Biogeochemistry (2012) 108:359–380
DOI 10.1007/s10533-011-9605-z

Effect of nutrient loading on biogeochemical processes in tropical tidal creeks

Jodie Smith · Michele A. Burford · Andrew T. Revill · Ralf R. Haese · Julia Fortune

Received: 27 April 2010 / Accepted: 19 April 2011 / Published online: 22 May 2011

Abstract The effect of increased nutrient loads on biogeochemical processes in macrotidal, mangrove-lined creeks was studied in tropical Darwin Harbour, Australia. This study uses an integrative approach involving multiple benthic and pelagic processes as measures of ecosystem function, and provides a comparison of these processes in three tidal creeks receiving different loads of treated sewage effluent. There were significant differences in process rates between Buffalo Creek (BC) (hypereutrophic), which receives the largest sewage loads; Myrmidon Creek (MC) (oligotrophic–mesotrophic) which receives smaller sewage inputs; and Reference Creek (RC) (oligotrophic) which is comparatively pristine. Benthic nutrient fluxes and denitrification were more than an order of magnitude higher and lower, respectively, in BC and denitrification efficiency (DE) was <10%. Pelagic primary production rates were also much higher in BC but respiration exceeded primary production resulting in severe drawdown of O_2 concentrations at night. Hypoxic conditions released oxide-bound phosphorus and inhibited coupled nitrification–denitrification, enhancing benthic nitrogen and phosphorus fluxes, leading to a build-up of excess nutrients in the water column. Poor water quality in BC was exacerbated by limited tidal flushing imposed by a narrow meandering channel and sandbar across the mouth. In contrast to BC, the effect of the sewage load in MC was confined to the water column, and the impact was temporary and highly localized. This is attributed to the effective flushing of the sewage plume with each tidal cycle. Denitrification rates in MC and RC were high (up to 6.83 mmol N m^{-2} day^{-1}) and DE was approximately 90%. This study has identified denitrification, benthic nutrient fluxes and pelagic primary production as the biogeochemical processes most affected by nutrient loading in these tidal creek systems. Physical process play a key role and the combined influence of nutrient loading and poor tidal flushing can have serious consequences for ecosystem functioning.

Keywords Benthic fluxes · Coupled nitrification–denitrification · Hypoxia · Nutrient loads · Primary production

J. Smith (✉) · R. R. Haese
Marine and Coastal Environment Group, Geoscience Australia, GPO Box 378, Canberra, ACT 2601, Australia
e-mail: jodie.smith@ga.gov.au

M. A. Burford
Australian Rivers Institute, Griffith University, Brisbane, Australia

A. T. Revill
CSIRO Marine and Atmospheric Research, Hobart, Australia

J. Fortune
Aquatic Health Unit, Northern Territory Department of Natural Resources, Environment, the Arts and Sport, Darwin, Australia

Introduction

Estuaries are complex, open systems that often experience large inputs of organic matter and inorganic nutrients from land. Biogeochemical processes subsequently determine the extent of nutrient transformations, retention and export to the ocean. Tropical estuaries are among the most biogeochemically active regions in the biosphere, but the processes are complex due to factors such as highly variable hydrodynamics, particularly in macrotidal systems (e.g. Wolanski et al. 1980), large organic matter inputs from fringing mangroves (e.g. Dittmar et al. 2006), large monsoonal freshwater inputs (e.g. Sarma et al. 2009), as well as heavy bioturbation in intertidal sediments (e.g. Pratihary et al. 2009).

Changes to the structure and function of estuaries due to increased anthropogenic nutrient loadings arising from such diverse sources as urban and rural run-off, sewage discharges and aquaculture are well known (Nixon 1995; Herbert 1999; Cloern 2001; Clarke et al. 2006). The increased input of nutrients to shallow marine environments, including estuaries, and the accompanying stimulation of primary production enhance organic matter supply to sediments, increasing benthic metabolism and resulting in greater nutrient release and rates of oxygen consumption (Richardson and Jørgensen 1996; Herbert 1999; Cloern 2001). Hypoxia is a common effect of nutrient loading in coastal marine ecosystems and the effects are most severe in areas such as shallow embayments or where tidal flushing is limited (Herbert 1999; Diaz and Rosenberg 2008). Hypoxia influences biogeochemical processes that control nutrient concentrations in the water column (Conley et al. 2009) and can lead to dead zones which have serious consequences for ecosystem structure and functioning (Diaz and Rosenberg 2008). Thus, increased nutrient loads can have important consequences for the structure of estuarine communities, aquatic food webs and estuarine water quality.

Nutrient loading is considered to be the most widespread problem in estuaries around the world and is likely to increase in the future (Howarth et al. 2002). The impact is expected to be greater in the tropics than at higher latitudes (Downing et al. 1999) and on a global scale, tropical regions such as southeast Asia are particularly vulnerable in terms of ecosystem alteration due to anthropogenic nutrient loading (Mackenzie et al. 2002; Jennerjahn et al. 2004; Halpern et al. 2008). The effects of altered nutrient cycling in tropical ecosystems can be understood most easily in the context of nutrient dynamics in undisturbed or minimally disturbed tropical ecosystems, however, nutrient processing in tropical estuaries, in general, is poorly studied relative to temperate environments (Downing et al. 1999; Bianchi 2007) and there are even fewer studies comparing biogeochemical cycles in disturbed and undisturbed tropical systems (Trott et al. 2004; Kristensen et al. 2008). Additionally, these studies are often limited in the suite of processes measured, with much of the information available tending to be focused on individual processes (Boynton et al. 2008). This study uses an integrative approach involving multiple benthic and pelagic processes as measures of ecosystem function, and provides a comparison of these processes across a gradient of nutrient loads in a tropical estuary. This study also provides the first reported measurements of denitrification in Darwin Harbour.

The aim of this study was to determine the effect of increased nutrient loads on multiple biogeochemical processes within tropical tidal creeks in Darwin Harbour and to identify which processes are most effective in determining eutrophication impacts in tidal creeks. Darwin Harbour is an N-limited system and is subject to anthropogenic nutrient inputs from urban and rural-runoff, as well as treated sewage effluent. Impacts on water quality in Darwin Harbour as a result of seasonal and point source nutrient inputs have been reported previously (e.g. McKinnon et al. 2006; Burford et al. 2008) and fish kills have occurred in tidal creeks receiving sewage effluent. There is potential for more severe impacts on water quality and overall ecological health in the future due to increasing population and land development. Indeed, Darwin has the most rapid population growth in Australia. Considering the rapid changes occurring in tropical estuaries as a result of nutrient enrichment associated with point and non-point sources, understanding the functioning of these systems and their interactions is important to be able to correctly assess the health of estuaries (Bouillon and Connolly 2009).

Materials and methods

Study area

The study was performed in three tidal creeks in Darwin Harbour in northern Australia (Fig. 1). Darwin Harbour is a large macrotidal estuary with a maximum tidal range of 7.8 m. The harbour is fringed by dense mangroves and during low tide, extensive intertidal mudflats are exposed (Fig. 1). The region is influenced by a tropical monsoonal climate characterized by high year-round temperatures and a highly seasonal rainfall pattern, with over 1,300 mm falling during the monsoon season (December–March). River flow into the harbour is also highly seasonal with maximum flow between January and March and a cessation in flow between May and July. Although the harbour experiences a distinct wet season, the catchment is relatively small and wet season runoff has relatively little impact over the whole harbour. Most of the freshwater runoff occurs in the form of a few discrete flood events during which the upper reaches of the harbour may become fully fresh. However, there is no marked river plume exiting the harbour and salinity remains almost constant at the mouth of the harbour throughout the year, implying that freshwater runoff is strongly diluted by the time it reaches the mouth (Williams et al. 2006).

The majority of nutrients that enter the harbour are imported from the ocean and are typically in the particulate or organic form (Burford et al. 2008). Nutrients also enter the harbour from the surrounding catchment and include both diffuse sources, such as urban and rural runoff, and point sources such as treated sewage effluent which is discharged into both the main body of the harbour and several tidal creeks on the fringes. Overall, the harbour is considered relatively pristine (McKinnon et al. 2006).

Field stations and sampling

Sediment and water column sampling was carried out at two sites in three tidal creeks; an unnamed creek (herein referred to as Reference Creek, RC) and Myrmidon Creek (MC) in East Arm of Darwin Harbour, and Buffalo Creek (BC) in Shoal Bay (Fig. 1). RC and MC have similar geomorphology with predominantly straight channels, widening downstream (Fig. 1a, b). At low tide, intertidal mudflats, several metres wide, are exposed along the length of the creeks. The upper reaches of the creeks may be fully drained at low tide, however the creeks contain water at all times. BC consists of a long, narrow channel with large meander bends at the downstream end (Fig. 1c). Upstream the channel becomes even narrower and meanders through dense, overhanging mangroves. Intertidal mudflats occur on the meander bends and along sections of the main channel. A large intertidal sand bar across the mouth inhibits tidal movement to a significant degree.

Reference Creek is considered to be near-pristine with no known impact from urbanization or land development (Woodroffe et al. 1988). MC and BC receive sewage effluent from sewage treatment plants (STP) which use waste stabilization ponds to remove organic matter and nutrients. MC receives 69 t TN $year^{-1}$ and 18 t TP $year^{-1}$ and the treated sewage effluent is discharged into the mangroves close to site MC1 (Fig. 1b). BC receives 79 t TN $year^{-1}$ and 43 t TP $year^{-1}$ and the treated sewage effluent is discharged into dense mangroves at the upstream end of the creek (Fig. 1c). While the sewage loads entering BC and MC are similar, the dimensions and hence water volume are much lower in BC than in MC. The sewage discharge is gravity-fed, i.e. there is only discharge when the tide level is below the outflow pipe. At high tide, flow is stopped.

