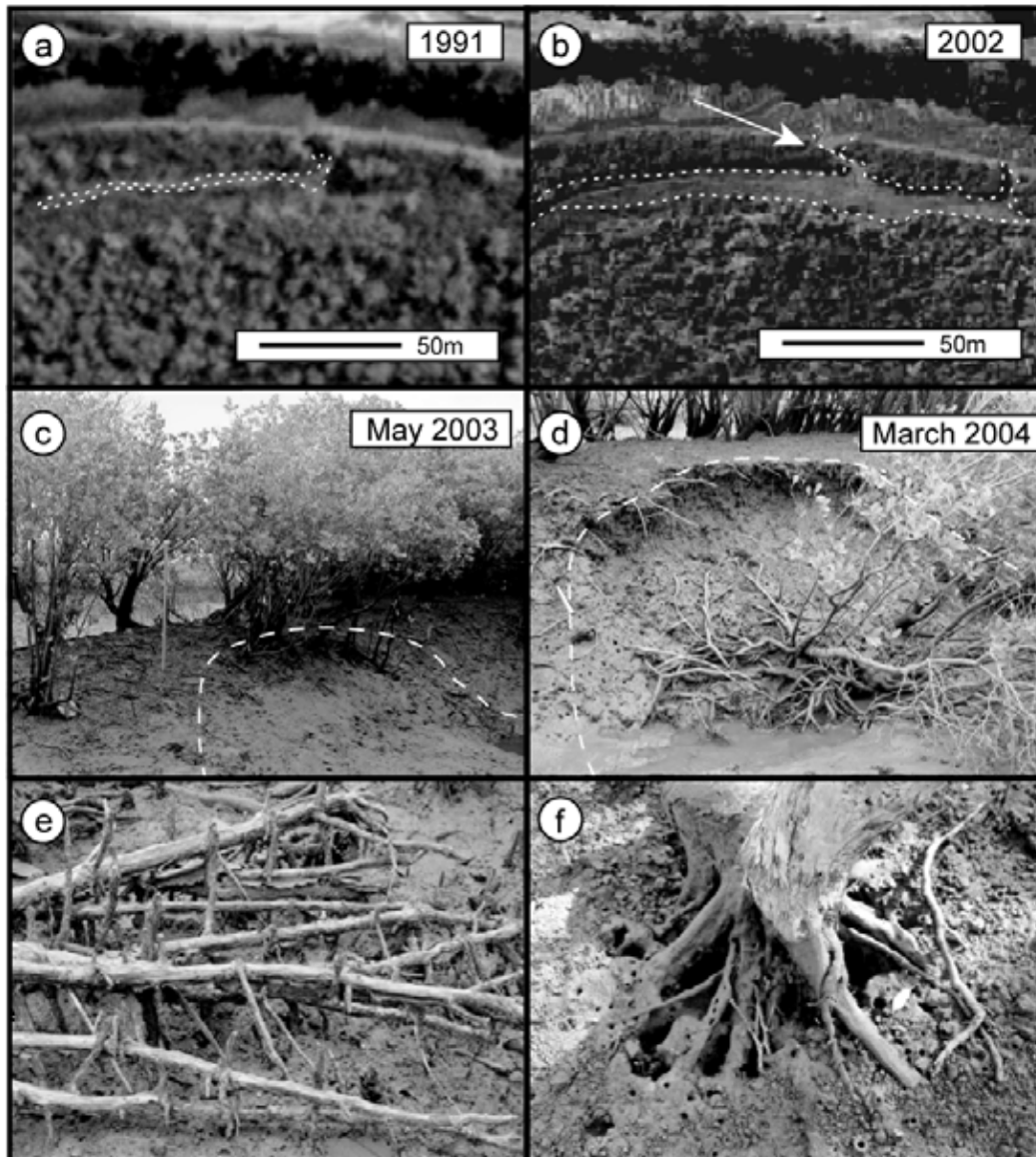
Figure 5. Sediment remobilisation in dieback regions. (a) Pre-dieback aerial photograph (1991) of mangrove distribution in Fursden Creek along exposed tidal drainage channel (0.0035 ha; dashed outline). (b) Post-dieback aerial photograph (2002) of mangrove distribution in Fursden Creek with large gap along same drainage channel (0.32 ha; dashed outline). Arrow points to location of photographs in c-d. (c) Erosion monitoring site across tidal creek gully in May 2003. Dashed line outlines region of slumping in d. (d) Same bank after slumping event, March 2004. (e) Exposed cable roots of dead *Avicennia marina* near drainage channel along the north bank of the Pioneer River, photographed 9 May 2003. (f) Exposed cable roots of dead *A. marina* in severe dieback region within Barnes Creek, photographed 14 July 2004.

The consequences of mangrove loss on nearshore water quality are likely to vary substantially among catchments of the GBR lagoon. While mangroves can be very efficient in trapping sediment and associated nutrients (e.g. in the Hinchinbrook Channel, mangroves accumulate mud at rates of ~1000 t km^{-2} yr^{-1}, Wolanski et al. 1998b), estuarine sediment retention is ultimately determined by

multiple factors, including catchment soil erosion rate, estuarine geomorphology, residence time, grain size and biological activity. As a result, while some estuaries (e.g. Fly River estuary, Papua New Guinea, Wolanski et al. 1998a) trap nearly all sediment delivered to the coast, others export the majority of riverine sediment to the sea (e.g. Mekong River estuary, Vietnam, Wolanski et al. 1996). In yet other systems (e.g. Fitzroy Estuary, Western Australia, Wolanski & Spagnol 2003), flood-deposited sediments may be resuspended by wind waves and strong tidal currents and transported back into the estuary. With a large tidal range, fast currents and high winds present throughout the year, it is likely that much of the sediment delivered by the Pioneer River to the nearshore is redeposited within Bassett Basin and its associated creek network. However, as the Pioneer has high freshwater outflow during flood pulses (Hacker 1988), the associated nutrients (both dissolved and particulate) in catchment runoff are likely to be utilised immediately in the N-limited coastal zone to support phytoplankton communities (Furnas et al. 2005)

