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ORIGINAL PAPER

Biogeochemical Zones Within a Macrotidal, Dry-Tropical Fluvial-Marine Transition Area: A Dry-Season Perspective

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Abstract The Fitzroy River delivers large amounts of nutrients and fine sediments to Keppel Bay (contiguous with the Great Barrier Reef Lagoon) during intermittent flow events. This study explores sources, forms and transformations of nutrients in Keppel Bay, and develops a functional process zonation that integrates seabed geochemistry and water column nutrient characteristics which are controlled by suspended sediment. The water column and seabed properties were investigated over two dry seasons, with supplementary core incubations taken to measure carbon decomposition rates and nutrient fluxes. Keppel Bay can be divided into three zones, the: zone of maximum resuspension (ZMR); coastal transitional zone (CTZ); and blue water zone (BWZ). Mineralisation of predominantly terrestrial organic matter occurs in the ZMR where nutrient uptake by phytoplankton is light limited. The CTZ and BWZ had higher light penetration and phytoplankton growth was likely limited by N and P, respectively. The identified zones conform to the bathymetry and hydrodynamic characteristics of the bay, allowing for the development of an integrated conceptual model accounting for the benthic and pelagic biogeochemical processes. Recognition of these different zones shows that considerable variation in benthic and water column properties is possible within a small system with the bathymetric and hydrodynamic characteristics of the fluidized bed reactor.

Keywords Resuspension · Dissolved nutrients · Seabed geochemistry · Nutrient limitation · Tide-dominated embayment · Sub-oxic fluidized bed reactor

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1 Introduction

Coastal zones play a dominant role in the storage and cycling of sedimentary organic carbon (Hedges and Keil 1995; Jahnke 1996). Tropical coastal regions are of especial importance as 60–70% of the world's delivery of sedimentary organic carbon occurs in these regions (Milliman and Syvitski 1992; Ludwig and Probst 1996). A major characteristic of these regions is massive subaqueous deltaic complexes of mud banks, both at the mouth, and further down current. The best studied examples are: the Amazon (Keuhl et al. 1986), the Fly and neighbouring rivers in the Gulf of Papua (Milliman 1995; Aller et al. 2004); and the subtropical Yangtze and Huanghe Rivers entering the East China Sea (Liu et al. 2006). These tropical zones are not only areas of high deposition (at least on a seasonal time scale) but can also be highly efficient sites for remineralisation of terrestrial organic matter as well as in situ primary production leading to productive fisheries (Alongi 1995). The specific mechanism responsible for this extensive and highly efficient remineralisation has been characterised as a "sub-oxic fluidized bed reactor" (Aller 1998; Aller and Michalopoulos 1999) and requires frequent cycles of resuspension and deposition of the fine sediments so that the attached organic carbon is repeatedly exposed to oxic and sub-oxic environments. There is thus a strong nexus between the geomorphic characteristics of the initial deposition zone especially the depth of deposition and extent of exposure to tide, wave and storm action causing repeated resuspension of the initially deposited sediments, and the mineralisation of particulate nutrients.

Keppel Bay, the seaward embayment adjoining the mouth of the Fitzroy estuary, in Queensland, Australia, shares many of the common physical characteristics of the paradiagmatic fluidized bed reactors of the Amazon and the French Guyanian mud banks and the Gulf of Papua. It receives large quantities of terrestrial sediments, possesses a relatively shallow topset deposition zone bisected by several distributary channels, and is macrotidal. It has been recognised physiographically as being a semi-tropical example (Flemming 2002) of a "muddy coast"—a hall mark of the Amazon and Gulf of Papua also. The biogeochemical behaviour of this area has not been investigated so far despite the intrinsic scientific interest as a relatively small scale fluidized bed reactor, as well as the important practical consequences. In the context of nutrients and sediments having potentially deleterious impacts on in-shore corals (Fabricius and De'Ath 2004), understanding the biogeochemical function of Keppel Bay, especially the storage, transformation and remineralisation of land-derived particulate nutrients, is of direct relevance to the management of the Great Barrier Reef and its preservation.

Keppel Bay is a macrotidal sediment-starved embayment (Ryan et al. 2007). Net shore-normal transport of particulates enhances sediment accumulation in the inter-tidal and shallow sub-tidal areas near the estuary mouth (Ryan et al. 2007). The shoreward transport also produces shore-normal gradients in seabed physical characteristics (i.e. grain size and sorting coefficients; Ryan et al. 2007) and water column optical properties (Oubelkheir et al. 2006). Superimposed on this spatial variability are semi-diurnal tides with a maximum range of ~ 5 m which impose short-timescale variability on water column properties through advection of water masses and resuspension of the seabed sediment (Webster et al. 2006). This variability makes the design of effective monitoring programs and the analysis of data much more difficult than in most aquatic systems. Moreover, there remain gaps in our understanding of the biogeochemical functioning of dry-tropical environments (Eyre 1994), particularly in relation to the processing and storage of biogeochemically reactive elements (carbon, nitrogen, phosphorus and iron) in the near-shore zone in the intervening periods between flood events.

Here we explore the sources, forms, availability (for primary production) and transformations of nutrients in Keppel Bay, and develop a functional process zonation that integrates seabed geochemical characteristics and the water column properties which are controlled by suspended sediment. From a consideration of the inherent water column optical properties, Oubelkheir et al. (2006) alluded to three zones in the estuary–coast–ocean transition: turbid estuarine waters, coastal mixed turbid waters and ocean blue waters. However, these zones, which are evident in Landsat images (e.g. Fig. 2a), were not specifically defined nor were their biogeochemical characteristics elucidated. The zones have the potential to provide an organising and simplifying structure for describing the interactions between the geochemistry and biogeochemistry of the seabed, and spatial and temporal variation in water column characteristics, and are referred to as the zone of maximum resuspension (ZMR), blue water zone (BWZ) and coastal transition zone (CTZ). However, the combination of interacting physical and biogeochemical processes, especially macrotidal sediment resuspension and episodic inputs of terrestrial soils and nutrients is not unique to Keppel Bay. The process conceptualisation and descriptive zonation we develop is likely relevant to other coastal systems. We draw particular attention to the many northward facing bays in the Great Barrier Reef catchment area (Larcombe and Woolfe 1999).

2 Study Area

The Fitzroy River Basin covers an area of $\sim$144,000 km^2 (Fig. 1), and is the largest Queensland catchment discharging to the Great Barrier Reef Lagoon. Situated in the dry tropics, the climate of the catchment is described as sub-tropical. The geology of the Fitzroy River Basin is complex with more than 100 different types of rocks and has been

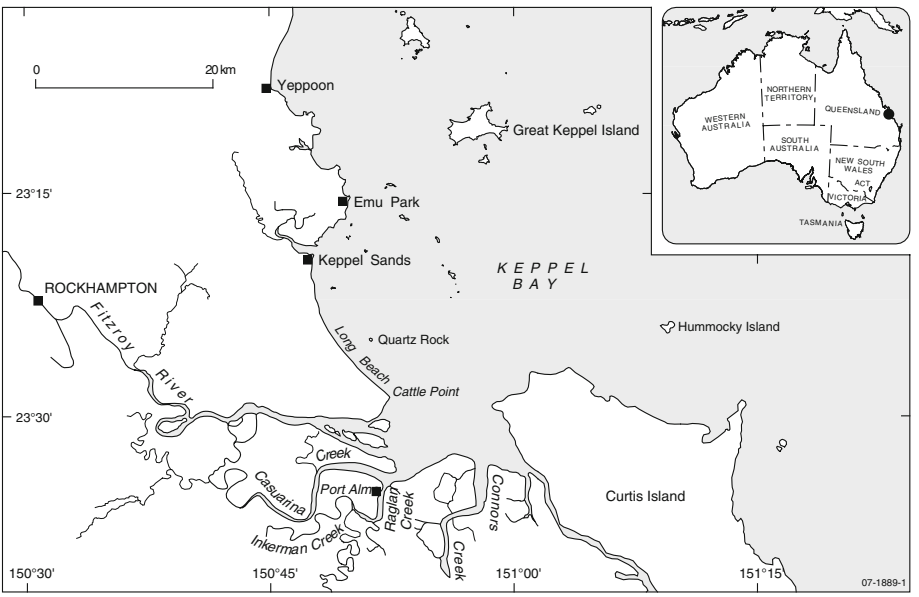

Fig. 1 Location map of the Fitzroy Estuary, Keppel Bay and tidal creeks

divided into five major structural units (Douglas et al. 2006). Approximately 60% of the native vegetation cover in the catchment has either been cleared or has been subject to thinning (Furnas 2003). Rangeland beef grazing occurs over at least 80% of the total area of the Fitzroy River Basin and is the principal land use in the catchment (Furnas 2003). The Fitzroy River Basin is divided into five large river sub-catchments. During the infrequent flood events the Fitzroy River carries high concentrations of fine suspended sediments (>1,000 mg l^{-1}; Packett et al. 2009). Consequently the river is one of the largest sources of sediment to the Great Barrier Reef Lagoon (Furnas 2003).

The Fitzroy Estuary/Keppel Bay region embodies many of the general characteristics of a dry tropical savannah tidal estuary having episodic freshwater deliveries (Depetris and Paolini 1991; Martins and Probst 1991). The catchment is subject to highly episodic rainfall and infrequent river runoff events which occur mainly in the austral summer (December–March). Reflecting the episodic character, the inter-annual average discharge over the last 40 years of the Fitzroy River has varied by a factor of more than 100, and sediment and nutrient deliveries have varied by a somewhat greater degree (Packett et al. 2009). The mean long-term annual discharge is 4.8 million ML $year^{-1}$ (Packett et al. 2009). There is very limited freshwater discharge in the dry season (usually <1 m^3 s^{-1}).