This study was conducted during 2007–2008 over three sampling periods. Rapidly changing tidal conditions limited boat access to many areas of the harbour and the sampling sites and times were chosen based on those areas that were accessible in practice. Therefore, we have to assume that the tidal creeks and sites within each creek were representative. Each sampling period lasted 5–6 days in between spring and neap tides during the 2-week tidal cycle. Surveys during the wet and dry season were undertaken to differentiate land runoff effects from sewage effluent inputs. Sewage effluent inputs are relatively constant all year round. RC and MC were sampled in the dry and wet seasons (October 2007 and March 2008). BC was sampled at the end of the dry season (early December 2008). We have assumed that our sampling periods were representative of the seasonal cycles and we have no reason to believe environmental conditions (e.g. STP discharge, water quality

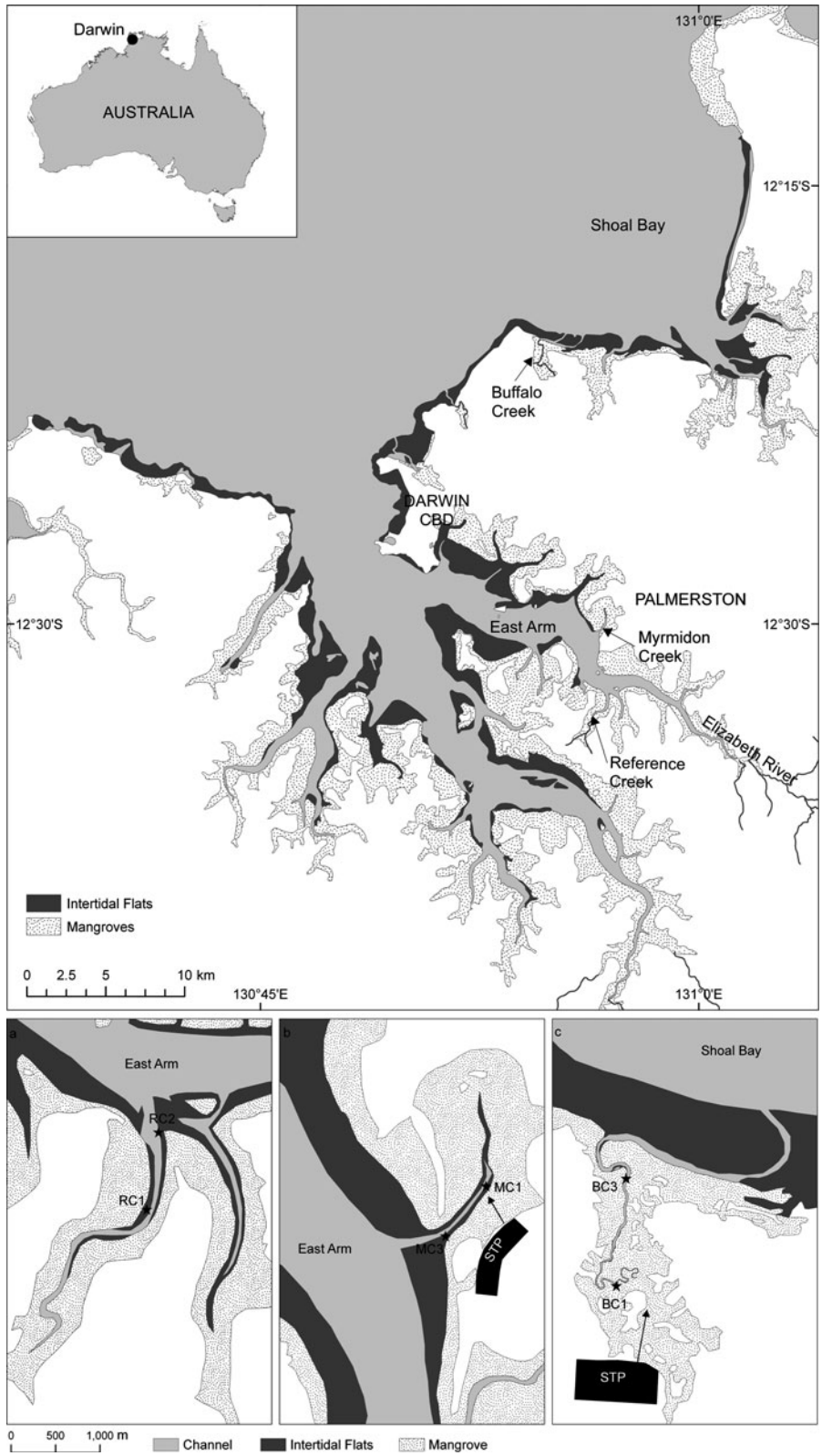

Fig. 1 Map of Darwin Harbour, Australia showing the three tidal creeks and sampling sites in:
a Reference Creek,
b Myrmidon Creek and
c Buffalo Creek

conditions) would be significantly different at other times during each season.

Water column physico-chemical conditions

Water sampling was conducted at least twice (typically on consecutive days) at each site in MC and RC during the ebb tide. In BC, initial field observations indicated rapidly changing physico-chemical conditions during the tidal cycle so water sampling was conducted every 1–2 h during the benthic chamber deployments and additional sampling conducted on consecutive days.

Water column parameters (temperature, salinity, dissolved oxygen) were recorded at each site with a YSI sonde (6000XLM). Photosynthetically active radiation (PAR) was measured during the middle of the day at water depth intervals of 0.5–1 m using a LI-COR light meter with a 4π quantum underwater sensor (LI-192) and this data used to calculate the euphotic depth (Z_{eu}). Surface water samples were collected in 1 l bottles. Total suspended solids (TSS) was determined by filtering water samples using pre-weighed membrane filters (0.45 μm, Millipore), drying at 60°C and re-weighing. Sub-samples were filtered (0.45 μm, Bonnet) into 30 ml tubes and frozen until analysis for nutrients. Samples for chlorophyll *a* (chl *a*) were collected by filtering water from just below the surface through GF/F filters (Whatman) using a manual pump. The filters were placed in cryotubes and stored in liquid nitrogen until analysis.

During the December 2008 field campaign in MC, continuous measurements of physico-chemical parameters were made using a YSI sonde over a 5 h period from high tide to low tide to measure the treated sewage effluent plume as it emerged from the mangroves. Surface water samples were collected at approximately 1 h intervals and were measured for TSS, total nutrients and chl *a*.

Pelagic primary productivity and respiration

Water column primary production was measured using ^{13}C-uptake incubations. Water samples collected just below the surface were stored in buckets during transport to the field laboratory. 500 ml acid-washed polycarbonate bottles were filled with water collected from each site. Triplicate bottles from each bucket were incubated at 0, 5, 14, 25, 50 and 100% of surface light using shade bags of appropriate light attenuation. ^{13}C-sodium bicarbonate was added to bottles to give a final enrichment of between 3 and 5% of the total bicarbonate concentration.

The bottles were incubated in a large tank with flowing water at ambient water temperature. Bottles were incubated on either side of local apparent noon (when the sun was highest in the sky) for 2–3 h. Known volumes of water from the bottles were filtered onto precombusted glass fibre (Whatman GF/F) filters which were frozen until analysis. Hourly primary production rates were calculated as the change in carbon concentration at each light level. Maximum productivity (P_{max}, mmol C m^{-3} h^{-1}) was estimated from the 100% light incubation. Daily depth-integrated net primary production (NPP, mmol C m^{-2} day^{-1}) was calculated by integrating primary production rates through the water column based on the ^{13}C-bicarbonate incubation and light data, based on a 10 h daylight period.

Maximum production and respiration were also measured by means of oxygen production and consumption, respectively. Surface water was collected and incubated in four (two transparent, two opaque) gas-tight, 100 ml glass syringes (Hamilton). The syringes were incubated within the water column for 3–4 h. Four samples were removed from each syringe during the incubation for O_2 analysis, transferred into 12 ml gas-tight glass vials with glass stoppers, preserved with saturated $HgCl_2$ and stored submerged just below ambient temperature in the dark until analysis. P_{max} and respiration (mmol O_2 m^{-3} h^{-1}) were estimated as the change in oxygen concentration during light and dark incubations, respectively. Daily depth-integrated community respiration (CR, mmol C m^{-2} day^{-1}) was calculated assuming that respiration rates were constant with depth and respiration rates converted to carbon units assuming a respiratory quotient (RQ) of 1 (Laws 1991). Gross primary production (GPP) was calculated as the sum of NPP and CR during a 10 h daylight period, and the productivity:respiration (P:R) ratio calculated as the ratio GPP:CR.

Surface sediments

Sediment cores (6 cm dia.) were collected at each site using a push corer. Surface sediment (to 1 cm depth)

from one core was transferred into clean glass jars and homogenized. Clean aluminium foil was placed between the lid and contents to minimize organic contamination. The samples were frozen until analysis for TOC, TN and stable isotope composition. Subsamples were taken for chl *a* analysis and placed in cryo-vials in a liquid nitrogen dry shipper. Surface sediment from a second core was transferred to plastic vials and frozen for total phosphorus (TP) analysis. Porosity was determined on a subsample by weight difference between wet and dry sediment following freeze-drying.