While it is still unclear whether the loss of mangroves in the Pioneer estuary affects the water quality of downstream coastal waters, the estuary itself has been altered by changes in catchment runoff. Flood delivery of catchment sediments since European land clearing caused the river bar (mapped as the -3 m contour) to prograde by 600 m between 1887 and 1979 and has led to the development of a large sand island (Cullen Island) within the estuarine reaches of the lower Pioneer (Hacker 1988). Additionally, the recent dieback of a substantial proportion of mangroves was a direct downstream effect of upper catchment land care practices, whether caused by a chemical agent or the less likely hypothesis of sediment burial. Meanwhile, this loss of mangrove area has consequences for the Mackay fishing industry: Manson et al. (2005) demonstrated that mangrove area and perimeter in Queensland were the dominant factors explaining catch-per-unit-effort of commercially important species (e.g. banana prawns, mud crabs, and barramundi) that use mangroves as juvenile habitat.

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Coral communities on the southern reef flat of Derwent Island. Photographed 8 March 2006.

Coral Reef Communities of the Mackay Great Barrier Reef Region

Introduction

Coral assemblages vary naturally in community structure along gradients of differing scales, relating to depth, reef habitat, distance along shelf, latitude, and biogeographic province (Huston 1985, Veron 1995, Bellwood and Hughes 2001, Harriott and Banks 2002, DeVantier et al. 2006). As disturbance frequency and intensity are important drivers of diversity within communities, there is growing concern that rapid rates of anthropogenic change are increasing rates of disturbance that lead to unfavourable shifts in coral communities (Jackson et al., 2001; Pandolfi et al., 2003).

Field studies from recent decades suggest that coral assemblages from sites within proximity to land are shifting in response to both local and diffuse

sources of terrestrial pollution (Smith et al. 1981, Cortes and Risk 1985, Lapointe 1997, van Woesik et al. 1999, Fabricius et al. 2005). Along natural and anthropogenically enhanced water quality gradients, scleractinian corals living closest to terrestrial and fluvial sources are generally characterised by: (1) high rates of partial mortality; (2) low rates of recruitment; (3) reduced skeletal density; and (4) reduced depth distributions (van Woesik 1992, Kleypas 1996, van Woesik et al. 1999, Nugues and Roberts 2003, Fabricius 2005, Fabricius et al. 2005, Restrepo et al. 2006). These changes in coral communities are often associated with: increased algal cover (van Woesik et al., 1999; Fabricius et al., 2005); increased abundance and rates of bioerosion by macroborers (Sammarco and Risk, 1990; Risk et al., 1995; Tribollet and Golubic, 2005); and reduced octocoral abundance and diversity, particularly from zoothanthellate clades (Fabricius et al., 2005; Fabricius and McCorry, 2006).

As a starting point to determine whether coral communities living at Mackay region reefs are influenced by episodic disturbance from large flooding events, we surveyed reef locations at a gradient of distance from the Pioneer River mouth in March 2006 (Figure 1). This chapter reports on the initial findings from those surveys.

Line Intercept Surveys

As a rapid assessment of benthic communities across all sites, a line intercept method (Loya 1972) was used to characterise benthic cover every 0.5 cm along 20 m into six categories: live hard coral, soft coral, macroalgae, turf and crustose coralline algae, substratum (e.g. rubble, consolidated pavement, sand) and other (dominated by the giant clam, *Tridacna gigas*, and encrusting sponges, with minor contributions from large molluscs (e.g. *Trochus* sp.), hydroids, anemones and ascidians, particularly at the outer reefs). Forty-four transects were conducted in shallow depths (1-7 m) parallel to the reef flat at 7 locations (Round Top Island, Keswick Island, Scawfell Island, Derwent Island, Little Kindemar Reef, Big Kindemar Reef), with a minimum of 4 transects per site.

We observed high cross-shelf variability in live hard coral cover, though in general, current benthic habitat composition in the Mackay region reflects expected inshore to offshore trends (Table 1). The sites closest to the mainland (Round Top, Keswick and St. Bees islands) were all characterised by low live
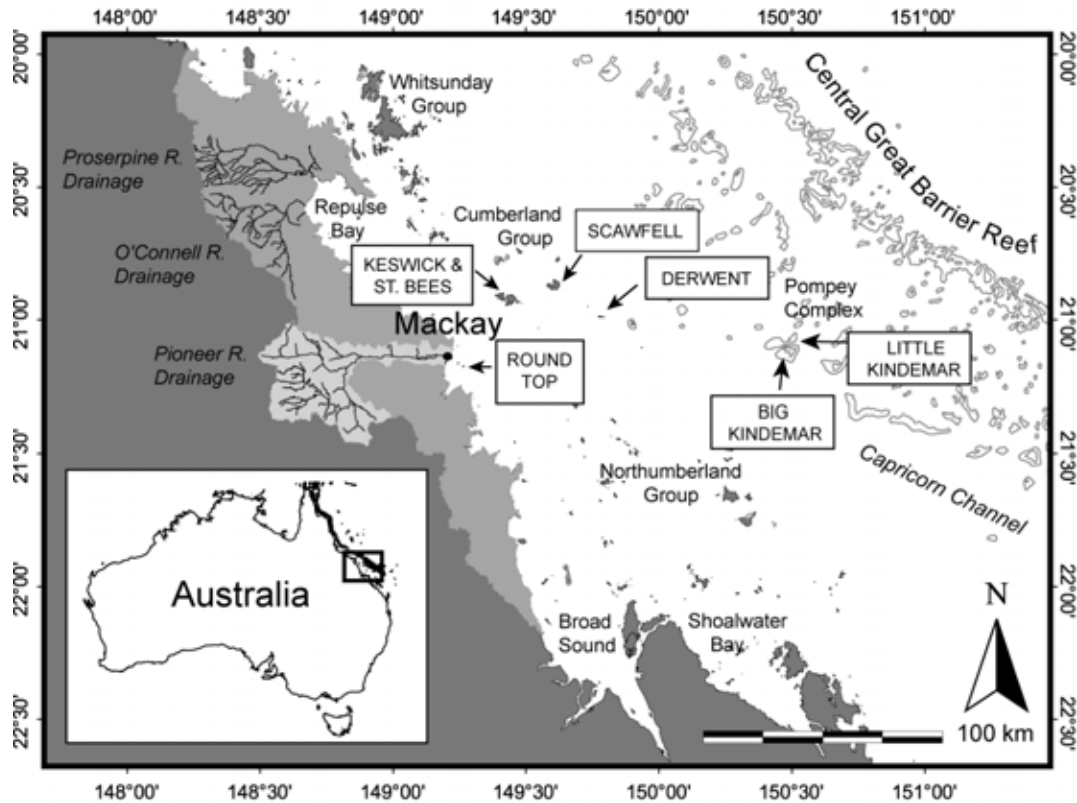
Figure 1. Reef habitat survey locations (boxes) in the Mackay section of the Great Barrier Reef along a gradient of distance from the Pioneer River mouth.