The landward limit of the Fitzroy Estuary is defined by the barrage at Rockhampton approximately 60 km upstream from the estuary mouth (Fig. 1). Within the Fitzroy estuarine floodplain to the south of the estuary are a series of tidal creeks which have a combined area similar to that of the Fitzroy Estuary. From a geologic perspective, the Fitzroy Estuary is transitional between a tide-dominated estuary and a delta because most of the accommodation space for sediment has been filled (Ryan et al. 2007). The geomorphology and the flow regime have important consequences for the transport and transformation of dissolved nutrients and nutrients attached to sediments. Flows larger than the estuary volume ($\sim 2.5 \times 10^8$ m^3) will pass quickly through the estuary and discharge their nutrients and sediments directly into Keppel Bay (a 30 × 20 km shallow (average depth 10 m) embayment which is part of the Great Barrier Reef Lagoon). Calculated nutrient loads of individual flood events (1994–2008) range from 0.05 to 5.5 kt for TP and 0.2 to 12.8 kt for TN (Packett et al. 2009). About 2/3 of nutrients are delivered in particulate form, mainly as organic constituents on soil particles, whilst the remainder is in dissolved forms (Ford et al. 2005). The high flows (maximum 10,000 cumecs) persist for about 1–2 weeks and fine particles and nutrients are rapidly transmitted through the estuary which flows fresh to beyond its mouth, and then as a brackish surface plume exiting Keppel Bay to the east and north (Devlin and Brodie 2005). It appears that the bulk of the fine sediment and particle-attached nutrients flocculate out on mixing with saline water (Kranck 1973, 1984) and settle rapidly from the flood plume. This process leads to deposition of fine mud in Keppel Bay. Tides in Keppel Bay are mixed, semi-diurnal and their ranges vary from ~1 m (neap) to ~5 m (spring). The vigorous tidal currents (maximum > 1 m s^{-1}) in the bay resuspend sediment and redistribute it through the bay.

3 Materials and Methods

3.1 Field Program

Three dry season surveys were conducted in Keppel Bay and Casuarina Creek in the periods September 4–12, 2003, August 15–September 1, 2004 and May 4–9, 2006. Logistic

and safety considerations as well as the long shallow sand bars radiating from the mouth of the estuary prevented sampling on a regular grid. The sampling strategy adopted covers all three water and sediment zones identified from satellite imagery and local knowledge. Measurements of physical and chemical properties of the water column and underlying sediments were undertaken during the September and August surveys at a series of locations (Fig. 2). In addition, during the August 2004 survey, the research vessel was anchored at seven stations for periods of 24 h, and samples for nutrients and total suspended matter (TSS) were collected at hourly intervals over the initial 12 h. Results from the 24-h stations are presented in Oubelkheir et al. (2006) and are not considered in detail here. Core incubation experiments were undertaken at eight sites during each of the August 2004 and May 2006 surveys (Fig. 2b, c).

3.2 Water Column Measurements

3.2.1 Total Suspended Matter

Water samples for total suspended solids (TSS) and nutrient (see below) analyses were collected from ~50 cm below the water surface. The samples were vacuum filtered through pre-weighed filter papers (diameter: 47 mm; nominal pore size: 0.45 μm), which were subsequently refrigerated. In the laboratory, the filter papers were oven-dried at 60°C before weighing.

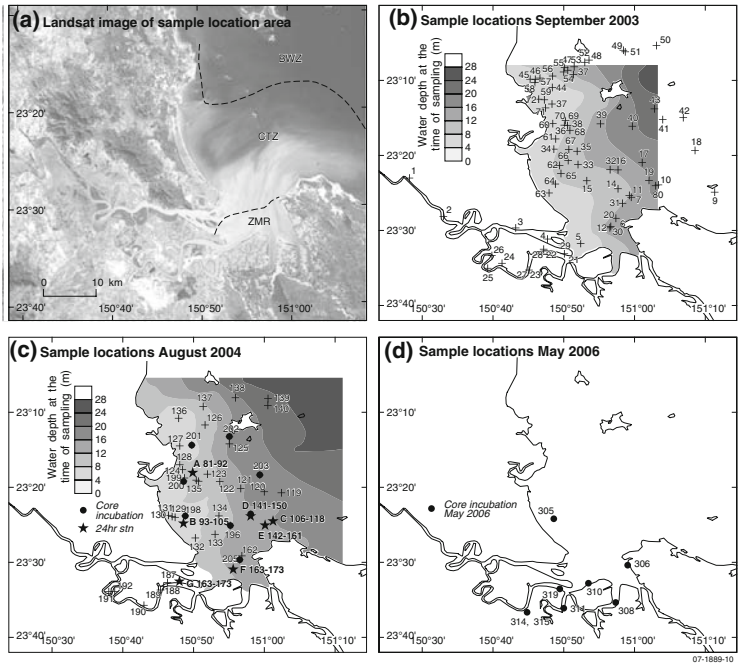

Fig. 2 **a** Landsat image of study area and maps showing sampling locations for each of the September 2003 (**b**), August 2004 (**c**) and May 2006 (**d**) surveys. Abbreviated names correspond to the zone of maximum resuspension (*ZMR*); Coastal Transitional Zone (*CTZ*); and blue water zone (*BWZ*)

3.2.2 Nutrients

Collected 1 L water samples were vigorously mixed. Water for filterable reactive dissolved nutrient analyses was syringe-filtered through 0.45 μm nylon membrane filters into clean environmental-grade HDPE bottles. A component of the remaining unfiltered water was analysed for total nutrients. The samples were stored on ice immediately after collection, and were frozen on the evening of collection for transport to the laboratory. The filtered samples were analysed for filterable reactive phosphorus (FRP), total oxidised nitrogen (NO_x), ammonia (NH_4^+) and silicate (SiO_4^{2-}) simultaneously using an automated LACHAT 8000QC flow injection system and by the following Standard Methods (Anonymous 1998: 4500-P G (FRP); 4500-NO_3 I; 4500-NH_3 H and 4500-SiO_2 F). The uncertainties on TN, TP and dissolved inorganic nutrient analyses were 0.005, 0.002 and 0.001 mg L^{-1}, based on In-House Reference Materials that were prepared at varying concentrations across the analysis range, and that were analysed with every analytical run. Samples for total nitrogen (TN) and total phosphorus (TP; unfiltered water), and total dissolved nitrogen (TDN) and total dissolved phosphorus (TDP; filtered water) were digested using a modified version of the simultaneous persulfate procedure (Hosomi and Sudo 1986). The digests were then analysed using the same instruments and procedures as those described for NO_x and FRP. Dissolved organic nitrogen (DON) and dissolved organic phosphorus (DOP) concentrations were calculated as follows: DON = TDN − (NO_x + NH_4^+); DOP = TDP − FRP. Total particulate nitrogen (PN) and total particulate phosphorus (PP) concentrations were calculated from: PN = TN − TDN; and PP = TP − TDP. The uncertainty on DON, DOP, PN and PP concentrations are 0.005, 0.002, 0.007 and 0.003 mg L^{-1}, respectively.

3.3 Bottom Sediment Properties

3.3.1 Sample Collection and Preparation

Undisturbed bottom sediment samples (top 2 cm) were collected using a hand-deployed sediment grab sampler. A sub-sample of this sediment was removed for grain size and carbonate analysis. The remaining sample was first centrifuged (and the supernatant was decanted), and then freeze-dried and ground prior to the determinations outlined in Sects. 3.3.2–3.3.4.

3.3.2 Major and Minor Element Oxides

Major and minor element concentrations (including TP) were determined by X-ray fluorescence (XRF) using a modified version of Norrish and Hutton's (1969) method, whereby no heavy absorber was added to the flux. The instrumentation used was a Philips PW2404 4 kW sequential spectrometer, and was calibrated using a range of USGS and SARM (South African Reference Material) international standards. Ferrous iron (FeO, Fe(II), Fe^{2+}) was determined using a modified version of the Shapiro and Brannock (1962) method.

3.3.3 Sediment Organic Carbon and Nutrients

Total organic carbon (TOC) concentrations were determined from finely ground sediments using a LECO combustion furnace (RC412) after acid pre-treatment. Sediment samples for nitrogen analysis were digested in an automated process based on Standard Methods 1998–4500-Norg D (Anonymous 1998), with modifications to allow analysis for freshwater,

saline waters and sediments. Analyses for total kjeldahl nitrogen (TKN) were then performed on the digest using a segmented flow instrument (BRAN+LUEBBE) and Standard Methods 1998–4500-NH_3 H, using sodium salicylate instead of phenol. A subset of sediment samples (25) were analysed at Primary Industries Research Victoria, for the following P fractions: total P, organic P, Fe/Al bound P including loosely exchangeable phosphate (non-apatite phosphorus), Ca-bound P (apatite-P) and residual inorganic P using a modification of the extraction schemes of Strom and Biggs (1982). The scheme differed from the Strom and Biggs scheme in the first and last extractions. 2 M NaCl was used in place of NH_4F to estimate exchangeable P because Strom and Biggs (1982) indicated that NH_4F is inappropriate in calcareous sediments. In addition, boiling H_2SO_4 and H_2O_2 (a modified Kjeldahl digest) were used in the final extraction to determine residual-P, whereas Strom and Biggs (1982) used warm nitric/perchloric/sulphuric acids. Extraction of standard sediments demonstrated that the digest was quantitative.

3.3.4 δ13C

Sediments (after acidification with 6% HCl twice) were analysed for $\delta^{13}C$ at Geoscience Australia using a Thermo Finnigan Flash EA series 1112 interfaced to a Thermo Finnigan Conflo (II)I. The isotopic measurements were carried out on a Finnigan Mat 252 using ISODAT NT software. The Flash EA (operated with EAGER software) was packed with copper oxide and silver cobaltous oxide and operated at 900°C. The reduction furnace was packed with pure copper and operated at 600°C. Combustion products were separated on a packed GC column run isothermically at 400°C. The acidified samples were weighed into tin foil cups and placed in an auto-sampler alongside a series of blanks and standards used for the isotope correction. The standards ANU Sucrose and TO2 were used along with caffeine for isotopic calibration. Samples were corrected for the apparent offsets of reference materials (as measured against the working gas) from their expected value on an international scale (i.e. δsample/international scale = δsample/working standard + δoffset + δsample/working standard × δoffset/1,000). Samples were run in duplicate or triplicate. The standard deviations on the replicate analyses ranged from 0.01 to 0.38‰ (average 0.12‰).

3.3.5 Surface Area Analysis

The surface area of a small number of samples (Keppel Bay seabed sediments and riverine flood and weirs sediments from Douglas et al. (2006)) was determined by methods outlined in Keil et al. (1997) using a Quantachrome Quantasorb Analyser at CSIRO Land and Water, Adelaide.

3.3.6 Core Incubations

One sediment box core was collected at each of eight sites in August 2004 and May 2006 (Fig. 2b, c) for measurement of dark respiration rates (as an indicator of carbon reactivity). Cylindrical cores of sediment were extracted from the box cores by hand-pushing polycarbonate tubes (~400 mm length; 80 mm diameter) into the captured sediment. The core barrels were sealed at the bottom, and contained 200–240 mm of sediment. Each core barrel was filled to capacity (i.e. 200–250 mm) with bottom water collected with the box core. A gas-tight lid sealed the top of each core, and the lid was fitted on the underside with a magnetic stirrer rotating at 7 rpm to avoid stratification. Following a pre-incubation

period of 1–2 h, core incubations proceeded in darkness and at near in situ water temperatures for approximately 24 h.