Sediment primary productivity

Sediment cores (4.5 cm dia.) were collected at each site for measurement of primary productivity in the sediment. Capped cores were transported with overlying water from the study site to the field laboratory. Primary productivity was measured at 0, 10, 50 and 100% of surface light using shade bags of appropriate light attenuation. ^{13}C-sodium bicarbonate was added to bottles to give a final enrichment of between 40 and 50% of the total bicarbonate concentration to the overlying water.

The cores were incubated in a large tank with flowing water at ambient water temperature around local apparent noon for 2–3 h. The temperature was logged throughout the incubations. Cores were then kept in the dark until processed. The top 2 cm was sliced off each core and frozen until analysis.

Benthic flux incubations

Benthic chamber incubations were used to quantify the flux of dissolved inorganic nutrients ($f\mathrm{NH_4^+}$, $f\mathrm{NO}_x$, $f\mathrm{PO_4^{3-}}$, $f\mathrm{SiO_4}$) and dissolved gas (fDO, fDIC, $f\mathrm{N_2}$). Four manually operated benthic chambers (two transparent, two opaque), as described by Haese et al. (2007), were deployed at each site. Self-logging probes (YSI-600XL) continuously measured temperature, salinity and oxygen concentration inside and outside of the chambers. The incubation began after manually closing the chamber lid. Five or six chamber-water samples with a volume of 100 ml were taken during an incubation period typically lasting 3–5 h. Water samples for nutrient analysis were filtered immediately (0.45 μm) into 30 ml tubes and frozen until analysis. Samples for DIC were filtered (0.45 μm) into gas-tight vials (3 ml, Exetainer), preserved with saturated $\mathrm{HgCl_2}$ and stored in the dark until analysis. Samples for $\mathrm{N_2}$ were transferred into 12 ml gas-tight vials with glass stoppers, preserved with saturated $\mathrm{HgCl_2}$ and stored submerged just below ambient temperature in the dark until analysis.

Benthic nutrient and gas fluxes were calculated from concentration changes over time, accounting for the incubated sediment surface area and water volume and corrected for the replenishment of sample volumes by ambient bottom water. During high tide, the light chambers were beyond the photic zone, and data collected during these periods were used in the calculation of dark fluxes. Only the linear proportion of the concentration versus incubation time curve was used in the flux calculations. Water incubated by benthic chambers never reached oxygen concentrations below 20% saturation, with the exception of BC1 where ambient water was at or below this level at the start of the incubation. Denitrification efficiency (DE) was calculated from the dissolved inorganic nitrogen fluxes:

$$\mathrm{DE}\% = f\mathrm{N_2}/(f\mathrm{N_2} + f\mathrm{NH_4} + f\mathrm{NO}_x) \times 100 \qquad (1)$$

Benthic production (P) and respiration (R) were calculated as the change in carbon concentration during light and dark incubations, respectively. GPP was calculated as the sum of P and R during a 6 h light period, and the productivity:respiration ratio calculated as the ratio GPP:R.

Analytical methods

Dissolved inorganic nutrients, $\mathrm{NH_4^+}$, NO_x, $\mathrm{PO_4^{3-}}$ and $\mathrm{SiO_4}$ from the filtered surface water and benthic chamber samples were analyzed by automated flow injection analysis (Lachat). Dissolved inorganic carbon (DIC) was analyzed on an infrared gas analyzer (LiCOR 7000). $\mathrm{N_2}$ from the benthic chamber samples and $\mathrm{O_2}$ from the surface water syringe incubations were measured using a membrane inlet mass spectrometer (MIMS) (Kana et al. 1994). Filters from the ^{13}C-uptake incubations were dried at 60°C for 24 h before being analyzed for $^{13}\mathrm{C}/^{12}\mathrm{C}$ ratio and % carbon on a mass spectrometer (GV Isoprime, Manchester, UK). Sediment cores from benthic ^{13}C-uptake incubations were analyzed in the same way following treatment with 6 N hydrochloric acid to remove carbonates.

Chl *a* was extracted from sediment and water column filters prior to analysis by high performance liquid chromatography following the procedures outlined in Cook et al. (2004) and Haese et al. (2007), respectively. Sediment samples for stable isotope analysis ($\delta^{13}C$ and $\delta^{15}N$) were processed and analyzed as described in Cook et al. (2004). Results are presented in standard δ notation:

$$\delta(‰) = \left[\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1\right] \quad (2)$$

where $R = {}^{13}C/{}^{12}C$ or ${}^{15}N/{}^{14}N$. The standard for carbon is Vienna Pee Dee Belemnite (VPDB) while that for nitrogen is air. The reproducibility of the stable isotope measurements was ±0.2‰ for carbon and ±0.5‰ for nitrogen.

Sediment total P (TP) was determined by X-ray fluorescence using a Philips PW2404 4kW sequential spectrometer according to a modified version of Norrish and Hutton's (1969) method. The instrument was calibrated using United States Geological Survey (USGS) and South African Reference Material international standards. The reported precision was better than 5%.

Hydrodynamic calculations

A simple tidal prism model (Seabergh 2006) was used to estimate the exchange of water in the tidal creeks with marine water in the main body of the harbour, as this is the dominant influence on water quality (McKinnon et al. 2006). The tidal prism is computed as follows:

$$p = 2 * a(b) * A(b) \quad (3)$$

Where $a(b)$ is the tidal amplitude or ½ the tidal range and $A(b)$ is the water area. The exchange calculation is:

$$T_{(d)} = \frac{V}{(e * (0.78 * p))} * 0.5 \quad (4)$$

Where T is the residence (or flushing) time in days, V is the water volume of the tidal creek, 0.78 is a correction factor for the sinusoidal nature of tidal cycles, e is exchange efficiency, and 0.5 accounts for the semi-diurnal tides. The exchange efficiency (e) was estimated as 1 for RC and MC, 0.5 for BC3 and 0.2 for BC1 based on creek geometry. All other values used in the calculations are given in Table 1. This model assumes no significant freshwater inflow into the tidal creeks, which is valid since the largest measured cumulative runoff during an exceptional flood was only 1% of peak tidal discharge at the mouth of the harbour (Williams et al. 2006).

Statistical analysis

Statistical analysis was carried out using Statistica Version 6.0 (StatSoft). Differences in $P_{\max}$ measured using O_2 and ${}^{13}C$ measurements were compared using a t test. A 2-way analysis of variance (ANOVA) was carried out on log-transformed RC and MC wet and dry season data with site and season as factors. A 1-way ANOVA was carried out on log-transformed dry season data only from RC, MC and BC. The significance level (alpha) was specified as 0.05. A sequential Bonferroni (Sokal and Rohlf 1995) was used to correct the alpha for multiple testing. In some

Table 1 Flushing times (T) calculated using model parameters for the tidal creeks

Model parameter	RC1	MC1	BC3	BC1
L (m)	1,500	1,000	500	2,500
W (m) (at mouth)	300	250	75	75
W (m) (at site)	150	100	40	10
$A(b)$ (m^2)	337,500	175,000	28,750	106,250
Mean Water Depth (m)	4	4	3	3
V (m^3)	1,350,000	700,000	86,250	318,750
$a(b)$ (m) (spring tide)	5.0	5.0	4.0	3.0
$a(b)$ (m) (neap tide)	2.0	2.0	1.5	1.0
e	1	1	0.5	0.2
p (spring)	3,375,000	1,750,000	230,000	637,500
p (neap)	1,350,000	700,000	86,250	212,500
T (day) (spring)	0.3	0.3	0.5	1.6
T (day) (neap)	0.6	0.6	1.3	4.8

Creek dimensions were estimated from satellite imagery, mean water depth was estimated from field measurements at the sampling sites, tidal amplitude ($a(b)$) was estimated from tide charts, and e was estimated from creek morphology. BC1 and BC3 were calculated separately due to the decreased e value upstream as a result of the meandering nature of the creek. *Note*: All parameters are estimates only

RC reference creek; *MC* Myrmidon Creek; *BC* Buffalo Creek; L length, W width, $A(b)$ water area, V water volume, $a(b)$ tidal amplitude, e exchange efficiency, p tidal prism

cases, variances in the compared groups were heterogeneous (as indicated by Cochran's *C*-test). However, ANOVAs are robust to violations of the assumption of homogenous variances, provided that sample sizes are similar (Zar 1999), as was the case for most tests undertaken. The significance level was defined as 0.01 when Cochran's tests were violated to further reduce the chance of a type I error (falsely identifying a significant difference). Where significant differences were detected, post-hoc analysis was carried out using Tukey's HSD test. The assumption that the data points from the six sample sites share equal independence may be violated as there are two sampling locations within each creek (upstream and downstream). However, while downstream sites may be somewhat influenced by upstream sites, they are also strongly influenced by marine waters in the main body of the harbour due to the macrotidal regime. Therefore, for the purposes of this study it was assumed that all six sites share equal independence.