coral cover: percent cover at the inner-most site (Round Top Island: 8.2 ± 3.7%) was slightly higher than at Keswick Island, though the differences in coral cover among all three sites are not significant (single factor ANOVA, arcsine square-root transformed, p = 0.33). At Refuge Bay on Scawfell Island, mean live coral cover (22.4 ± 3.3%) was within range of cover (27%) observed by van Woesik and Done (1997) on both Scawfell and Cockermouth island reefs. Percent cover peaked at Derwent Island (34.8 ± 6.9%, 61 km from river mouth), and dropped slightly, but not significantly, at the outermost sites (Little Kindemar: 31.7 ± 4.0%; Big Kindemar: 27.9 ± 3.3%; single factor ANOVA, arcsine square-root transformed, p = 0.77), located ~130 km from the Pioneer mouth and ~70 km (perpendicular distance) from the outer shelf edge of the Pompey Complex. The range of values measured from our three outermost sites is within range of live hard coral cover observed by the Australian Institute of Marine Science' long-term monitoring surveys of offshore reefs in the Pompey Sector (Sweatman et al. 2005). Coral cover in this region may be reduced by high energy waves

propagating through the Capricorn Channel, as evidenced by the highly detrital framework of cored outer reefs on the Pompey Complex (Kleypas & Hopley 1992).

While trends in live coral cover were not unexpected, reef structure and composition varied substantially between sites. Sand and consolidated pavement were the dominant benthic cover types at Round Top Island (60.9 ± 6.9%), with sparse, small colonies settled on rock or rubble covered in turf algae and thick sediment (Figure 2a) and little macroalgae (2.4 ± 1.2%). At Keswick and St. Bees Islands, however, macroalgae, particularly *Sargassum* spp. and *Podina* spp., dominated the assemblage (69.5 ± 3.0% and 63.0 ± 3.6%, respectively), growing attached to sand and dead reef framework (Figure 2b). Very little macroalgae was observed at Scawfell in Refuge Bay, with shallow, often turbid reefs dominated by soft corals (35.1 ± 6.4%; Figure 2c) fringing the embayment on the northwestern portion of the island. Low macroalgal cover was also recorded from the south side of Derwent Island, along the outer edge of a well-developed reef flat bound together with high abundance of crustose coralline algae and dropping steeply to rubble and pavement at ~10 m (Figure 2d). The eastern, more exposed side of the reef flat had high occurrences of a boring sponge, *Cliona* sp. (Figure 2e). The outermost sites, both broad reef platforms stretching between 9 to 13.5 km, had low abundance of macroalgae (Little Kindemar: 0.1 ± 0.1%; Big Kindemar: 0.6 ± 0.4%) but higher cover of soft coral (Little Kindemar: 8.6 ± 2.3%; Big Kindemar: 11.9 ± 2.4%; Figure 2f), such that the totals of live hard coral and soft coral were very similar to that observed at Derwent Island. These differences in community structure will be discussed in more detail below.

Table 1. Results of line intercept surveys of benthic cover for six categories: live hard coral, soft coral, macroalgae, turf algae and crustose coralline algae (CCA), substratum (sand, rubble, consolidated pavement), and other. Values are reported as mean percent cover ± 1 standard error.