Measurements and samples were taken at the beginning and end of each experiment in August 2004 and at approximately 6 h intervals in May 2006. As a sample was withdrawn, it was replaced with an equivalent amount of site water (maintained in the dark at the same temperature as the incubated core) from a gravity-feed reservoir. Samples for alkalinity were filtered through 0.45 μm disposable filters into gas-tight, glass scintillation bottles (no head space), and were refrigerated prior to analysis. Alkalinity was determined by Gran titration, whilst the carbonate alkalinity (CA) was estimated by subtracting the alkalinity contribution of $B(OH)_4^-$. Carbon dioxide (TCO_2) was estimated from pH and carbonate alkalinity (Mehrbach et al. 1973). Nutrient samples were collected and processed as outlined in Sect. 3.2.2.

Oxygen and CO_2 fluxes were calculated from the slopes of the linear regressions of (all five points) with time. Apart from samples 314 and 315, the slope of the full five-point regressions and that obtained using only the beginning (0 h) and end (24 h) points were identical.

3.3.7 Carbonate Content

Surface sediment samples were analysed for percentage mud, sand and gravel (dry weight) after wet sieving through nested 2 mm and 63 μm sieves. Carbonate contents were determined on bulk sediments using the carbonate bomb method of (Muller and Gastner 1971). Twenty percent orthophosphoric acid, warmed to 50°C, was placed in a warm (35°C) Perspex container. Dried and crushed sediment samples, weighing 0.9 g, were introduced to the chambers. Pressure gauges were screwed onto the top of the chambers, forming a seal. The chambers were then agitated until all the carbonate dissolved, producing CO_2 gas. The mass of carbonate is determined by a calibration curve of the CO_2 gas pressure as a function of carbonate content. The accuracy of the method is ±0.5%.

3.4 Data Analysis

Spatial patterns and significant relationships between the physical and chemical variables in the bottom sediment data set were investigated by principal components analysis (PCA) using STATISTICA 6™. The input variables for the PCA included the major and minor element concentrations, percent mud, carbon and nutrient concentrations. Al_2O_3/K_2O ratios were used as weathering indices (Smith et al. 2008). FeII/FeIII, TS:FeII and Fe(II):TOC ratios and TOC, TS and FeII as molar percentages of TOC + TS + FeII were used as indicators of sediment redox condition. Data were transformed (log_{10}) prior to analysis to produce approximately normal distributions. Contour maps of the distributions of various physical and chemical parameters were generated using the default kriging options in SURFER7®.

4 Results

4.1 Seabed Geochemistry

The PCA identified three main groups of seabed samples (Fig. 3a). One pair, the mud and sandy-mud (-M&sM), muddy-sand (-mS) and sand (-S) samples form a band from negative

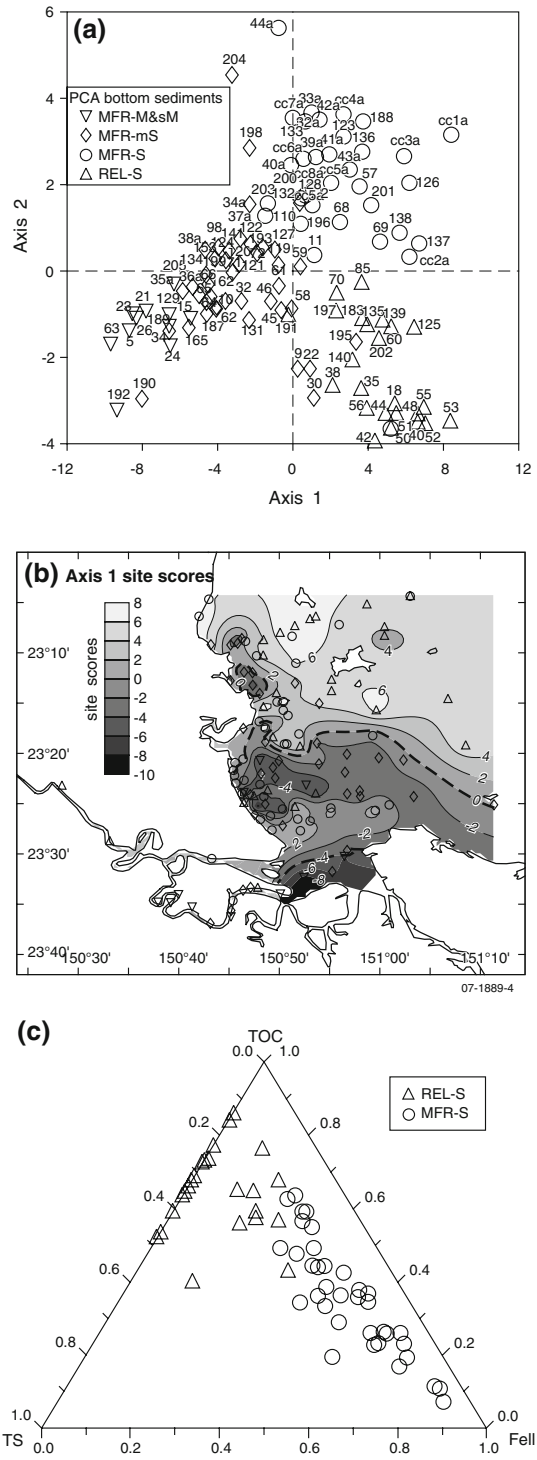

Fig. 3 Results of the PCA on bottom sediment geochemistry and grain size data: **a** axis 1 versus axis 2 site scores; **b** map showing the distribution of site scores for axis 1; **c** triplot of TOC, FeII and TS in sandy sediments. Indicated grain sizes are based on Folk et al. (1970) and include mud and sandy-mud (*M&sM*), muddy sand (*mS*) and sands (*S*) of the modern Fitzroy River (*MFR*) and relict sands (*REL-S*)

to positive loadings across both axis 1 and 2 (Fig. 3a) and are derived from the modern Fitzroy River (MFR; Ryan et al. 2007). These MFR sediments are mainly found on the landward side of the zero-contour on the map of axis 1 site scores (Fig. 3b), and occur in the ZMR and in two distinct lobes in the CTZ (i.e. the near-shore areas along the northern part of Curtis Island and along the western coastal margin). The 3rd group are sands with negative scores on axis 2 and positive scores on axis 1 called Outer Bay Relict Sands (REL-S) in the terminology of Ryan et al. (2007). They are found in the BWZ.

Axis 1 explained 53% of the variance in the data set, and differentiated seabed sediments on the basis of grain-size, major and minor element, nutrient and TOC concentrations and Al_2O_3/K_2O ratios (Table 1). The correlations between total iron, Al and the weathering index (Al_2O_3/K_2O) with axis 1 were particularly strong.

Hydrodynamic sorting has created the dispersion of axis 1 site scores indicative of the degree of weathering of the seabed sediment (e.g. Fe and Al_2O_3/K_2O ratio; Table 1). Axis 2 explained 11.1% of the variance, and identified two groups of sands (MFR-S and REL-S)

Table 1 Factor coordinates of variables on axes 1, 2 and 3 of the bottom sediment PCA

Variables	Axis 1	Axis 2	Axis 3
Al_2O_3:K_2O	**−0.97**	0.07	−0.06
Fe(tot)	**−0.97**	0.10	0.03
Al	**−0.96**	0.10	0.08
TOC	**−0.92**	−0.17	0.16
TP	**−0.92**	0.08	−0.02
TN	**−0.90**	−0.20	−0.13
Zn	**−0.90**	0.14	−0.01
FeIII	**−0.89**	−0.17	0.20
Mg	**−0.89**	0.05	−0.32
Na	**−0.89**	0.08	−0.06
%Mud	**−0.88**	−0.14	−0.04
S	**−0.86**	−0.27	0.02
Ti	**−0.85**	0.19	−0.12
K	**−0.85**	0.19	0.14
Cr	**−0.84**	0.07	0.01
Ni	**−0.81**	−0.13	0.21
Cu	**−0.79**	0.28	0.16
TN:TP	**−0.75**	−0.33	−0.18
FeII	−0.69	0.59	0.02
%TOC-(TOC+TS+FeII)	−0.50	−0.58	0.17
Mn	−0.48	0.24	0.03
TS:FeII	−0.42	0.05	0.19
FeII:FeIII	−0.26	**0.72**	0.03
Ca	−0.21	0.11	**−0.89**
Carbonate	−0.12	−0.01	**−0.92**
FeII:TOC	0.11	**0.86**	−0.13
%FeII-(TOC+TS+FeII)	0.25	**0.83**	−0.09
%S-(TOC+TS+FeII)	0.46	−0.51	−0.15
Quartz	**0.77**	0.05	0.47
Si	**0.87**	0.04	0.32

Variables with loadings greater than 0.7 (absolute value) are shown in bold

with different values for the redox indicators (Table 1). Figure 3c confirms that Fe(II) varied systematically with TOC in the sandy seabed sediments, causing the differentiation of sands on axis 2.

TP concentrations typically fell within a range from 360 to 470 mg kg^{-1} (median 420 mg kg^{-1}; Table 3), which is comparable to those from a suite of Australian estuaries compiled by Eyre (1993). All the seabed samples were enriched in P relative to the Redfield ratio (Redfield et al. 1963), with molar TN:TP ratios ranging from 1.1 ± 0.5 in sands to 3.3 ± 0.6 in mud. Sediment P was predominantly associated with the Ca–P pool (>50%), with lesser amounts occurring in organic matter, Fe/Al–P or the residual pool (Fig. 4a). About 30–45% of the TP in the mud and sandy-mud sediments was potentially available (Fig. 4a), on the assumption that all of the organic-P and Fe/Al–P can be mobilised through degradation (Slomp et al. 1996). The TOC concentrations of Keppel Bay surface sediments fell into a range that is typical for river-influenced continental shelves (Keil et al. 1997), with TOC values of 0.41 ± 0.23% in the mud and sandy-mud sediments decreasing to 0.07 ± 0.09% in sands (Table 3). Both the MFR and REL sands had TOC:TN ratios and $\delta^{13}C$ signatures that suggested bacteria were the principal component of the organic matter, whilst the muddy-sand samples plotted within the fields of expected values for marine phytoplankton and bacteria (Fig. 4b). The mud and sandy-mud samples were mainly confined to the marine phytoplankton field.