A multivariate ordination technique was used to examine the major source of variation in the process rate data. Principal component analysis (PCA) was carried out using benthic and pelagic processes as variables. The variables displayed strong collinearity due to the extreme values measured in BC, therefore variables were either excluded in cases where multiple variables were measures of the same biogeochemical processes, or ratios were used. Variables included in the PCA, and the processes and covariables they represent were: P_{max} as a measure of pelagic metabolism (negatively correlated with respiration); *f*DIC as a measure of benthic remineralization (positively correlated with fNH_4, fNO_x, fPO_4, $fSiO_4$, negatively correlated with *f*DO, fN_2); DE as a measure of nitrogen release to the water column (negatively correlated with fNH_4, positively correlated with fN_2); benthic primary production (bPP); $fDIC/fPO_4$ as a measure of phosphorus retention in the sediments; and $fDIC/fO_2$ as a measure of aerobic versus anaerobic organic matter degradation.

Results

Water column physico-chemical data

Water quality in RC and MC were similar and varied seasonally (Table 2). Water temperature was relatively constant all year (approx. 30°C). The surface waters were well saturated with oxygen (>77%) but varied with tides, being typically lower during low tide. During the dry season, MC and RC had high salinity (up to 37), very low nutrient concentrations (<0.3 μM DIN and <0.21 μM PO_4^{3-}) and very low N:P ratios (<1.5). During the wet season survey, freshwater from the Elizabeth River flowed into East Arm and was pushed into the tidal creeks during the flood tide, lowering the salinity (22–29) and increasing nitrogen concentrations (up to 1.9 μM). N:P ratios increased during the wet season, particularly in RC (up to 12.5). Concentrations of chl *a* in the water column remained relatively low all year round (<3 μg l^{-1}). The euphotic depth decreased during the wet season and was also lower during low tide.

Sewage effluent strongly affected physico-chemical parameters in the water column. It was observed that sewage effluent entered the creek at MC1 from the mangroves following the tidal maximum and rapidly changed water quality conditions. Surface water during periods of sewage effluent discharge in MC had a higher temperature (>32°C) and lower salinity (~28) than the surrounding creek water (MC-S; Table 2), resulting in a temporary surface plume. Mean TSS and nutrient concentrations increased dramatically, chl *a* concentrations were elevated (9.9 μg l^{-1}) and the N:P ratio was higher than typical creek water (6.4). The sewage effluent plume caused a decrease in light penetration (Z_{eu} = 3 m) and oxygen saturation (69%). As the tide receded, nutrient and TSS concentrations gradually decreased as the plume was dispersed and diluted. Within several hours the impact of the plume was undetected with nutrient concentrations and salinity returning to background levels.

Water quality in BC varied considerably over short sampling periods (4–5 h) in December 2008 as indicated by the high standard deviation values for most parameters (Table 2). Overall, during our sampling periods, salinity was lower and highly variable (20.6 ± 10.0) due to the influence of tides, terrestrial freshwater inputs and sewage effluent. Dissolved oxygen concentrations in BC were also much lower (43 ± 25%) than in the other two creeks and highly variable. Measured DO saturation ranged from <10% to supersaturation, with the lowest values occurring early in the mornings. The high phytoplankton

Table 2 Mean (±SD) physico-chemical parameters in the water column in three tidal creeks in Darwin Harbour during the sampling periods

Variable	Reference Creek		Myrmidon Creek			Buffalo Creek
	Oct-07	Mar-08	Oct-07	Mar-08	MC-S[b]	Dec-08
Water temperature	31.4 (0.5)	29.4 (0.6)	30.3 (0.8)	29.9 (0.7)	32.1 (1.1)	30.7 (2.0)
Salinity	37.0 (0.3)	22.5 (3.5)	36.5 (0.4)	29.3 (1.3)	28.2 (7.7)	20.6 (10.0)
Suspended solids	17.1 (3.5)	12.3 (4.6)	15.8 (5.6)	28.3 (5.5)	116.2 (40.1)	97.7 (131.3)
DO saturation (%)	85.8 (10.3)	77.6 (9.4)	84.7 (9.4)	86.2 (8.2)	69.1 (14.8)	43.3 (25.2)
DO concentration (mg l^{-1})	5.1 (0.6)	5.2 (0.6)	5.2 (0.5)	5.5 (0.5)	4.3 (0.8)	2.9 (1.8)
Euphotic depth (m)	5.2 (2.1)	3.7 (1.3)	5.9 (1.9)	3.8 (0.3)	3.0 (0.6)	1.6 (0.8)
Chl *a* (μg l^{-1})	1.8 (0.4)	2.3 (0.2)	2.8 (1.3)	1.7 (0.04)	9.9 (3.8)	90.0 (37.6)
NH_4 (μM)	0.15 (0.09)	1.11 (0.36)	0.15 (0.17)	0.33 (0.11)	12.4 (10.4)	35.5 (24.2)
NO_x (μM)	0.13 (0.13)	0.77 (0.40)	0.07 (0.06)	0.27 (0.21)	6.5 (6.7)	14.1 (10.2)
PO_4 (μM)	0.21 (0.07)	0.15 (0.02)	0.14 (0.13)	0.13 (0.03)	5.8 (8.3)	7.2 (4.9)
SiO_4 (μM)	10.6 (4.4)	26.4 (2.3)	4.4 (3.8)	5.7 (0.8)	49.6 (34.2)	38.4 (21.4)
Molar N:P ratio[a]	1.3 (0.4)	12.5 (3.7)	1.4 (0.7)	4.5 (2.2)	6.4 (4.6)	8.4 (4.9)

Oct-07 dry season; *Mar-08* wet season; *Dec-08* dry season

[a] DIN:phosphate ratio ($NH_4 + NO_x$:PO_4)

[b] MC-S values are the mean of all samples collected from the sewage effluent plume in MC across all three field surveys

biomass (chl *a*) and TSS concentrations limits light penetration, with the euphotic depth much lower ($Z_{eu} = 1.6$). The mean nutrient concentrations in BC were several orders of magnitude higher than in the other two creeks, including the mean sewage effluent plume concentrations in MC (MC-S) (with the exception of SiO_4) and nutrient concentrations in BC decreased downstream (data not shown).

Tidal flushing is restricted in BC by a sand bar across the mouth, a narrow channel and several large meander bends (Fig. 1c) and the estimated flushing time varied from 0.5 to 5 days, depending on location in the creek and the nature of the tides (Table 1). The degree of flushing decreased upstream and during neap tides. In contrast, RC and MC have wide open mouths and relatively straight channels (Fig. 1a, b), allowing efficient flushing. Hence, estimated flushing times were shorter (~0.5 days; Table 1) and both creeks were well flushed with water from East Arm during each tidal cycle. This is consistent with the observed sewage effluent plume in MC1 which was diluted and dispersed following each low tide.

Sediment characteristics

Sediment TOC, TN and TP concentrations were higher at the upstream sites reflecting the higher mud content (as indicated by porosity). Mean TOC concentrations ranged from 1.8 to 4.6 wt% and were highest at RC1 and BC1. TN concentrations ranged from 0.08 to 0.42% and were highest in BC. TP concentrations were highest in BC (997–1,363 mg kg^{-1}) and MC1 (762–825 mg kg^{-1}) compared to the other sites (<646 mg kg^{-1}). The molar C:P ratios in BC and MC were lower than typical terrestrial and marine C:P ratios (C:P < 106) suggesting an additional phosphorus source, most likely from sewage. The mean $\delta^{13}C$ values ranged between −25.7 and −23.3‰ and the mean $\delta^{15}N$ values ranged from 2.3 to 12.6‰ with the most enriched values in BC and at MC1 (Table 3). Benthic chl *a* concentrations ranged from 17 to 60 mg m^{-2} in RC and MC and were higher in BC, ranging from 161 to 532 mg m^{-2} (Table 3).

Pelagic primary production and respiration

P_{max} rates measured as both O_2 and ^{13}C gave comparable results (data not shown) with no significant differences between the two methods ($p = 0.977$, *t* test). The ^{13}C results are reported herein since this method was used to calculate depth-integrated production. P_{max} rates in BC were significantly higher (1-way ANOVA, $p < 0.02532$, Fig. 2)

Table 3 Surface sediment characteristics at the upstream and downstream sites in three tidal creeks in Darwin Harbour

Site	Chl *a* (mg m^{-2})	Porosity	%TOC	%TN	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)	TP (mg kg^{-1})	C:N (mol:mol)	N:P (mol:mol)	C:P (mol:mol)
RC1 dry	37	81.9	4.6	0.22	−24.9	3.7	583	24.1	8.4	203
RC1 wet	34	83.2	3.5	0.29	−25.7	4.2	628	13.8	10.3	142
RC2 dry	17	74.4	2.6	0.15	−25.0	4.1	478	20.5	7.0	143
RC2 wet	41	76.5	3.9	0.17	−25.1	4.1	559	26.6	6.8	181
MC3 dry	31	72.0	1.8	0.13	−23.5	2.7	646	16.3	4.5	73
MC3 wet	42	75.5	1.8	0.08	−24.7	2.3	635	27.5	2.7	73
MC1 dry	60	78.8	3.0	0.22	−25.0	6.6	825	15.7	5.9	93
MC1 wet	50	80.7	2.4	0.22	−25.6	6.9	762	12.7	6.4	82
BC3	161	78.7	2.8	0.28	−23.3	8.8	997	11.6	6.3	73
BC1	532	83.3	4.5	0.42	−25.3	12.6	1,363	12.8	6.7	86

than in the other two creeks with values ranging from 23.5 to 42.7 mmol C m^{-3} h^{-1} and these two sites were significantly different from each other. Mean P_{max} rates in MC and RC were similar, ranging from 1.17 to 2.93 mmol C m^{-3} h^{-1} and there were no significant differences between sites or season, however there were significant interactions between site and season (2-way ANOVA, $p < 0.05$, Table 4). Mean respiration rates in BC ranged from 4.5 to 10.8 mmol O_2 m^{-3} h^{-1} and were significantly higher at BC1 (1-way ANOVA, $p < 0.02532$, Fig. 2) compared to other sites. In RC and MC, respiration rates were similar and low, ranging from 0.73 to 1.82 mmol O_2 m^{-3} h^{-1} with no significant differences in season or site (Table 4). The sewage effluent plume in MC was sampled on one occasion during the October 2007 survey (MC-S) and P_{max} (measured using the O_2 syringe method) and respiration rates (19.1 and 8.6 mmol O_2 m^{-3} h^{-1}, respectively) were significantly higher than other sites in RC and MC but comparable to BC1 and BC3.