Site	Live Hard Coral	Soft Coral	Macroalgae	Turf + CCA	Substratum	Other
Round Top Island	8.2 ± 3.7	2.1 ± 0.7	2.4 ± 1.2	26.3 ± 4.4	60.9 ± 6.9	0.1 ± 0.1
Keswick Island	5.0 ± 2.1	1.6 ± 1.1	69.5 ± 3.0	2.7 ± 1.5	20.8 ± 2.8	0.5 ± 0.5
St. Bees Island	10.1 ± 2.9	0.3 ± 0.3	63.0 ± 3.6	14.0 ± 2.7	12.4 ± 3.4	0.1 ± 0.1
Scawfell Island	22.4 ± 3.3	35.1 ± 6.4	0.3 ± 0.3	40.8 ± 3.8	0.8 ± 0.6	0.8 ± 0.6
Derwent Island	34.8 ± 6.9	1.1 ± 0.5	1.3 ± 1.0	50.0 ± 2.9	1.5 ± 0.8	11.3 ± 4.4
Little Kindemar Reef	31.7 ± 4.1	8.6 ± 2.3	0.1 ± 0.1	43.5 ± 6.6	14.9 ± 4.2	1.2 ± 0.5
Big Kindemar Reef	27.9 ± 3.3	11.9 ± 2.4	0.6 ± 0.4	50.6 ± 3.7	7.8 ± 3.3	1.2 ± 0.5
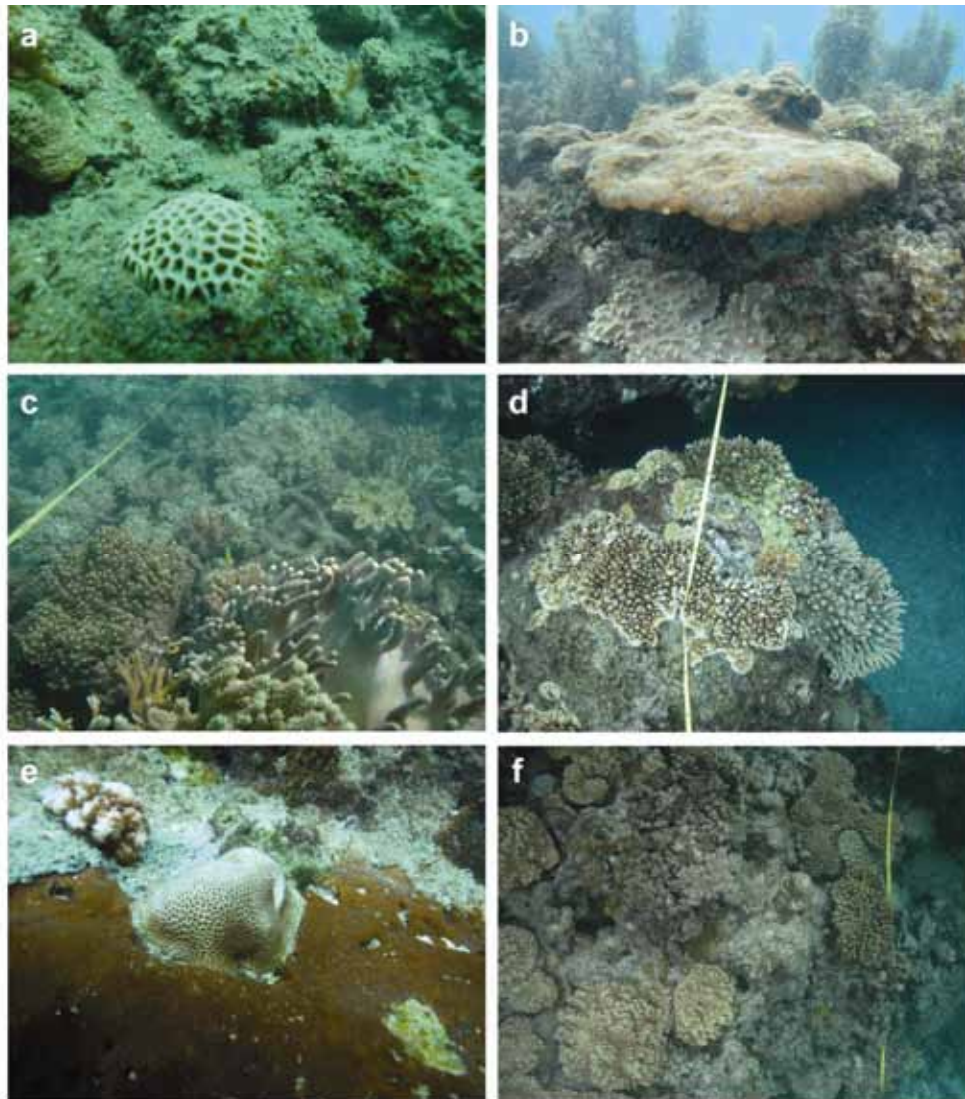
Figure 2. Photographs representative of transect conditions. (a) Small coral colony settled on rock covered in sediment and turf algae at Round Top Island. (b) Hard and soft corals surrounded by large *Sargassum* sp. stands at Keswick Island. (c) Soft coral assemblage in Refuge Bay, Scawfell Island. (d) Coral colonies at the edge of the reef flat surrounded by crustose coralline algae on the south fringing reef of Derwent Island. (e) Bio-eroding sponge (orange) surrounding small coral colonies on the southeast reef flat of Derwent Island. (f) Diverse hard and soft coral community at Little Kindemar Reef. All photographs taken between 6-12 March 2006.

Community Structure Analysis

In addition to the line intercept surveys, a total of 20 transects were surveyed for comprehensive analysis of coral assemblages and benthic cover across all of the locations except Round Top Island, where high turbidity prevented adequate resolution of photographs. From each location, photographs taken at 2 m intervals over 0.5 m quadrats along a 50 m measuring tape were

analysed by the CPCe random point count method (Kohler & Gill 2006) using 50 points per quadrat. Community structure was categorised by quantifying total cover of hard coral, halimeda, macroalgae, soft coral, bio-eroding sponge, substratum (including intact dead coral, coral rubble, reef matrix, and sand) and other. To determine the variability in coral assemblages, coral cover was further categorised into dominant families (Acroporidae, Pocilloporidae, Poritidae, Faviidae and Other), and variability in morphology of Acroporidae was separated into growth forms (arborescent, caespitose, cuniform, digitate, tabular, plating and encrusting). Mean percent cover of each category analysed through CPCe is presented in Table 2. In addition, the same transects were surveyed for incidence of coral disease and degree of coral bleaching gauged by scoring against CoralWatch colour charts. No disease was found and levels of bleaching overall were modest, with relatively no occurrences at the three most inshore sites and the highest mean occurrence (2.13 ± 1.7%, Table 2) at Derwent Island.