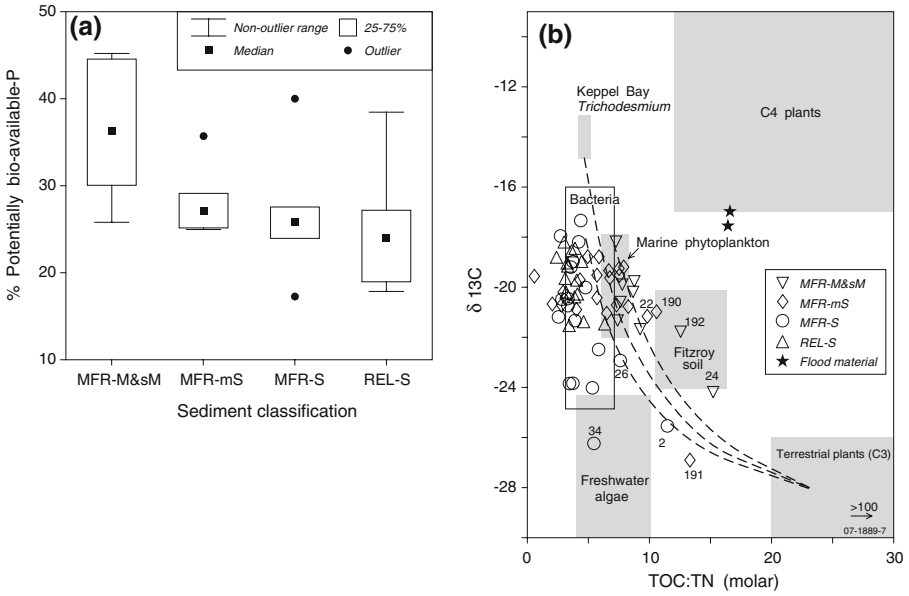

Fig. 4 **a** Percentages of P in biologically available forms (i.e. organic-P + Fe/Al-bound P) and **b** $\delta^{13}C$ signatures versus TOC:TN ratios for the different sediment types in Keppel Bay and Casuarina Creek (see Fig. 3). The *shaded boxes* refer to expected values for fresh marine phytoplankton (based on Bird et al. 1995 and Gagan et al. 1987), soil organic matter (Ford et al. 2005), fresh terrestrial-C3 plant debris (Meyers 2003), C4 plants (Eyre and McKee 2002; Meyers 2003; Holtvoeth et al. 2005), fresh lacustrine algae (Meyers 2003) and *Trichodesmium* collected from Keppel Bay (P. Ford, unpublished data). The *open box* denotes the area of marine bacteria $\delta^{13}C$ signatures and TOC:TN ratios reported by Fukuda et al. (1998) and Goni et al. (2005). Three example *mixing lines* extending from the terrestrial organic matter field to each of the marine phytoplankton, bacteria and *Trichodesmium* fields are also shown. The flood samples are based on analyses made on material reported in Douglas et al. (2006)

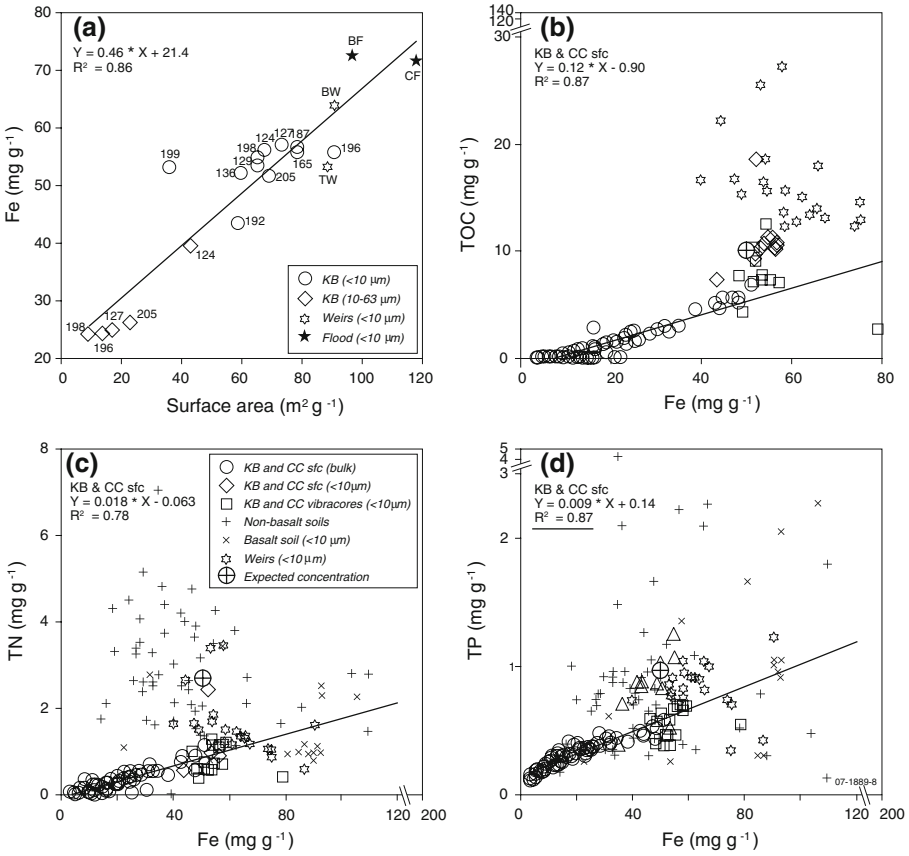

Fig. 5 **a** Sediment Fe versus surface area of Keppel Bay sediment. **b** Sediment/soil TOC versus sediment/soil Fe; **c** Sediment/soil TN versus sediment/soil Fe; **d** Sediment/soil TP versus sediment/soil Fe. The soil and weir samples are from Douglas et al. (2006), the vibracore data are from Bostock, unpublished data and the expected TOC concentration are from Ford et al. (2005). The expected P and N concentrations are derived from the results of Smith et al. (2008) and Douglas et al. (2006). CC refers to Casuarina Creek and KB refers to Keppel Bay

The approximate direct proportionality shown in Fig. 5a suggests that total iron can be considered a useful surrogate for surface area. Assuming this to be the case, the carbon and nutrient concentrations per Fe surface area equivalent of seabed sediments were low compared to most non-basaltic soils from the Fitzroy catchment (Douglas et al. 2006), concentrations of TOC in incoming flood material (Ford et al. 2005), and to expected concentrations based on the results of a sediment tracing study (Smith et al. 2008; Fig. 5b, c, d). The expected P and N concentrations are derived from the area weighted mean abundances of N and P in the five major catchment soil types identified in Keppel Bay multiplied by the average N and P concentrations of these respective soils. They were ~65 and ~50% higher than those measured in Keppel Bay (at the same Fe concentration) for N and P, respectively (Fig. 5c, d), whilst the TOC of the incoming flood material was ~40% higher (Fig. 5b).

Table 2 O_2, CO_2 and nutrient fluxes from the core incubation experiments

Zone	Sample	O_2 flux (mM m^{-2} day^{-1})	CO_2 (mM m^{-2} day^{-1})	O_2 drop (mg L^{-1})	DIN Flux (mM m^{-2} day^{-1})	FRP flux (mM m^{-2} day^{-1})
CTZ	196	−10.7	18.1	1.91	−0.16	−0.02
CTZ	198	−18.5	21.3	3.78	−0.05	−0.01
CTZ	200	−8.5	9.9	0.96	−0.04	0.02
CTZ	204	−10.9	9.8	2.33	N/A	N/A
CTZ	205	−15.9	41.2	1.74	N/A	N/A
CTZ	305	−6.3	3.6	1.05	0.05	0.01
CTZ	306	−11.7	22.9	1.88	1.77	−0.02
BWZ	201	−7.5	19.3	1.4	−0.53	−0.01
BWZ	202	−8.7	8.0	1.91	−0.94	−0.08
BWZ	203	−15.0	31.2	2.28	−0.15	0.01
ZMR	308	−6	11.9	1.07	0.22	0.06
ZMR	310	−8.3	15.9	1.49	0.07	−0.01
ZMR	311	−7.5	17.7	1.21	0.33	−0.04
ZMR	314	−8.3	49.5	1.39	1.99	−0.07
ZMR	315	−6.8	53.6	1.15	0.39	−0.03
ZMR	319	−6.9	12.5	1.13	0.42	−0.02

Negative fluxes imply uptake by sediment and positive fluxes imply release from sediment

4.2 Benthic Processes

Results of the core incubation experiments are shown in Table 2. Most benthic CO_2 fluxes were <48 mmol m^{-2} day^{-1}, and thus fell in a range that is considered oligotrophic for Australian coastal ecosystems (Eyre and Ferguson 2002). Oxygen concentrations dropped between 0.96 and 3.78 mg L^{-1} over the course of the incubations, and oxygen uptake fluxes ranged from −15.9 to −6 mmol m^{-2} $day^{-1.}$ Most of the O_2 and TCO_2 fluxes formed a roughly curve (Fig. 6), which peaked in samples 203 and 205 and declined in samples 314 and 315. With one exception (305), O_2:CO_2 flux ratios were less than 1.3, which is the ratio expected from aerobic degradation with complete nitrification. There was net release of DIN to the water column in all the samples from the ZMR, net uptake of DIN in the three samples from the BWZ and a mixture of uptake and release in the CTZ (Table 2). There was no distinct regional pattern in either the O_2 or CO_2 fluxes (Fig. 6a). There was reasonable agreement between the DIN fluxes into the ZMR water column measured in the core incubations (0.7 (SD 0.8) mmol m^{-2} day^{-1}) and the flux inferred from changes in salinity and NO_x concentration in ZMR (0.38 mmol m^{-2} day^{-1}; described below).

4.3 Water Column Properties

During the dry season, the salinity in the study region tended to be highest in the Fitzroy estuary, tidal creeks and in the eastern reaches of Keppel Bay and along its western shore. This salinity enhancement over offshore waters is attributed to evaporation. NO_x and FRP concentrations measured in the ZMR increased approximately linearly with salinity. This increase was much greater than that expected due to concentration by evaporation (Fig. 7).