Mean depth-integrated primary production (NPP) ranged from 10.1 to 248.5 mmol C m^{-2} day^{-1} and there were significant differences between the six sites (1-way ANOVA, $p < 0.01$, Fig. 3). Net primary production rates were similar at RC1, RC2 and MC3, ranging between 10.1 and 16.5 mmol C m^{-2} day^{-1}. Net primary production at MC1 was significantly higher (40.8 mmol C m^{-2} day^{-1}) than at other sites in MC and RC, and in BC, NPP was significantly higher than all sites in MC and RC, ranging from 130.9 to 248.5 mmol C m^{-2} day^{-1}.

Mean community respiration ranged from 50.4 to 519 mmol C m^{-2} day^{-1} (Fig. 3). Mean community respiration rates were significantly higher at BC1, and MC1 and BC3 were also significantly higher than other sites in MC and RC (1-way ANOVA, $p < 0.02532$). Respiration exceeded production at all sites and the GPP:CR ratio was ≤ 1 at all sites with the lowest values (0.5–0.7) at sites in MC and RC, and higher values in BC (0.9–1.0).

Benthic respiration and production

Mean dark DIC fluxes ranged from 58.8 to 390.8 mmol C m^{-2} day^{-1} and were significantly higher in BC (1-way ANOVA, $p < 0.01$, Fig. 2). Mean dark DO fluxes varied from −40.0 to −90.5 mmol m^{-2} day^{-1} and there were no significant differences between the six sites. There were no significant differences in DO or DIC fluxes between sites or seasons in MC and RC (Table 4).

There was diurnal variation in DIC and DO fluxes, with reduced DIC efflux and DO influx measured in all light chambers. However, the semi-diurnal, macrotidal regime generates constant variations in light conditions at the sediment surface. Light conditions varied both within and between sites and were not reproducible between sites or sampling periods. Therefore, it was not possible to calculate light fluxes on a mmol m^{-2} day^{-1} basis. The reduced DIC and increased O_2 fluxes measured in the light chambers suggest the presence of microbenthic algae (MBA) at all sites. This was confirmed by measurable benthic

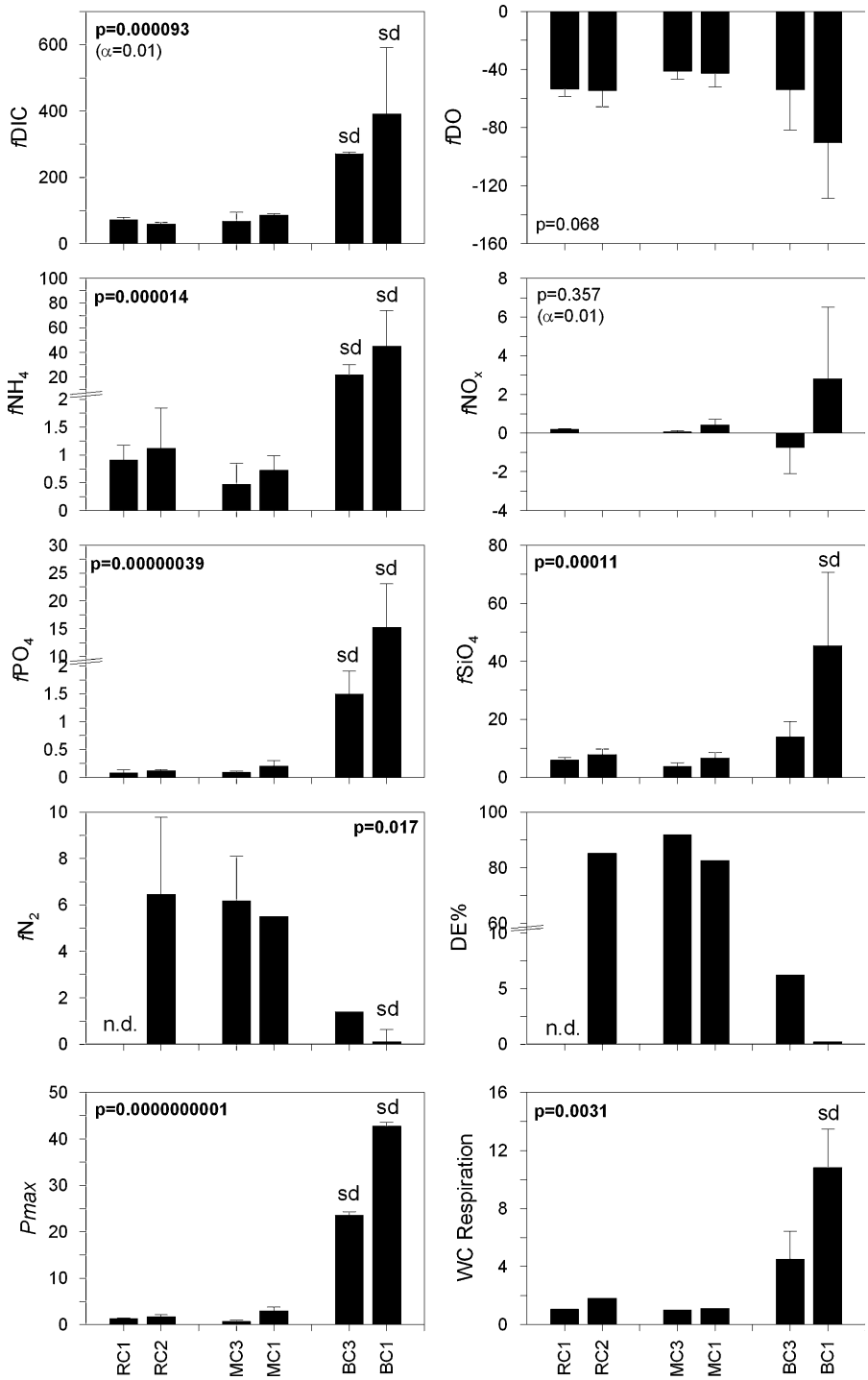

Fig. 2 Mean dry season benthic fluxes (mmol m^{-2} day^{-1}), DE (%), water column primary production (P_{max}) and respiration (mmol m^{-3} h^{-1}) in RC, MC and BC. *Error bars* SE of replicate samples. n.d. no data. 1-way ANOVA results are shown (*p* values) with significant differences highlighted in *bold* (adjusted $\alpha = 0.02532$, unless otherwise stated). Sites which are significantly different (as identified in post hoc comparisons) indicated as sd

Table 4 Results of 2-way ANOVA tests (*p* values) comparing pelagic and benthic processes in MC and RC during the dry and wet seasons

Process	α	Season	Site	Interaction	Post-hoc results
P_{max}	0.05	0.5240	0.2227	**0.0002**	Significantly higher at MC1 dry and MC3 wet
Respiration	0.05	0.4736	0.6497	0.2032	
*f*DIC	0.05	0.1420	0.9125	0.3960	
*f*DO	0.05	0.2561	0.8792	0.2039	
fNH_4	0.05	0.1160	0.6235	0.4376	
fNO_x	0.01	0.0347	**0.0006**	0.7339	Significantly higher at MC1
fPO_4	0.05	0.3099	0.4730	**0.0078**	
$fSiO_4$	0.05	**0.0087**	0.6497	0.3051	Significantly higher in the dry season
fN_2	0.05	0.7671	0.8993	0.7911	
Benthic PP	0.01	0.6238	0.0222	0.0186	
Chl *a*	0.01	0.1487	0.0378	0.0330	