Table 2. Results of mean percent cover (or occurrence) ± 1 standard error (SE) of: coral morphology and family, reef community structure, and bleaching and disease.

		Keswick 33km		St Bees 35km		Scawfell 50km		Derwent 61km		Little Kindemar 125km		Big Kindemar 135km	
		Av.	±SE	Av.	±SE	Av.	±SE	Av.	±SE	Av.	±SE	Av.	±SE
Coral Composition	Acroporidae	2.82	0.4	9.20	0.7	14.41	1.2	16.54	0.9	12.82	0.7	19.07	1.8
	Arborescent	2.05	2.0	3.24	1.4	4.31	2.2	0.41	0.3	1.72	0.9	2.36	2.0
	Caespitose	-	-	1.41	0.7	2.46	1.7	0.42	0.2	3.83	0.7	4.45	2.1
	Cuniform	-	-	0.54	0.3	0.66	0.4	2.09	0.1	1.44	0.8	4.15	3.8
	Digitate	-	-	1.02	0.8	3.37	2.1	11.00	5.1	1.26	0.4	3.18	2.5
	Tabular	-	-	0.45	0.3	-	-	1.20	0.7	0.10	0.1	0.52	0.5
	Plating	0.64	0.6	2.16	1.8	1.53	1.4	0.13	0.1	1.11	0.6	1.75	1.7
	Encrusting	0.14	0.1	0.36	0.2	2.09	2.0	0.31	0.2	1.45	0.9	0.92	0.4
	Other	-	-	-	-	-	-	1.20	0.7	0.10	0.1	0.52	0.5
	Pocilloporiidae	0.00	0.0	0.00	0.0	0.69	0.2	0.84	0.4	1.88	0.4	2.78	1.0
	Faviidae	0.00	0.0	0.00	0.0	0.34	0.3	5.20	1.0	0.87	0.2	0.65	0.6
	Poritidae	0.00	0.0	0.18	0.2	0.66	0.5	0.13	0.1	1.32	0.8	0.75	0.7
	Other Coral	0.42	0.4	0.72	0.2	1.59	0.7	0.53	0.2	7.56	2.4	5.68	0.9
Community Structure	Total Coral	3.25	3.2	10.10	2.7	17.68	3.0	23.25	6.6	24.44	2.2	28.92	2.1
	Halimeda	0.07	0.1	0.09	0.1	0.05	0.0	0.00	0.0	3.35	2.6	8.71	8.4
	Macroalgae	80.12	7.2	62.68	7.1	0.27	0.2	0.00	0.0	0.22	0.2	0.00	0.0
	Soft Coral	0.14	0.1	0.04	0.0	31.32	4.6	10.55	3.8	8.75	3.0	8.76	4.0
	Bioeroding Sponge	1.03	0.1	0.95	0.5	0.24	0.2	9.70	6.2	0.57	0.1	-	-
	Other	-	-	0.05	0.0	0.04	0.0	0.37	0.1	0.89	0.1	0.52	0.5
	Substrate	15.38	3.7	26.08	7.1	50.40	3.9	56.14	3.6	61.78	6.0	53.09	14.0
	Dead Coral Intact	2.12	0.5	-	-	14.77	3.5	1.72	0.2	4.47	0.8	1.64	0.2
	Coral Rubble	1.06	1.1	3.78	3.8	0.92	0.9	0.30	0.3	3.69	1.9	2.19	1.9
	Reef Matrix	8.84	2.2	13.78	1.0	34.32	3.2	52.93	3.6	47.47	6.1	46.52	11.9
	Sand	3.37	2.7	8.53	4.1	0.39	0.4	1.19	0.3	6.16	2.7	2.74	0.4
Health	Coral bleaching	0.00	0.0	0.18	0.2	1.74	1.2	2.13	1.7	1.28	0.4	1.67	0.6
	Coral disease	-	-	-	-	-	-	-	-	-	-	-	-