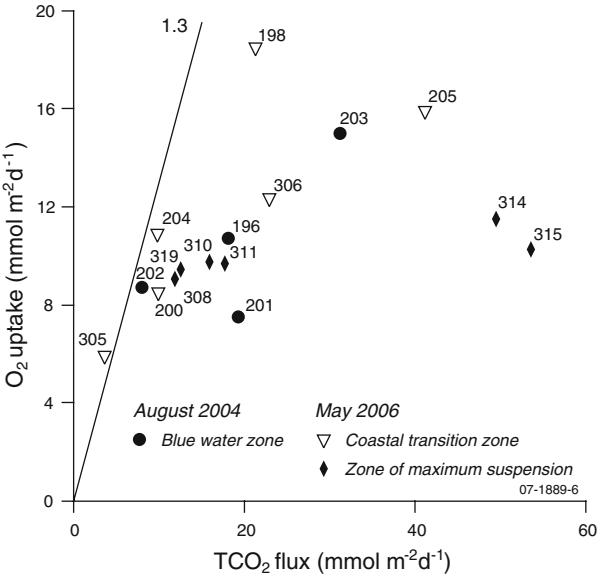

Fig. 6 Benthic O_2 flux versus benthic CO_2 flux. The *y*-axis is reversed to highlight the stoichiometry between O_2 uptake by sediment and CO_2 release. Negative fluxes imply uptake by sediment. The *regression line* pertains to data collected during the August 2004 survey only

Rather, we speculate that the nutrient increase arises from benthic mineralisation leading to a dissolved nutrient flux into the water column within the ZMR zone. Based on the observed salinity difference between the coast and further offshore and assuming an average ZMR water depth of 5 m and an assumed evaporation rate of 5 mm day^{-1}, a simple box model of the salt balance yields a characteristic residence time of the water in the ZMR of $\sim$40 days. With this exchange time scale, the observed NO_x and FRP concentrations are consistent with benthic fluxes into the water column of 380 and 60 μmol m^{-2} day^{-1} of NO_x and FRP, respectively. The DIN: DIP flux ratio is 6.3:1 (it is worth noting that this ratio is dependent on the concentration only). The calculated net uptake of oxygen by the sediment based on Redfield C:N:P of 106:16:1 and a O_2/C quotient of 1.45 (Anderson 1995) is 3.7 or 9.3 mmol m^{-2} day^{-1} depending on whether the C:N or C:P is used.

NO_x and FRP concentrations from the BWZ were below analytical detection, whilst those from the CTZ had mixed properties (i.e. showing evidence for a source, conservative evaporation and conservative mixing and uptake). Figure 8a shows that the regions of significant nutrient input or uptake were approximately defined by the zero and −4 contours of axis 1 of the bottom sediment PCA (Fig. 3b), and the 2.5 and 40 mg L^{-1} contours in the map of interpolated TSS concentrations for the combined dry-season surveys (Fig. 8a). There was also a change in predominant nutrient form across the regions (Fig. 8b), with particulate nutrients dominating near the mouth and tidal creeks, dissolved organic nutrients dominating in the BWZ and no clear pattern of nutrient predominance in the CTZ.

Total suspended matter (TSS) concentrations ranged from <1 to >300 mg L^{-1} in September 2003 and from <1 to 140 mg L^{-1} in August 2004. The map of combined TSS concentrations shows that dry season suspended sediment concentrations were highest near the estuary mouth and in the tidal creeks, and that they declined to the north and east in Keppel Bay (Fig. 8a). PP, PN, NO_x and FRP concentrations tended to increase with TSS and linear relationships were observed in some months (Fig. 9a, b, c). The FRP

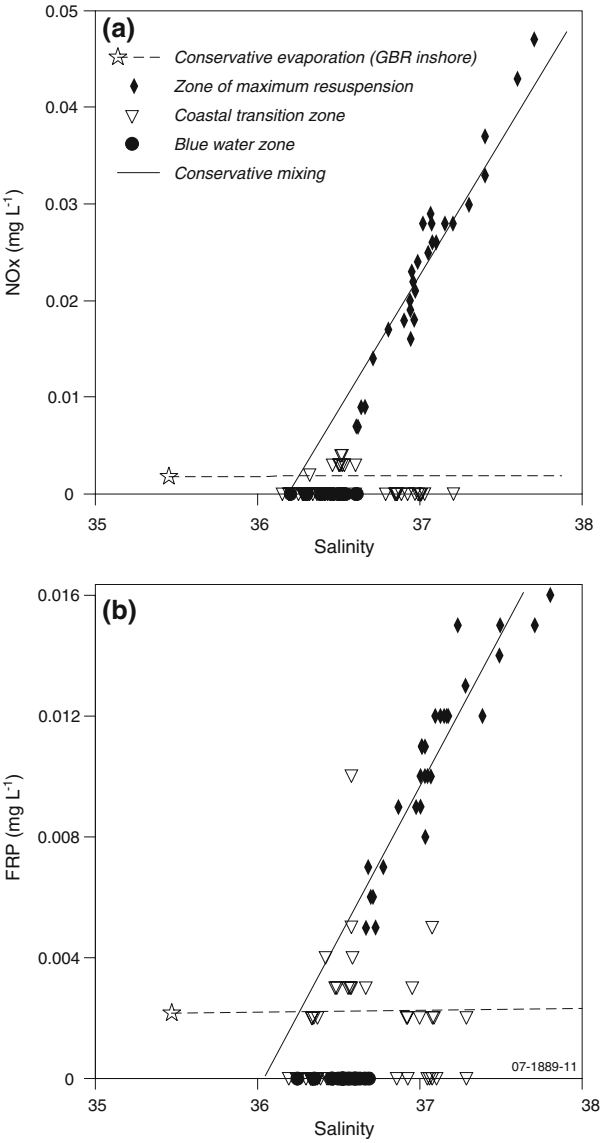

Fig. 7 Mixing diagrams (nutrients versus salinity) for NO_x and FRP data sets (August 2004 only). Average of data for the inner GBR waters (Swains Reefs; Furnas and Brodie 1996) is also shown and forms the basis of the conservative evaporation trend which extends through the origin

concentrations were near constant when TSS was higher than ~ 30 mg L^{-1} (Fig. 9d; samples 1, 2, 227–229 from the Fitzroy Estuary excluded).

5 Discussion

5.1 Biogeochemical Zonation

Despite the inherent complexity of the system, there were distinct patterns in most bio-physical characteristics, allowing Keppel Bay to be divided into three *functional process*

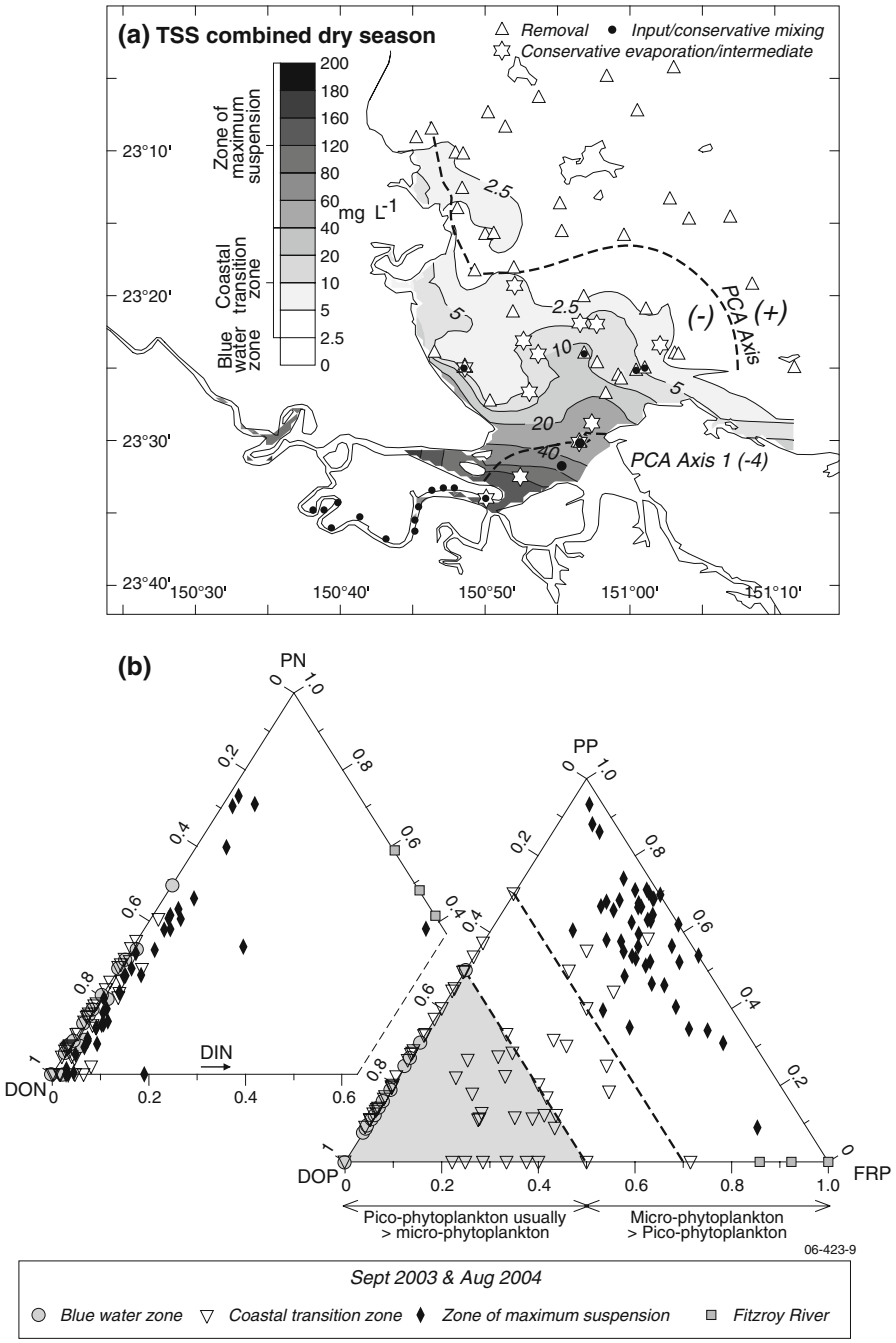

Fig. 8 **a** TSS map of Keppel Bay based on combined data from September 2003 and August 2004 with overlays showing the zero and −4 contours from axis 1 of the PCA (Fig. 3b) and whether the sites were areas of nutrient input (with conservative mixing), nutrient removal or intermediate between these end-members (see Fig. 7). **b** Triplots showing the proportions of the different nutrient forms (organic, inorganic and particulate) in the different regions of Keppel Bay