Significant differences are highlighted in bold

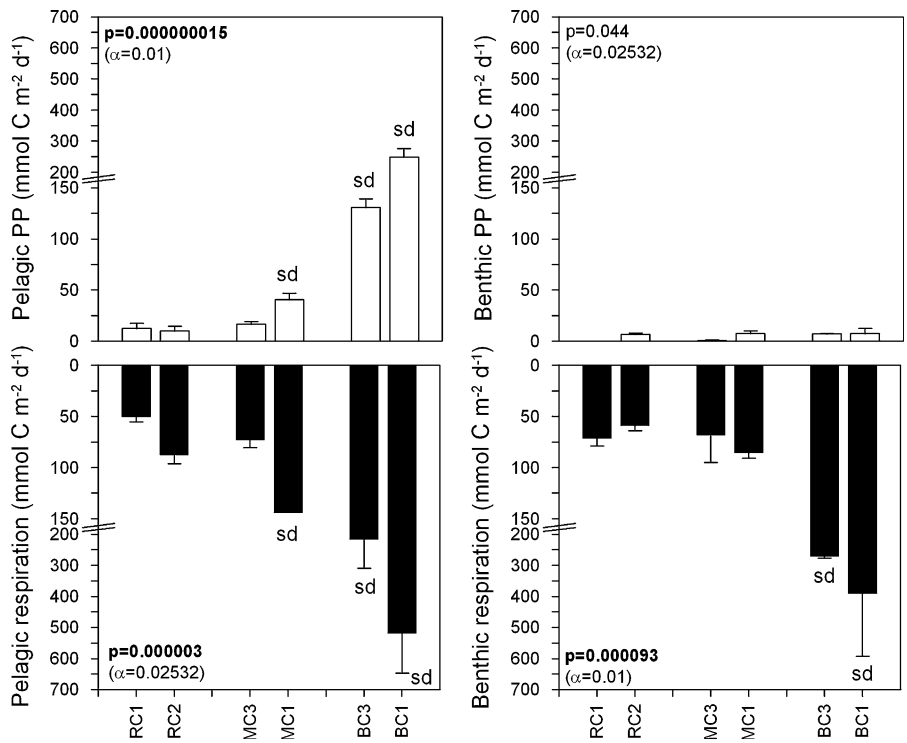

Fig. 3 Mean benthic and pelagic respiration and primary productivity. *Error bars* SE of replicate samples. 1-way ANOVA results are shown (*p* values) with significant differences highlighted in *bold* (adjusted α also shown). Sites which are significantly different (as identified in post hoc comparisons) indicated as sd

primary productivity rates, indicating uptake of DIC by MBA, with the exception of RC1 where primary productivity rates were below detection limits. However, sediment chl *a* concentrations at this site were similar to other sites in RC and MC (Table 3). Sediment primary production rates were all low and similar in all three tidal creeks (<8 mmol C m^{-2} day^{-1}, Fig. 3), despite higher benthic algal biomass in BC. The P:R ratio of the sediments was very low at all sites (<0.25).

Dissolved nutrient fluxes

Benthic nutrient fluxes were very high in BC compared to the other two creeks where similar fluxes were measured (Fig. 2). At all sites, the sediments

were a source of inorganic nutrients for the overlying water with a net efflux of DIN, PO_4 and SiO_4. There were no significant differences in nutrient fluxes between seasons in RC and MC, except for SiO_4 fluxes which were significantly higher in the dry season (2-way ANOVA, $p < 0.05$, Table 4).

In RC and MC, mean dark NH_4^+ fluxes ranged from 0.32 to 1.12 mmol N m^{-2} day^{-1}, accounting for >65% of the DIN flux. There were no significant differences between seasons or sites (Table 4). In BC, mean dark NH_4^+ fluxes were significantly higher (1-way ANOVA, $p < 0.02532$, Fig. 2), ranging from 21.9 to 45.0 mmol N m^{-2} day^{-1}, accounting for >94% of the DIN flux in this creek. NO_x fluxes were highly variable with the standard deviation at each site typically exceeding the mean fluxes. NO_x fluxes were significantly higher at MC1 compared to other sites in MC and RC (2-way ANOVA, $p < 0.01$, Table 4). However, when comparing all six sites, there was no significant difference in NO_x fluxes (Fig. 2). Mean PO_4^{3-} fluxes in RC and MC ranged from 0.06 to 0.21 mmol P m^{-2} day^{-1} and there were no significant differences in sites or seasons. A significant interaction was found between season and site (2-way ANOVA, $p < 0.05$, Table 4), however the post hoc comparison (Tukey's HSD test) failed to identify where these interactions occurred. PO_4^{3-} fluxes were significantly higher in BC compared to sites in RC and MC (1-way ANOVA, $p < 0.02532$, Fig. 2), ranging from 1.50 to 15.2 mmol P m^{-2} day^{-1}, and these two sites were also significantly different from each other. Mean SiO_4 fluxes ranged from 3.26 to 45.4 mmol Si m^{-2} day^{-1} and the flux at BC1 was significantly higher than at the other sites (1-way ANOVA, $p < 0.02532$, Fig. 2).

Denitrification (net N_2 fluxes)

Measured N_2 fluxes in RC and MC were consistently high ranging from 5.50 to 6.83 mmol N m^{-2} day^{-1} (Fig. 2). Variability was sometimes high among replicate chambers, but in all cases N_2 fluxes were greater than the DIN fluxes. No data was collected from RC1.

There were difficulties calculating N_2 fluxes in BC due to missing data and highly variable rates in replicate chambers, with both positive and negative fluxes calculated. However, overall mean N_2 fluxes in BC were lower than the N_2 fluxes in the other two tidal creeks and fluxes at BC1 were significantly lower ($p < 0.02532$, Fig. 2).

Denitrification removed a major portion of the N cycled through the sediments in RC and MC. The mean DE ranged from 83 to 97% at sites in RC and MC. In contrast, the majority of N flux to the water column in BC was in the form of NH_4^+ and denitrification only removed a small proportion (DE < 10%) of the N cycled through the sediments.

Principal component analysis

The first two PCA axes cumulatively explained 94.4% of the total variation in biogeochemical data and the discussion will be limited to these main axes. PCA axis 1, which alone accounted for 81.4% of the variation, was highly correlated with variables related to benthic remineralization (*f*DIC) and pelagic metabolism (P_{max}). DE, the degree of anaerobic respiration ($fDIC/fO_2$) and phosphorus retention ($fDIC/fPO_4$) were strongly negative on this axis (Fig. 4a). PCA axis 2, which accounted for only 13.0% of the variation, was determined by benthic primary production (bPP) and phosphorus retention ($fDIC/fPO_4$) to a lesser degree.

Sites in BC had high positive scores on axis 1 and there was a downstream gradient with higher scores at BC1 than BC3 (Fig. 4b). All sites in MC and RC had similar scores on axis 1 and were all slightly negative, except for MC1 in the dry season which was close to zero on this axis. Sites in MC and RC were spread across axis 2 with no obvious trends between sites or seasons. The three sites with strongly negative scores on this axis all had the highest benthic primary productivity values. Sites with negative axis 1 scores and positive axis 2 scores typically had very low benthic primary productivity rates and high $fDIC/fPO_4$ ratios indicating strong phosphorus retention in the sediments.

The position of the sites in the ordination space indicates the main similarities and differences in biogeochemical variables between sites. Sites in BC were most different from sites in the other two creeks, and were also different from each other. This is consistent with the significant differences observed in benthic and pelagic processes between sites in BC and the other two creeks (Figs. 2, 3). Although there were differences between sites in MC and RC along axis 2, this axis only explains a small proportion

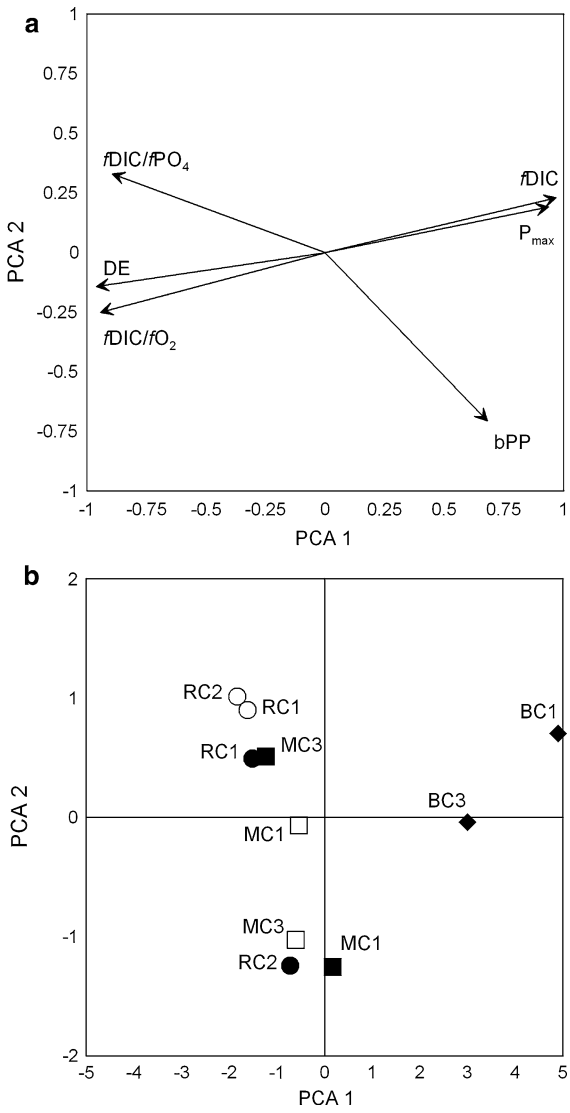

Fig. 4 Vector diagram (**a**) indicating the loadings on PCA1 and PC2 and biplot of sites (**b**). *Closed symbols* dry season; *open symbols* wet season

(13.0%) of the variance and is therefore less important that the differences observed along axis 1.

Discussion

Effect of nutrient loads on biogeochemical processes

Our results, which integrate multiple biogeochemical processes in three tropical tidal creeks, indicate a substantial impact of sewage effluent on rates of benthic and water column nutrient cycling in the hypereutrophic creek (BC), but effects on pelagic processes only in the oligotrophic–mesotrophic creek (MC) relative to the reference site (RC). There was a downstream gradient in the creeks receiving sewage effluent, with the greatest effects measured at BC1and MC1, closest to the sewage discharge points.