Corals from the family Acroporidae dominated at all sites, even with varying coral cover across locations (Figure 3a,b). At low-richness reef sites, acroporid corals are often underrepresented compared with favids, which suggests that they are less resilient in marginal settings, such as turbid nearshore environments (Bellwood & Hughes 2001). Yet, as acroporid corals are fast growing, they may often dominate coral assemblages following extreme disturbances (Done et al. 1991): for example, after severe coral mortality from crown-of-thorns (*Acanthaster planci*) outbreaks in the central GBR during 1982-83 at Rib and John Brewer reefs, the majority of larval recruits observed were *Acropora* spp. (Done 1988). Yet taxonomic identification of corals to family level
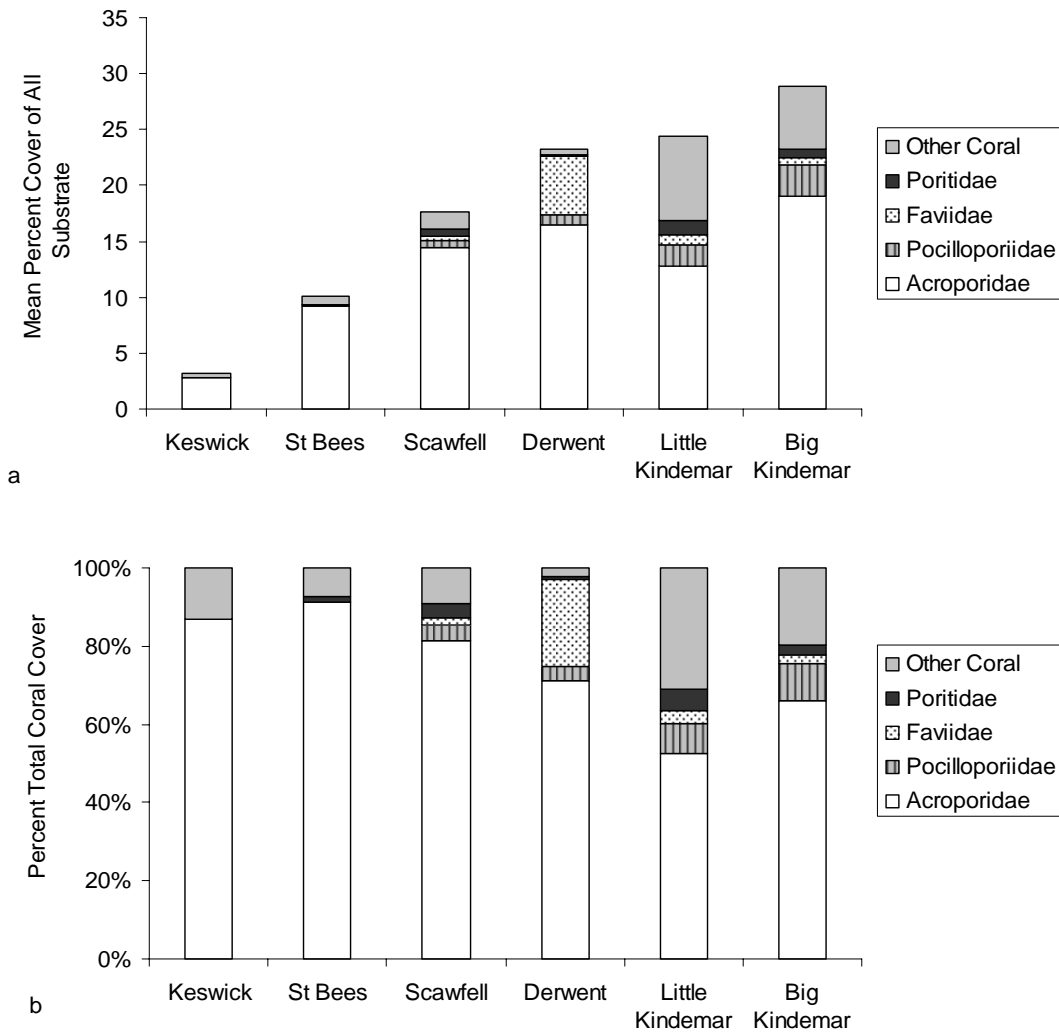

Figure 3. (a) Mean percent coral cover (of total substrate analysed) at each site (total), broken down by proportion occupied by each family. (b) Percent of total coral cover occupied by each family group. (Acroporidae: white; Pocilloporidae: grey striped; Faviidae: polka dot; Poritidae: black; Other coral: grey)

alone is unlikely to yield detectable differences in community assemblages related to terrestrial disturbance gradients as a large majority of taxa can live in highly turbid nearshore waters: Devantier et al. (2006) recorded just 4 of 362 species from the entire GBR province that were restricted in their distributions to mid- or outer-shelf reefs, while 18% of species were only recorded 1-3 times in the 599 sites surveyed. The authors concluded that disturbance along the GBR leads to local removal of species rather than a shift to separate suite of taxonomic groups, but this was only resolved by identification to the species level. Therefore, the high proportion of *Acropora* spp. at Keswick and St. Bees may give little indication of the overall disturbance regime without reference to other data on community assemblage and exposure to terrestrial pollution.

In order to determine which sites were most distinct and most similar to assess whether the most inshore sites (Keswick and St. Bees islands) were likely
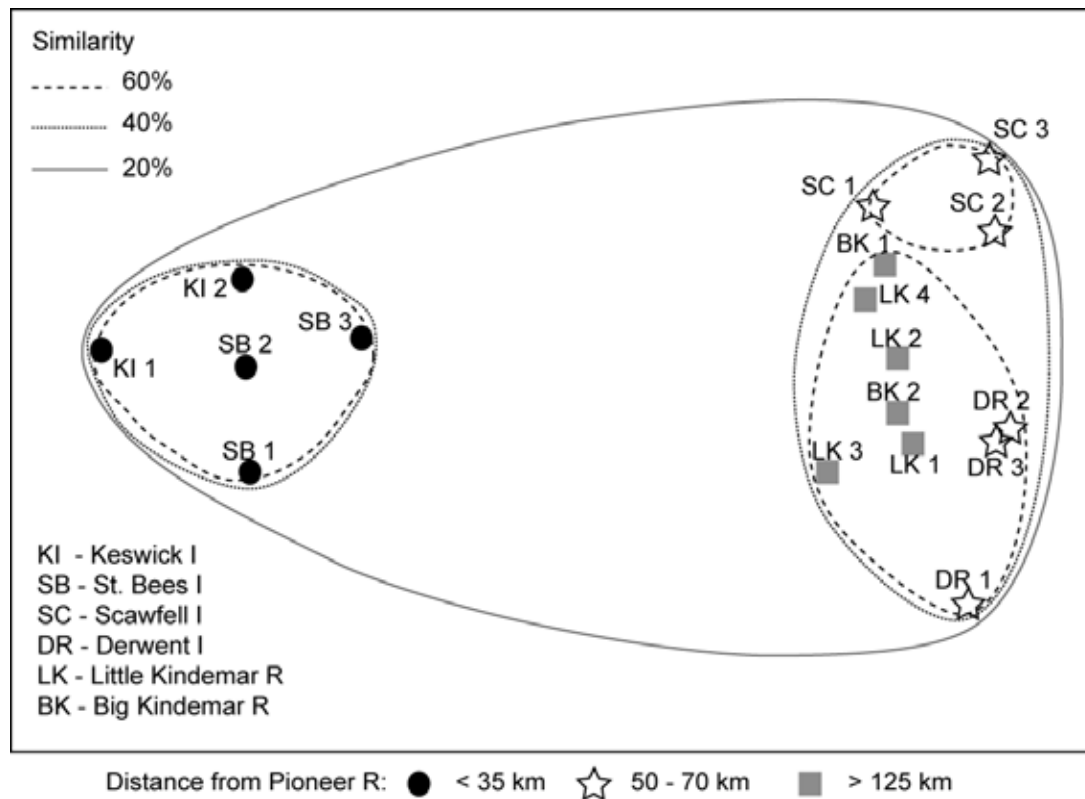