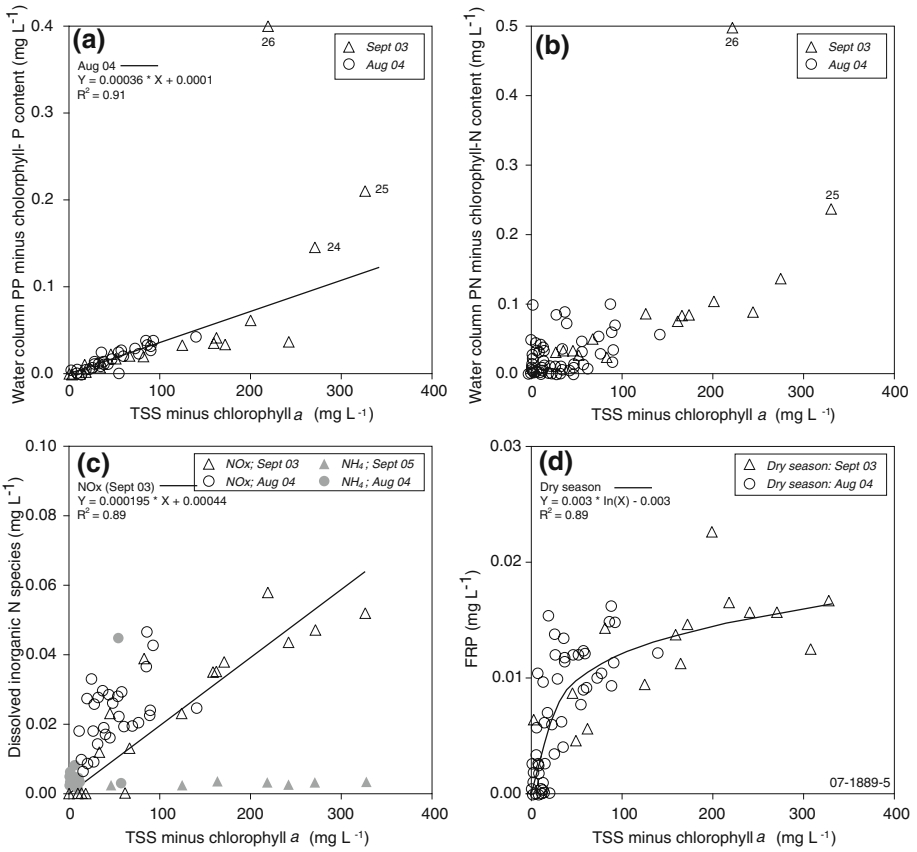

Fig. 9 Cross plots of TSS versus **a** PP; **b** PN; **c** inorganic nitrogen; and **d** FRP for the September 2003 and August 2004 surveys. The TSS data were corrected for the total weight of chlorophyll in the samples, whilst the concentrations of PN and PP were corrected for the estimated weight of N and P in the chlorophyll (assuming a C:chlorophyll weight ratio of 50 and Redfield stoichiometric proportions; Redfield et al. 1963)

zones (*sensu* Thorp et al. 2006), albeit with somewhat fuzzy boundaries. These zones are based on statistically significant differences in physical and chemical attributes of the underlying sediment, TSS concentrations and the forms and availability of dissolved inorganic nutrients (Table 3). This investigation spanned two dry seasons. The results are clearly influenced by antecedent conditions, and it is a legitimate question as to how persistent the zonation is. Anecdotal long term knowledge in the local fishing community recognises an ecological boundary which corresponds to our boundary between the CTZ and BWZ. Banana Prawns dominate prawn catches in the CTZ, whilst King Prawns dominate in the BWZ. This suggests that the zones may thus represent the approximate long-term (multi-year) average condition as they ultimately derive from the prevailing bathymetry and hydrodynamics which control the distribution of sediments initially delivered by flood events. In the discussion that follows, components of the seabed geochemistry and the framework of sediment deposition, biogeochemical processes and water column properties are integrated into the zonation that is summarised in the format of conceptual models of particulate and dissolved inorganic nutrient dynamics (Fig. 10).

Table 3 Some physical, chemical and ecological characteristics of the water column and bottom sediments of different regions of Keppel Bay: Fitzroy mouth and approaches (ZMR); inner Keppel Bay (CTZ); and outer Keppel Bay (BWZ)

Variable	Fitzroy mouth and approaches (ZMR)	Inner Keppel Bay (CTZ)	Outer Keppel Bay (BWZ)
Water column nutrients and TSS (medians; 25th–75th percentile range; minimum—maximum)			
Nutrient behaviour	Input; conservative mixing	Input; removal; conservative evaporation	Removal
Limiting factor	Light	Nitrogen	Phosphorus
TSS (mg L^{-1})	56; 31–90; 13–326	*** 4.5; 2.0–7.6; <1–45.5 ***	0.9; 0.6–1.6; <1–4
NO*x* (mg L^{-1})	0.026; 0.018–0.035; 0.007–0.058	+ BD; BD; BD-0.023 +	BD; BD; BD
FRP (mg L^{-1})	0.012; 0.009–0.014; 0.005–0.17	+ BD; BD-0.002; BD-0.01 +	BD; BD; BD
TN:TP (molar)	12; 10–15; 4–27	*** 30; 24–36; 10–58 ***	41; 30–50; 18–103
DIN:FRP (molar)	4.9; 4.4–6.1; 2.2–14.2	*** 2.2; 2.2–5.2; 1.7–6.2 +	N/A
Water column pigments (medians; 25th–75th percentile range; minimum—maximum)			
Chlorophyll *a* (μg L^{-1})	1.6; 1.4–1.9; 0.8–2.6	*** 0.2; 0.2–0.2; 0.0–0.9 ***	0.18; 0.15–0.23; 0.0–0.94
%Picophytoplankton	22; 20–24; 16–26	* 43; 25–47; 22–53 **	47; 44–53; 33–76
%Microphytoplankton	71; 69–74; 66–79	** 46; 43–65; 38–70 **	38; 35–45; 11–53
Bottom sediment data (medians; 25th–75th percentile range; minimum—maximum)			
Sediment group	MFR–M&sM	MFR–mS&S	REL–S
%Mud	45; 12–78; 1–96	* 13; 2–31; <1–96 ***	<1; <1–2; <1–19
Fe (mg g^{-1})	37; 19–44; 8–48	** 18; 13–23; 9–51 ***	7; 5–10; 3–17
Available P (mg g^{-1})	0.16; 0.16–0.19; 0.11–0.2	** 0.07; 0.06–0.09; 0.03–0.21 ***	0.02; 0.02–0.03; 0.01–0.07
TOC (mg g^{-1})	3.9; 2.5–5.3; 0.38–6.01	*** 0.89; 0.36–1.84; 0.13–6.95 ***	0.23; 0.21–0.36; 0.13–0.75
TN (mg g^{-1})	0.51; 0.31–0.7; 0.08–0.93	** 0.31; 0.15–0.39; 0.06–1.15 ***	0.09; 0.07–0.11; 0.07–0.25
TP (mg g^{-1})	0.42; 0.36–0.47; 0.21–0.55	*** 0.32; 0.25–0.36; 0.2–0.59 ***	0.19; 0.16–0.23; 0.12–0.31
TOC:TN (molar)	3.4; 2.7–3.8; 1.9–7.6	*** 5.3; 3.7–5.5; 0.5–49.8 ***	8; 5.9–9.9; 4.6–13.4

The difference between two sample means (ZMR versus CTZ and CTZ versus BWZ) for all variables was analysed using a Wilcoxon rank sum test in *R* (R Development Core Team 2007), as the samples are either non-normal in distribution or heterogeneous in variance. The results show that the difference between two samples is statistically significant for all variables. Results (*p* values) are shown in the CTZ column: $p \leq 0.05$ (*); $p \leq 0.01$ (**); $p \leq 0.001$ (***); and indeterminable (+). Symbols on the left hand side of the numbers in the CTZ column refer to comparisons made between the ZMR and the CTZ, and symbols on the right hand side refer to comparisons between the CTZ and the BWZ. BD refers to nutrient concentrations that were below the limits of analytical detection

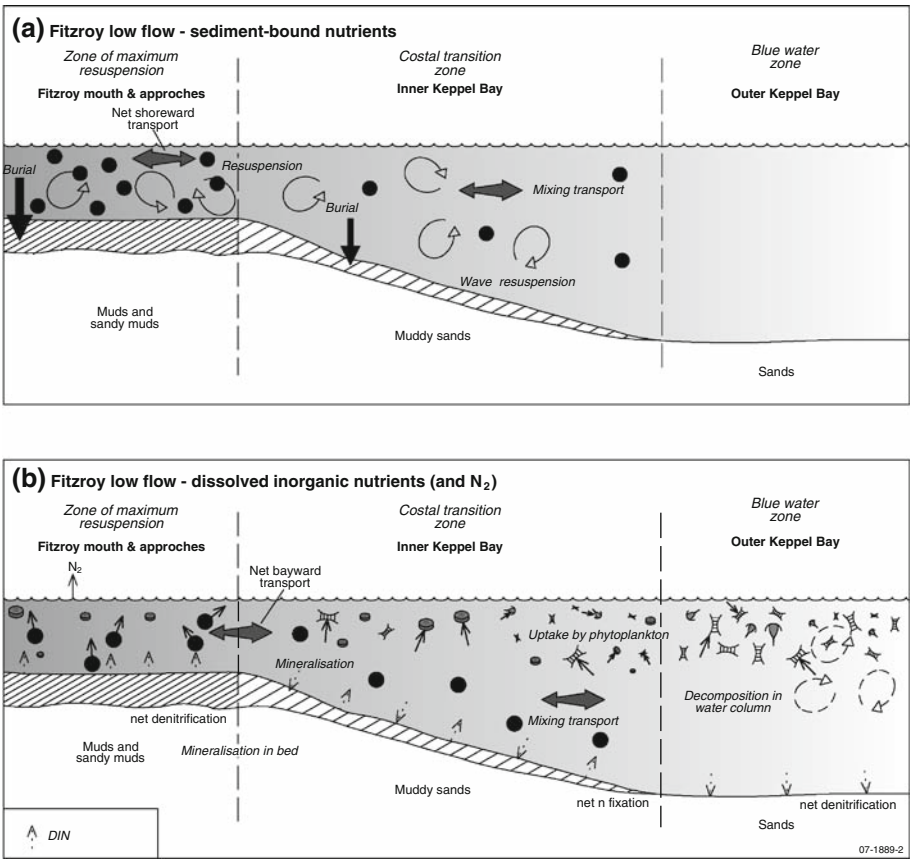

Fig. 10 Conceptual models of **a** particulate nutrient dynamics; and **b** dissolved inorganic nutrient dynamics in Keppel Bay. The diagrams are divided into three functional process regions: the Zone of Maximum Resuspension; the coastal transition zone; and the blue water zone which correspond to the Fitzroy mouth and approaches to the tidal creeks, and near-shore Keppel Bay, respectively. The elements pertaining to N-fixation are from Webster and Radke (2006)

5.1.1 The Zone of Maximum Resuspension

Processes occurring in turbidity maximum zones exert a fundamental control on nutrient cycling in coastal areas (Abril et al. 2000; Goni et al. 2005). This zone arises in Keppel Bay, because of the large currents, geomorphic factors and asymmetric tides. In other systems, tidal asymmetries, gravitational circulation and stratification all contribute (reviewed in Goni et al. 2005). MFR sediments form the seabed near the estuary mouth and in the near-shore area between Cattle Point and Keppel Sands (Fig. 3b). Sediment transport modelling has shown that these are the regions where the highest deposition rates of sediments occur under low- and moderate flood conditions (Webster et al. 2006). However, the ZMR encompassing the Fitzroy mouth (delta) and tidal creeks is shallow and had the highest percentage of sediment in the mud size fraction (Table 3). The co-occurrence of fine grain sizes with very high shear velocities was first described in the high-energy Severn Estuary (Hamilton 1979).