The most affected processes in BC were benthic nutrient fluxes (*f*DIN, *f*DIP), denitrification (fN_2) and primary production (P_{max}) which were 1–2 orders of magnitude higher or lower than in RC (Fig. 5c, d). The combination of increased DIN flux and decreased N_2 flux subsequently affected the DE which was up to three orders of magnitude lower in BC relative to RC (Fig. 5d). Denitrification provides a sink in the nitrogen budget and thereby plays an important role in controlling the degree of eutrophication in waters subjected to substantial anthropogenic input of nutrients (Seitzinger 1988; Rysgaard et al. 1995). The low DE in BC is consistent with studies in other estuarine systems which have demonstrated that as nutrient loads increase, denitrification removes a smaller proportion of the load (Sloth et al. 1995; Burford and Longmore 2001; Caffrey et al. 2007). The effect of nutrient loading on DE has important implications for the nutrient status of the system and has flow-on effects that alter the structure of higher trophic levels such as fish and invertebrate communities (Kemp et al. 2005).

Dissolved inorganic nutrient concentrations (DIN and PO_4) and phytoplankton biomass (chl *a*) were one to two orders of magnitude greater in BC than in RC (Fig. 5a). Depth-integrated primary production and respiration, sediment algal biomass and benthic respiration were also higher in BC but to a lesser degree (Fig. 5). The presence of a high phytoplankton biomass in BC limited light penetration, with the euphotic depth several times lower than in the other two creeks. Additionally, the high phytoplankton biomass, combined with high pelagic respiration rates, resulted in substantial diel fluctuations in O_2 concentrations. High benthic respiration rates in BC also emphasize the potential importance of this pathway to contribute to O_2 depletion (Boynton and Kemp 1985). The low DO saturation in the early mornings indicates high rates of night-time respiration and suggests BC experiences regular hypoxia. Overall, DO saturation in BC was approximately half

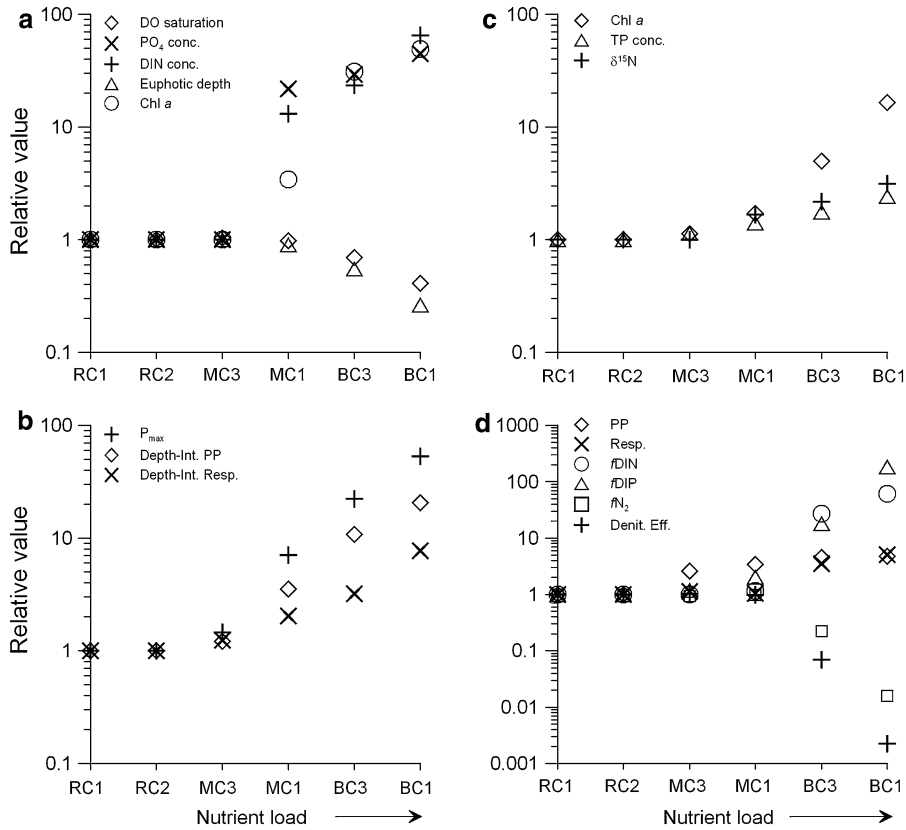

Fig. 5 *Plot* showing the relative impact on **a** water quality parameters, **b** pelagic processes, **c** sediment parameters and **d** benthic processes at each site compared to RC. Values for each site were calculated by dividing the mean rates and concentrations of each variable by the mean rates and concentrations measured in RC. Data from the dry and wet season were averaged for these calculations. Note the different *y*-axis scale in (**d**)

that found in RC (Fig. 5a). BC has experienced periodic fish kills along the entire length of the creek and it is likely a lack of oxygen is responsible.

In contrast, there was a relatively minor effect of increased, but smaller nutrient loads in MC relative to RC and importantly, the impacts were observed only in the water column at MC1, which is adjacent to the sewage discharge point. All variables at site MC3 were similar to sites in RC. Dissolved inorganic nutrient concentrations were most affected at MC1 and were approximately one order of magnitude greater than RC (Fig. 5a). Pelagic primary production, respiration and phytoplankton biomass were also affected to a lesser degree (Fig. 5a, b). There were minor differences in sediment quality and benthic processes at MC1 with sediment chl *a* and TP concentrations, δ^{15}N and DIP fluxes slightly higher compared to other sites in MC and RC. As such, small scale nutrient inputs appear to have a greater impact on pelagic rather than benthic processes and parameters, but at larger scale nutrient inputs, benthic processes are most affected (Fig. 5). This pattern is most likely due to differences in both the magnitude of effluent inputs and the hydrodynamics in the two creeks (see below).

Biogeochemical process rates measured in BC far exceeded any previously reported values for Darwin Harbour and other tropical estuaries (Table 5). Based on our study, BC is considered to be hypereutrophic (Nixon 1995). Pelagic metabolism and benthic nutrient fluxes in BC were similar to that found in other tropical hypereutrophic systems such as shrimp ponds (e.g. Alongi et al. 1999a; Burford and Longmore 2001). The high benthic nutrient fluxes and low DE in BC indicate the sediments were a major source of dissolved inorganic nutrients to the water column and, combined with the sewage effluent, contribute to increased algal biomass and poor water quality. The

Table 5 Comparison of pelagic (NPP and community respiration, mmol C m^{-2} day^{-1}) and benthic (respiration, ammonia and phosphate fluxes, mmol m^{-2} day^{-1} as C, N, and P, respectively) processes in tropical estuaries and coastal systems

Estuary/coastal system	Sampling location	Pelagic primary production	Pelagic respiration	Benthic Respiration	Benthic N flux	Benthic P flux	Reference
Buffalo Creek	Tidal creek	131–249	217–671	271–391	22–45	1.5–15	This study
Myrmidon & Reference Creeks	Tidal creeks	8–16	50–94	65–92	0.32–1.12	0.06–0.23	This study
Darwin Harbour, Australia	Estuary	82–180		65–74*	3.5–8.2	0.05–0.1	Burford et al. (2008)
Darwin Harbour, Australia	Shallow margins	31–53	43–88	77	0	−0.005	Burford et al. (2008)
Port Douglas, Australia	Tidal creeks	39–277			0.9–2.1	−0.02 to −0.06	Trott et al. (2004)
Fly River Delta, PNG	Coastal waters	11–58	0.5–3				Robertson et al. (1993)
Mandovi & Zuari estuary, India	Estuary	23–155	42–468				Ram et al. (2003)
Gautami-Godavari estuary, India	Estuary	−108 to 124	16–1,503				Sarma et al. (2009)
Hinchinbrook Channel, Australia	Tidal creeks	5–30	50–75				McKinnon et al. (2010)
Terminos Lagoon, Gulf of Mexico	Tidal channel	2.5–542					Rivera-Monroy et al. (1998)
Gulf of Papua, PNG	Coastal waters	13–52	59–135				McKinnon et al. (2007)
Mandovi Estuary, India	Estuary			35–99*	0.8–5.2	0.13–0.25	Pratihary et al. (2009)
Northern Queensland, Australia	Tidal creek, shrimp pond				11.3–45.8	0–0.58	Burford and Longmore (2001)
Phuket Island, Thailand	Mangrove forest			32–62	−2.2 to 1.74		Kristensen et al. (2000)
Peninsular Malaysia	Mangrove forest			11–79	−0.25 to −0.44		Alongi et al. (2004)
Hinchinbrook Channel, Australia	Mangrove forest			14–22			Alongi et al. (1999b)
Gulf of Thailand	Mangrove forest			5–73			Alongi et al. (2001)

The values with asterisk were measured as mmol O_2 m^{-2} day^{-1} whereas all other values were measured as mmol C m^{-2} day^{-1}

similarity between benthic primary productivity in all creeks, despite the higher benthic algal biomass in BC, suggests high TSS and phytoplankton biomass decreased light availability at the sediment surface. Additionally, in BC the dense algal mat, as demonstrated by the high chl *a* concentrations, is likely to cause self-shading.