Figure 4. Multidimensional scaling plot of coral community data from Keswick Island (KI), St. Bees Island (SB), Scawfell Island (SC), Derwent Island (DR), Little Kindemar Reef (LK) and Big Kindemar Reef (BK). Circles around clusters of transect data represent % similarity between sites.

to be recovering from flood-related disturbance, community structure data (including coral families and growth form) were square-root transformed and similarities were calculated using the Bray-Curtis similarity measure (Bray & Curtis 1957). Multidimensional scaling (MDS) was used to display ordination between sites and transects (Clarke & Warwick 2001), and hierarchical cluster analysis was performed to detect groupings between sites at 20, 40 and 60% similarity levels. SIMPER (SIMilarities PERcentages) analysis was used to determine which community structure categories contributed most to similarities between transects at each location and to dissimilarities between reef sites (Harriott & Banks 2002).
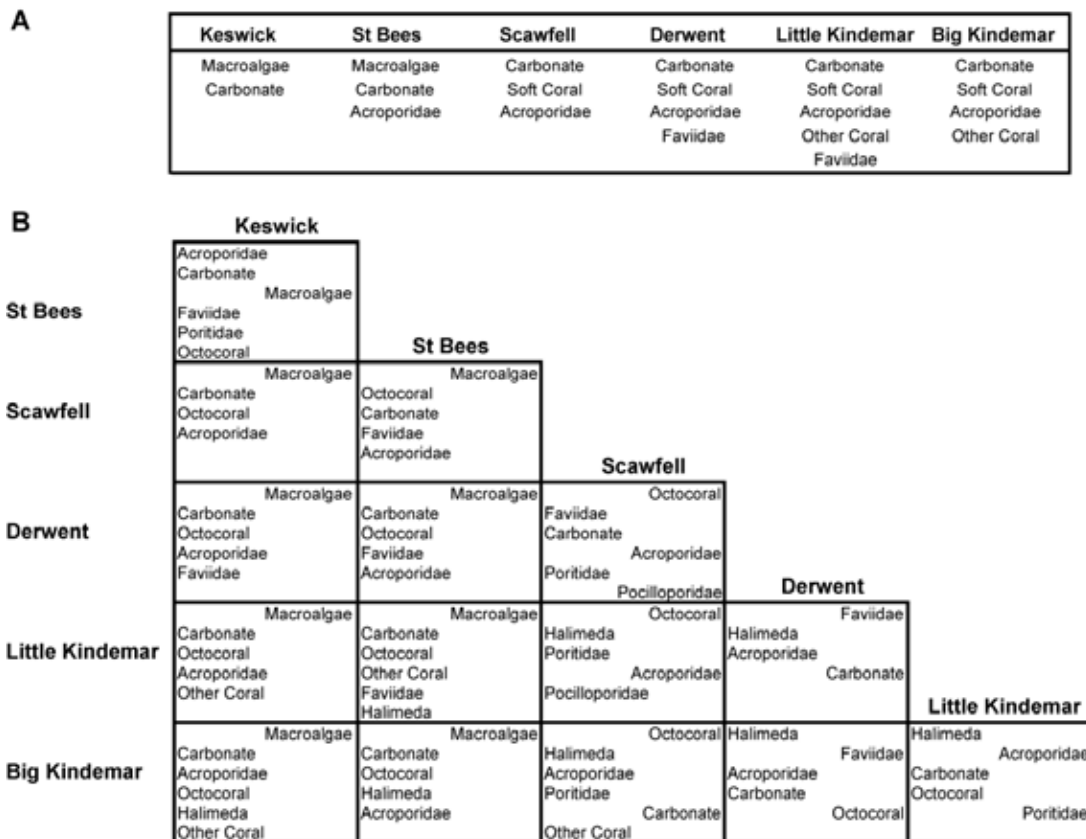
Figure 5. Results of SIMPER analysis showing benthic cover classes that contributed most strongly to (a) similarity between transects at each survey site and (b) differences between site groupings in the MDS analysis. Benthic cover classes are listed in order of their contribution to similarities between transects within sites and dissimilarities between sites.

The most notable results from the MDS analysis are that the community assemblages at Keswick and St. Bees are categorically different from the other

sites (Figure 4), and that this difference results from the overwhelming dominance of macroalgae (Figure 5). The significance of macroalgal dominance on nearshore GBR reefs is still debated (DeVantier et al. 1998). High percent cover of large macroalgae, particularly *Sargassum* spp., is often regarded as a sign of degradation from eutrophication (Bell & Elmetri 1995). For example, freshwater inundation from major flooding events can cause mass mortality on shallow reefs, and as a consequence, there may be overgrowth by fleshy macroalgae as the initial successional stage (DeVantier et al. 1998, McClanahan et al. 2001). Alternatively, the macroalgae may be a normal seasonal component of the community, which often is associated with fast-growing coral genera such as *Acropora* and *Montipora* whose rapid radial expansion (> 10 cm/yr) enable the colonies to overgrow algal holdfasts during periods of low biomass (Done 1982, DeVantier et al. 1998, 2006).