Fine sediments are delivered to Keppel Bay during floods, but most of these settle out near the mouth of the Fitzroy estuary due to flocculation. Subsequently, these sediments undergo cycles of settling and resuspension due to the strong tidal currents. Some sediment escapes and is transported towards the north-west by the prevailing current. Much of the sediment is pumped back into the Fitzroy estuary and tidal creeks through tidal asymmetry where it is ultimately buried (Ryan et al. 2007). The flood-tide is shorter in the estuary and thus faster than the ebb-tide, and resuspends more sediment on the inflow than the outflow. A study of Chesapeake Bay has highlighted that retention of PP and PN in an estuary depends critically on the retention of particulate organic matter (POM), which is controlled by geomorphology and circulation patterns (Boynton et al. 1995). Based on measured sedimentation rates and nutrient concentrations within the sediment column, the amount of nutrient buried appears to be approximately 30% and 50% of the modern inputs of TN and TP by the Fitzroy River to its estuary (Webster et al. 2006). Most of the sediment accumulation occurs on the floodplain and in the ZMR (Bostock et al. unpublished data). Indeed, deltas are the most important depocenters for organic carbon (C_{org}; and nutrients) in marine environments, accounting for about 50% of the global burial flux (Hedges and Keil 1995).

The dry season mixing diagrams had an inverse structure with the highest inorganic nutrient concentrations occurring at the highest salinity levels in the near-shore areas of the ZMR (Fig. 7). These inshore salinity levels were elevated by as much as one over values further offshore and are attributed to evaporation. Such conditions (evaporation exceeds precipitation giving rise to elevated salinity) typify inverse estuaries such as Shark Bay (Smith and Atkinson 1983), Spencer Gulf (Smith and Veeh 1989) and San Quintin Bay (Camacho-Ibar et al. 2003), which are found in the arid tropical to subtropical regions (Eyre 1998).

Both the core incubation experiments, and the simple box model based on the spatial distribution of salinity in the ZMR, show fluxes of NO_x and FRP from the sediments in this ZMR. In contrast the core incubation flux data in the other two zones (Table 2) indicates net up-take of DIN probably by benthic phytoplankton growing in the better (vis a vis ZMR) light climate. The FRP fluxes are too small to draw any valid conclusions. The measured O_2 fluxes for ZMR (average 7.9 (SD 0.9) mmol m^{-2} day^{-1}) fall between the values estimated from the DIN and DIP fluxes. The differences in O_2 fluxes between the different zones are slight and, if anything, the CTZ zone actually has a higher O_2 flux than the other two zones. This is contrary to the fluidized bed sub-oxic reactor paradigm as the mud zone with greatest resuspension usually has the highest metabolic rate. The benthic O_2 fluxes throughout Keppel Bay are all substantially less than those measured in the mud zone of the Gulf of Papua (Alongi 1995). This suggests that the reactivity of the organic matter is less in Keppel Bay.

Soil organic carbon is the principle form of organic matter entering the Fitzroy Estuary (Ford et al. 2005), and a mineral sediment also dominates TSS in the ZMR (Oubelkheir et al. 2006). Likewise, sediment-bound nutrients were the main form of nutrients near the Fitzroy mouth at the time of the dry season surveys (Figs. 8, 9). The ZMR seabed sediments had the highest carbon and nutrient concentrations for the bay because the delivery of mineral with high surface area is a key control on organic matter preservation in coastal margin settings (Keil et al. 1997). Terrestrial weathering has caused progressive fining of soil and increases in the specific surface area and secondary (reactive) iron mineral concentrations. The observed linear increase in Fe concentrations per unit mass of sediment with the specific area of these sediments (i.e. 0.46 mg Fe m^2 sediment; Fig. 5a) is consistent with the weathering process. The amount of carbon and nutrients per Fe surface area

equivalent of the Keppel Bay surface sediments were similar to those of underlying Holocene age sediment (vibracores in Fig. 5b, c, d), suggesting that most of the organic matter we see in surface sediments is refractory. Indeed, the carbon and nutrient concentrations of the seabed sediments were ~40–65% lower than those of the parent sediments/soils from the catchment (Fig. 5b, c, d) suggesting that there has been desorption or degradation of a significant component of the terrestrial POM. This result is consistent with global patterns: POM is delivered by rivers at approximately twice the rate that it accumulates in marine sediment (Keil et al. 1997). The ZMR is thus a zone where dissolved nutrients are being released from particulate terrestrially sourced sediments.

Terrestrial particles undergo major transitions in surface characteristics, chemistry and microbiology when they enter seawater, and even seemingly recalcitrant organic substances can be degraded in energetic deltaic settings and replaced with recently formed marine substances (Fig 4b; Aller et al. 1996). Physical disturbance and re-working of sediments, when coupled with the input of Fe-oxide rich debris, produces a particularly efficient decomposition system characterised by repetitive redox successions (oxic to sub-oxic, temporarily sulfidic), iron re-oxidation and metabolite exchange (i.e. the sub-oxic batch reactor; Aller et al. 1996).

The O_2:CO_2 in core incubation experiments on ZMR sediments (Fig. 6) lie substantially below 1.3 suggesting the involvement of sub-oxic processes in the remineralisation of the sediment organic matter. Iron-oxyhydroxide reduction is likely a dominant process because TS concentrations <0.1% and Fe concentrations in the range of 42.8–50 mg g^{-1} are geochemical features that ZMR muddy sediments share with Amazon shelf sediments where the sub-oxic batch reactor concept was developed (Aller et al. 1986). The ZMR bottom sediments are an important source of nitrate to the water column (Table 2) as in other tropical systems (Eyre 1994). Release of inorganic nitrogen to the water column would likely be facilitated by resuspension, as demonstrated in nearby Bowling Green Bay (Ullman and Sandstrom 1987).

Water column NO_x concentrations in the ZMR typically ranged from 0.018 to 0.035 mg L^{-1} (Table 3), which is higher than those observed during the dry-season in some tropical Australian estuaries with near-pristine catchments (Annan, Daintree and Jardine; Eyre and Balls 1999). These concentrations were also higher than those measured at the seaward end (salinity >30) of the Moresby Estuary, which is another tropical tide-dominated system with significant disturbance in the catchment (Eyre 1994). The median NO_x concentration (0.026 mg L^{-1}; Table 3) was also similar to those found in nine wave-dominated, subtropical deltas (Australia) subject to discharge of varying amounts of wastewater DIN (Eyre 2000). It is likely that some NO_x was derived from the nitrification of NH_4^+ previously adsorbed onto sediment particles because a cross-plot of sediment TN versus TOC (not shown) had a *y*-intercept of 0.32 mg g^{-1} TN for muddy sediments, indicating that there was an inorganic sediment N pool as well as another pool involving organic matter. In addition, NO_x concentrations correlated with TSS in September 2003 when the sampling of Casuarina Creek coincided with spring-tide conditions and higher TSS levels were observed (Fig. 9c). Chemical studies of the Tamar Estuary have shown that nitrification rates are often high in resuspension zones because waters over there are highly oxygenated and nitrifying bacteria occur attached to sediment particles (Owens 1986).

FRP concentrations in the ZMR typically ranged from 0.009 to 0.014 mg L^{-1} (Table 3). These concentrations are considerably higher than those observed in the near-pristine tropical estuaries during both the wet and dry seasons (Eyre and Balls 1999). The median concentration was 0.012 mg L^{-1} (Table 3) and was similar to average dry-season

concentrations reported for some wave- and tide-dominated deltas with greater catchment modification (Eyre 1994; Eyre and Balls 1999). Except at a few sites, the FRP concentrations tended to stabilize, with increasing TSS, at $\sim$0.015 mg L^{-1} (Fig. 9d). This was likely due to the phosphate buffer mechanism (Froelich 1988) because the shape of the FRP relationship with TSS resembled a Langmuir isotherm for phosphorus adsorption (Webster et al. 2001; Fig. 9d), and the role of adsorption to Fitzroy marine sediments in controlling phosphate concentration has been demonstrated (Payne et al. 2002). The strong correlation between TP and Fe in the underlying sediment (Figure 5d) also suggests that equilibration with solid phase ferric iron is an important control on FRP concentrations. The partially reversible adsorption of phosphate onto sediment usually regulates concentrations in estuaries at higher levels than we observed (i.e. 0.019–0.043 mg L^{-1}; reviewed in Eyre 1994). Many factors can influence the nature phosphate buffering including pH, ionic strength and sediment composition (reviewed in Eyre 1994).

Total suspended matter (TSS) concentrations were high (Table 3) compared to wet- and dry-season concentrations from other tropical tide-dominated systems (Eyre 1994; Eyre and Balls 1999), and undergo a pronounced semi-diurnal variation whose amplitude varies over the 14-day spring-neap tidal cycle. Interestingly, chlorophyll a concentrations were highest for Keppel Bay in the Fitzroy mouth region (Table 3; Oubelkheir et al. 2006), whilst estimated production rates, which varied by only a factor of three in Keppel Bay (August 2004), were comparatively low (Ford, unpublished data). The chlorophyll may have been derived from algae washed from the mud banks. Presumably, production was limited by the availability of light allowing dissolved inorganic nutrients to build up in the water column to the extent that the estimated timescale of dissolved inorganic nitrogen utilisation was in the order of a few days (Ford, unpublished data). This effect of TSS in delaying nutrient utilisation by phytoplankton has been observed in many rivers including the Mississippi (Lohrenz et al. 1999), the Changjiang (Tian et al. 1993) and the Amazon (Smith and DeMaster 1996). The ZMR thus appears to represent a zone in which inorganic nutrients are generated and then transported by tidal and wind-driven currents to further offshore where the light climate is more conducive to their biological utilisation.

5.1.2 The Blue Water Zone

The second zone in our classification is the clear blue low inorganic nutrient waters of outer Keppel Bay. The BWZ (Fig. 10) is roughly coincident with the distribution of relict sands (Fig. 3b). Ryan et al. (2007) sees the relict sands (REL-S) as a former sandy coastal plain that was drowned by rising sea levels in the early Holocene. These sediments have lower Fe, carbon and nutrient concentrations due to their extended presence in the marine environment (Table 3): the feldspars have broken down into clays, which have winnowed out of the seabed by hydrodynamic processes, whilst more resistant quartz has been retained. The effect of waves on resuspension is diminished due to larger depths (>10 m) and particle sizes, and TSS is mainly less than 2 mg L^{-1} (Table 3).

Phytoplankton dominate TSS in these clear offshore waters (Oubelkheir et al. 2006), and dissolved N and P pools were strongly dominated by organic nutrients (Fig. 8b). The transition to the BWZ may constitute a domain shift in the terminology of Karl et al. (2001) because it was marked by a parallel increase in phytoplankton diagnostic pigments indicative of cyanobacteria, and in the overall dominance of pico-phytoplankton (Table 3; Oubelkheir et al. 2006). The pico-cyanobacteria genera *Synechococcus* and *Prochlorococcus* usually dominate primary production and phytoplankton biomass in offshore Great Barrier Reef waters (Furnas et al. 2005), and likely also in Keppel Bay. Tufts of nitrogen-fixing

Trichodesmium were also frequently observed in near-surface waters. *Trichodesmium* is known to supply nitrogen to the GBR in amounts similar to those entering from the GBR catchment area, and community dynamics are expected to shift towards phosphorus limitation in the presence of such large amounts of fixed-N (Bell et al. 1999). Indeed, pico-phytoplankton biomass tends to be highest in oligotrophic and especially P-limited waters (Joint 1986; Agawin et al. 2004), whilst micro-phytoplankton are known to out-compete smaller species in areas of high nutrient supply (Donald et al. 1997). P-limitation has been documented in Moreton Bay (Eyre and McKee 2002) and in several estuaries in subtropical eastern Australia (Eyre 2000), whilst nutrient limitation was evident in the BWZ in NO_x and FRP concentrations that were always below the limits of analytic detection (Table 3).

Positive correlations between pico-phytoplankton biomass and TN:TP supply ratios have been observed in a few studies (Stockner and Shortreed 1988; Suttle and Harrison 1988; Takamura and Nojiri 1994), and are consistent with our observations. Most TN:TP ratios were in a range from 30 to 50 in outer Keppel Bay, compared to 24–36 in the CTZ and 10–15 near the estuary mouth (Table 3). The success of pico-phytoplankton in nutrient-depleted waters may in part rely on their ability to utilise numerous and sometimes novel organic P and N sources including cyanates and phosphonates (Fuller et al. 2005), and in part on their different uptake efficiencies. For example, Donald et al. (1997) demonstrated that P-starved *Synechococcus* possessed a lower half saturation concentration for inorganic-P uptake than certain diatoms, although the uptake of P by diatoms was faster under P-replete conditions. Moreover, some *Trichodesmium* are known to utilise components of the DOP pool for their P-nutrition (Mulholland et al. 2002), and that includes species found in Great Barrier Reef waters (Bell et al. 2005). *Trichodesmium* are also known to excrete up to 50% of the nitrogen they fix in the form of DON (Glibert and Bronk 1994). Therefore, uptake of DOP and/or release of DON by *Trichodesmium* (and other species) are possible explanations for higher TN:TP ratios in outer Keppel Bay (Table 3). The apparent P-limitation may be related to the low bio-available P concentrations of the seabed sediments (Fig. 4a; Table 3). The relict sands found in this region had the highest proportions of residual-P. The minerals that make up the residual-P pool may include resistant rare-earth phosphates such as xenotime and monazite. These minerals are likely to occur in the granitic terrain of the New England Fold Belt, and can contain as much as 25% phosphate by weight.

Based on very limited data (Table 3) the sediments of the BWZ were a net sink for DIN, and to a lesser extent FRP. Competition for water column DIN for heterotrophic and autotrophic metabolism increases with light availability (Ferguson et al. 2007), and may explain why only net uptake of nitrogen was observed in BWZ sediments but not elsewhere in the Bay. As with most GBR waters, the bulk of phytoplankton N and P demand in the BWZ is probably met by microbial cycling in the water column (Furnas and Brodie 1996).

5.1.3 The Coastal Transition Zone

The CTZ (Fig. 10) covers inner Keppel Bay, and is characterised by smaller tidal currents then the ZMR. However, being relatively shallow it is subject to resuspension due to the combined effects of tidal currents and waves. The CTZ was approximately coincident with the distributions of MFR sand and muddy-sand sediments (Fig. 3b) and the distribution of turquoise-coloured waters. MFR muddy-sand sediments are confined to near the coast of inner Keppel Bay by waves approaching from the east and southeast, and are transported

towards the north with the prevailing currents. Episodic winds from the north in summer and tidal mixing, account for the spread of these sediments in the direction of Hummocky Island (Fig. 3b).

Except at a few sites, nutrient concentrations in the CTZ tended to lie below the conservative mixing line evident in the ZMR (Fig. 7). Consequently, one might surmise that in this region nutrients are being utilised from the water column. The lower turbidity levels in this zone as compared to the ZMR would favour more vigorous uptake by primary producers in the water column and on the seabed here. TSS concentrations need to drop below about 10 mg L^{-1} in order that there is sufficient light for abundant phytoplankton growth (reviewed in Devlin and Brodie 2005). TSS in the CTZ was usually in a range from 2 to 8 mg L^{-1}, and the timescale of water column N-utilisation assuming that the measured photosynthesis rate was associated with nitrogen utilisation at Redfield, ratio (August 2004) ranged from <0.05–0.3 days (Ford, unpublished data). However, tidal advection and resuspension of sediment caused TSS to fluctuate to as high as 46 mg L^{-1} (Table 3). As a consequence, TSS concentrations in CTZ resuspension plumes could increase to above levels that are generally considered limiting to primary production. This would allow dissolved nutrients (mainly P) to in some cases follow the conservative mixing lines (Fig 7a) and move further offshore, as in river flood plumes (Devlin and Brodie 2005).

The CTZ was also unique in the respect that there was no clear pattern in the dominant form of P (i.e. dissolved organic, inorganic or particulate; Fig. 8b). This was also due to the fluctuations in TSS (and likewise PP concentrations) modulating light levels and the extent to which water column FRP could be utilised. The wide tidal excursion prevents any simple demarcation between the two end-members, and may have also allowed for the apparent co-dominance of pico-phytoplankton (mainly cyanobacteria) and micro-phytoplankton (mainly diatoms; Fig. 8b and Table 3; Oubelkheir et al. 2006). Nitrogen was probably the limiting nutrient during times of light sufficiency because DIN:FRP ratios were always less than 10:1 (reviewed in Eyre 2000; Table 3). Low inorganic nitrogen concentrations in the water column together with moderate concentrations of iron and available-P in the sediment (Table 3), may account for the apparent occurrence of benthic N-fixation in this region. Webster and Radke (2006) have estimated that benthic N-fixation supplies 3,200 ± 1,700 t N $year^{-1}$ to inner Keppel Bay, which is nearly half of the amount delivered from the catchment (Brooke et al. 2008). However, the implied N-fixation rates in this study were high (up to 3.5 mmol day^{-1}), and were based on correlations between sediment Fe^{3+} concentrations and net uptake of di-nitrogen observed in dark incubation experiments (no light incubations were undertaken). In addition, the negative N_2 fluxes were measured with the N_2/Ar method, and are the subject of controversy (C. Smith, written communication, Dec 5/2008). Notwithstanding, N-fixation contributes importantly to the N budgets of other tropical and sub-tropical coastal areas (Eyre and McKee 2002 and references therein). Thus, it is reasonable to assume that it also has an important role in Keppel Bay.

Sediment Fe(II) concentrations were high relative to TS and TOC (Fig. 3c). This relationship points to the widespread occurrence of iron oxyhydroxide reduction in the CTZ. Particularly high loadings (PCA axis 2) of FeII:FeIII were observed along the western beach fringe (Fig. 3) where wave-induced reworking of the bottom sediment likely leads to reoxidation of previously reduced Fe (and Mn) oxides, regenerating a readily available oxidant for further sub-oxic reactions. The sediments in this region are, by far, the best sorted in Keppel Bay (Ryan et al. 2007) supporting our hypothesised frequent reworking. Bacteria rather than macrofauna dominate benthic biomass where there is

frequent reworking of the seabed (Alongi 1995), and are another potential explanation for the low TOC:TN ratios in the sediment of the region (Fukuda et al. 1998; Fig. 5).

6 Summary

Keppel Bay receives large amounts of fine sediment with associated particulate nutrients delivered by infrequent flood events. Most of this material is deposited initially near the mouth of the Fitzroy Estuary. During the subsequent protracted low-river flow period, the vigorous tides repeatedly resuspend, transport and deposit the fine sediments, and the particulate-attached nutrients are mineralised as they are subject to oscillating redox conditions during transitory burial and resuspension. Under low-flow conditions the nutrient dynamics in Keppel Bay reflects the interplay of internal biogeochemical processes, biological utilisation and hydrodynamic factors which mix and transport nutrient and phytoplankton laterally, determine the redox conditions in sediments, and regulate light climate through the control on concentrations of fine-grained sediments in the water column. All these characteristics have a marked spatial variability. Consequently, Keppel Bay, rather than being an undifferentiated sub-oxic muddy fluidized bed reactor can be divided into three biogeochemical zones based on the nature of the underlying sediment, TSS levels (related to depth and macrotidal tidal forcing), phytoplankton functional groups and on the degree of input and biological uptake of dissolved inorganic nutrients. These zones: the Zone of Maximum Resuspension, the Blue Water Zone, and the Coastal Transitional Zone integrate our observations and provide a conceptual framework (Fig. 10), for a more differentiated understanding of terrestrially derived dissolved and particulate nutrient dynamics in "muddy" tropical coastal zones. Recognition of these zones in the relatively small-scale Fitzroy embayment points to possible nuances in biogeochemical processing in the "giant" fluidized bed sub-oxic reactors such as the Amazonian mudbanks and the Gulf of Papua.

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