Multiple Lines of Evidence to Assess Reef Community Shifts

Several approaches have been used in previous field studies to assess whether present-day coral communities dominated by macroalgae and low hard coral cover represent an ecological shift in response to changes in water quality. Along the GBR, a study comparing community characteristics from the reefs adjacent to the highly agricultural Wet Tropics catchments (16^0 to 18^0 S) and the relatively unmodified Princess Charlotte Bay catchments (14^0 S) found three major response variables (macroalgal cover, octocoral richness, and abundance of sensitive hard coral species) that were significantly correlated with a water quality index constructed from present-day water quality parameters sampled from each location (Fabricius et al. 2005). While the study shows a strong link between current ecological community structure and recent water quality, due to a lack of historical data, there is only inference that water quality was degraded at some sites from prior conditions. A different approach is to determine if there is a mismatch between present reef-building capacity and Holocene reef framework that increases along a gradient of declining distance from a river source (van Woesik and Done 1997; DeVantier et al. 1998; van Woesik et al. 1999). van Woesik et al. (1999) suggested that the limited modern reef-building at Calf and Pine islands in the Whitsunday Group was associated with recent increases in suspended particulate matter and nutrients delivered to Repulse Bay by the

Proserpine and O'Connell rivers. However, this technique does not distinguish between effects of terrestrial runoff and other possible effects suggested by Smithers et al. (2006), such as: reduced flushing from Repulse Bay following closure of the Holocene high energy window, when outer barrier reefs caught up with sea level (Hopley 1984); and changes to SSTs and aragonite saturation state associated with global warming that may have increased disturbance from bleaching and decreased calcification rates (Hoegh-Guldberg 1999; Kleypas et al. 1999).

In the present study, we can use our coral core records to evaluate likelihood of exposure at Keswick and St. Bees Islands to historical flood events of large magnitude with high terrestrial nutrient and sediment loads. Coral δ^{15}N data from a Keswick Island core (KIC) indicate that the colony was exposed to highly enriched land-derived nitrogen from extreme flood events in 1974 and in 1991, following Cyclone Joy (Chapter 5). The 1974 and 1991 floods were the highest magnitude discharge events from the Pioneer River between 1968 and 2004, and the peak δ^{15}N values (12.24‰ and 13.62‰ for 1974 and 1991, respectively) coincided with intense luminescence banding in the core (Chapter 5). Similarly, total REY abundance from a separate Keswick Island core (KIA) showed elevated values (large positive residuals in Figure 7, Chapter 6) from 1951, 1974 and 1990 (which likely included part of the flood band from Cyclone Joy), suggesting that Keswick and St. Bees were exposed to terrestrial material in high volumes of low salinity water during these events.

Extreme flooding has been previously related to large-scale death of coral assemblages in the southern GBR. In the Keppel Islands following Cyclone Joy in late 1990, floodwaters from the Fitzroy River damaged corals to 1.3 m, causing rupturing of epidermal cells and bleaching predominantly in acroporids and pocilloporids (van Woesik et al. 1995). In such cases, recovery to coral dominance can be slow: DeVantier et al. (2006) reported low coral cover and species richness from sites in the Northumberland Group and Keppel Islands surveyed in 1997 that were considered legacies from the 1990 death event. It is therefore possible that the community assemblages observed at Keswick and St. Bees Islands (high macroalgal cover, low coral cover of mainly acroporid species) represent an early successsional stage following large disturbance from recent, extreme flooding events bearing elevated nutrient loads from the Pioneer River,

particularly since agricultural intensification ~1950. However, without dating fragments of dead coral framework from the uppermost portion of the Keswick and St. Bees fringing reefs, we cannot be certain of the timing of coral death. Furthermore, surveys need to be repeated at these sites during winter to assess whether observed macroalgal dominance is a seasonal phenomenon or a permanent fixture of the community associated with coastal eutrophication.

Conclusions

Gross trends in benthic habitat cover do not deviate from expected cross-shelf trends on the Great Barrier Reef, with low live coral inshore and higher coral cover and diversity offshore. Acroporid corals dominated at all reef locations surveyed with photo-quadrats, and the prevalence of fast-growing acroporids at Keswick and St. Bees may represent communities in recovery from disturbance. The reef assemblages at Keswick and St. Bees are further distinguished by the dominance of large stands of brown macroalgae, particularly *Sargassum* spp. and *Podina* spp., which have often been cited as coral reef indicators of land-based eutrophication. When the coral community results are synthesised with historical coral core records of flood-related disturbance, it is evident that Keswick and St. Bees have been exposed to major flooding events 3 times since 1950 (1951, 1974, and 1991), with highly enriched, land-sourced δ^{15}N observed in 1974 and 1991 flood bands analysed from a Keswick core. These data suggest the possibility that these major floods may have led to massive coral mortality on shallow reef flats at Keswick and St. Bees due to reduced salinity, while enhanced nutrient levels may have promoted macroalgal growth. Further research is needed to determine the exact timing of coral death and to assess whether macroalgae are a seasonal or perennial component of the system.

Emerging evidence suggests that tropical storms, tied to changes in El Niño-Southern Oscillation strength, are likely to increase in intensity and be accompanied by higher rates of peak precipitation (Walsh et al. 2004). While we cannot say with certainty that the current macroalgal dominance at Keswick and St. Bees was a consequence of Pioneer River floods, there is cause for alarm that recovery to coral dominance may be hampered by more frequent and more extreme flood-related disturbances. Moreover, the 10 to 16-fold increase in accumulation rates of river-delivered nitrogen over natural baselines observed in

nearshore coral skeletons (Chapter 7) suggests that Pioneer River discharge is becoming increasingly eutrophic, which is favourable for rapid growth phytoplankton communities (Beman et al. 2005) that may further cause coral community shifts by decreasing light availability and depleting dissolved oxygen.

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