In MC, the impact of increased nutrient loads was restricted to the water column adjacent to the sewage discharge point, consistent with a locally mesotrophic system (Nixon 1995). The treated sewage effluent had a high proportion of ammonium, nitrate and phosphate relative to the typical creek water but lower relative concentrations of phytoplankton which is consistent with other studies (e.g. Jones et al. 2001). Therefore, while there may not be direct input of phytoplankton biomass with the sewage effluent, the additional nutrients stimulated in situ primary production in the creek water. The elevated TP concentrations and $\delta^{15}N$ signature of sediments at MC1 suggest sewage-derived material is deposited at this site, however, there was no increase in benthic metabolism and nutrient fluxes at this site, indicating the sewage-derived nutrients and associated primary

production were not being recycled through the sediments in MC.

Depth-integrated pelagic primary production rates in RC and MC were lower than values reported for the shallow margins of Darwin Harbour (Burford et al. 2008) as well as tropical coastal waters in Australia and around the world (Table 5). These tidal creeks are considered to be oligotrophic and are net heterotrophic (P:R ratios in the water column were ≤ 1). This is in contrast to the main body of the harbour which is autotrophic (Burford et al. 2008). The higher turbidity in the tidal creeks results in a shallower euphotic zone and therefore pelagic primary production is likely to be light limited relative to the main body of the harbour (McKinnon et al. 2006). The rates of benthic remineralization in RC and MC were similar to rates reported for other tropical mangrove environments including Darwin Harbour (Table 5). Denitrification rates in these creeks were high but comparable to the range of estimates for other estuarine and coastal marine sediments (Seitzinger 1988).

In comparison to the sewage-derived nutrient inputs, the seasonal input of nutrients associated with freshwater runoff during the wet season has no effect on biogeochemical processes in the tidal creeks. This is in accordance with the limited seasonal change in key parameters such as temperature and organic matter supply from mangroves. The seasonal variations in water column nutrient concentrations in MC and RC were minor compared to variations observed at sites affected by sewage effluent.

Controls on biogeochemical processes

Pelagic primary production was strongly associated with benthic remineralization in the PCA, suggesting benthic-pelagic coupling. The higher pelagic primary production, a P:R ratio close to 1 and low C:N and C:P ratios in BC all reflect a significant algal contribution and suggest phytoplankton detritus was an important source of organic matter to the sediments in this creek. Therefore, the increased benthic remineralization in BC was a response to the stimulated primary production in the water column. Additionally, primary production in the water column was stimulated by benthic nutrient fluxes. Benthic nutrient regeneration in BC was far greater than phytoplankton demand for net growth, which was limited by light availability below the surface. This results in the accumulation of DIN and PO_4^{3-} in the water column. Overall, there was strong coupling between benthic and pelagic processes in BC.

In RC and MC, depth-integrated primary production rates were much lower than the benthic remineralization rates, indicating phytoplankton production contributes only a small proportion of the overall organic matter pool in the sediment surface. Sediment organic matter was driving benthic metabolism rather than phytoplankton detritus in these two tidal creeks. In addition, benthic regenerated nutrients were not sufficient to supply all the nutrients required for phytoplankton growth in these creeks. The remaining nutrient requirements by phytoplankton are likely supplied by oceanic or terrestrial inputs (Burford et al. 2008; Ferrón et al. 2009). The high denitrification rates in RC and MC indicate this is the main process controlling nitrogen release to the water column in the tidal creeks and support the suggestion that nitrogen is limiting phytoplankton growth in Darwin Harbour (Burford et al. 2008). NO_3^- levels in the water column were low and only infrequently was there NO_3^- influx, indicating denitrification was controlled by coupled nitrification–denitrification, as is commonly found in coastal marine systems (Seitzinger 1988).

Denitrification efficiency and phosphorus retention were strongly associated with the degree of anaerobic degradation in the PCA, suggesting sediment oxygen consumption was important in controlling nitrogen and phosphorus release. In the tidal creeks, the community respiratory quotient ($CRQ = DIC/O_2$) was -2 in the oligotrophic creeks and -4 in the hypereutrophic creek, indicating a shift to dominance of anaerobic mineralization processes with the increased nutrient loading in BC. This shift from aerobic to anaerobic metabolism occurs during hypoxic events, caused by excess nutrient inputs, and involves profound changes in the biogeochemical cycles of phosphorus and nitrogen (Conley et al. 2009; Soetaert and Middelburg 2009).

One of the most prominent effects of hypoxia is the increased P flux from sediments (Conley et al. 2009). Phosphate fluxes are controlled by release from degradation of organic matter and by the buffering mechanism involving iron oxides at the sediment surface (Froelich 1988). The low oxygen conditions and dominance of anaerobic metabolism

pathways in BC contributed to the large benthic PO_4^{3-} flux. The ratio of DIC to PO_4^{3-} fluxes was low in BC indicating little or no phosphorus retention in the sediment. Under small or no increased nutrient loads in MC and RC, the ratio of DIC to PO_4^{3-} fluxes was high, indicating strong phosphate retention by the sediments. The low efflux of remineralized phosphate is likely controlled in the surface oxidized layer by sorption with iron oxyhydroxides (Patrick and Khalid 1974).

Hypoxia also affects nitrogen release to the water column which is strongly controlled by denitrification. Denitrification appears to be inhibited in BC and there are several possible mechanisms. It is likely the low oxygen conditions cause a breakdown in the nitrification–denitrification coupling by inhibiting nitrification. Nowicki (1994) found that highly reduced conditions in enriched sediments near sewage outfalls restricted O_2 penetration and limited nitrification. Additionally, sulfate reduction, the predominant pathway of anaerobic metabolism, produces sulfide which inhibits nitrification (Seitzinger 1988). Therefore, in BC where anaerobic metabolism dominates, denitrification rates could be indirectly affected by sulfide if nitrification is suppressed. This is supported by the large proportion of N present as NH_4^+.

Processes affected by hypoxia, such as denitrification and phosphorus retention, display threshold-like behavior (Webster and Harris 2004; Conley et al. 2009; Eyre and Ferguson 2009). Regime shifts, involving an abrupt change in ecosystem processes, can occur once specific thresholds of nutrient inputs are exceeded and this can cause changes in biological variables that propagate through several trophic levels (Conley et al. 2009). The breakdown of coupled nitrification–denitrification and subsequent low DE, as well as the large flux of PO_4^{3-} from the sediments to the water column, suggests that thresholds have been exceeded in BC. This is consistent with the theory that an ecosystem has reached a threshold when the system switches to one dominated by anaerobic processes (Conley et al. 2009) as was found in BC. The nutrient loads entering MC are sufficiently small to have not impacted these key biogeochemical processes, with PO_4^{3-} fluxes and denitrification efficiencies similar to those observed in the comparatively pristine tidal creek. While there is some evidence of sewage-derived material being deposited at MC1, the assimilation capacity of the sediments has not yet been exceeded.

The processes occurring in BC follow the generally accepted conceptual models of eutrophication (e.g. Nixon 1995; Cloern 2001) whereby an increase in the input of nutrients (in this case from sewage effluent) has stimulated primary production in the water column, leading to enhanced sedimentation of algal-derived organic matter, stimulation of microbial decomposition and oxygen consumption and depletion of water column oxygen. There has been a shift in dominance from aerobic to anaerobic metabolism and as a result, coupled nitrification–denitrification is inhibited and oxide-bound phosphorus released. Thus more nutrients are recycled back into the water column, further stimulating primary production (Kemp et al. 1990; Eyre and Ferguson 2002). Nutrient-generated increases in algal biomass fuel respiration and lead to light limitation of the phytoplankton and benthos, further generating hypoxic conditions. Ultimately, there is a positive feedback accelerating eutrophication through internal loading of nutrients (McGlathery et al. 2004).

Influence of physical processes

The effluent loads are similar between BC and MC but the response of many biogeochemical processes was far greater in BC (Fig. 5). This suggests that nutrient load alone was not responsible for the observed effects on biogeochemical processes in BC, and there must be consideration of additional processes or factors. The susceptibility of estuaries to eutrophication varies and it is now well recognized that physical attributes, including tidal mixing and associated residence times and optical properties, act as a filter to modulate the response to nutrient loading (Cloern 2001).

The estimated residence times in the three tidal creeks vary both spatially and temporally and are controlled by the tidal regime and geomorphology (Wolanski et al. 1992, 2000). The lower reaches of the tidal creeks are flushed efficiently by tidal action while significant trapping can occur in the upper reaches of BC, particularly during neap tides when tidal flushing is limited. This is typical of tropical mangrove-lined tidal creeks, for example, Wolanski et al. (2000) reported that water may reside in the upper reaches of tidal creeks for between 5 and

15 days, and flushing is rapid near the mouth. Longer residence times reduce export of nutrients (Nixon et al. 1996) and favour local degradation of phytoplankton detritus (Koné and Borges 2008), leading to low dissolved oxygen concentrations and nutrient enrichment (Boto and Bunt 1981; Trott and Alongi 1999) and enable benthic processes to have a greater impact on the system. Therefore, the impact on biogeochemical processes from excess nutrients is most severe in systems where tidal flushing is limited (Jickells 1998; Herbert 1999), as is the case in BC, and physical processes play a key role in reducing the risk of algal blooms, hypoxic events and subsequent changes in dominant biogeochemical processes in the tidal creeks.

Other physical processes may also influence biogeochemical processes, particularly sediment resuspension (Ståhlberg et al. 2006). Potential effects of resuspension include increased benthic mineralization, a decline in pelagic O_2 concentration, release of porewater nutrients to the water column, desorption of compounds from suspended sediment particles, decreased light availability and physical disturbance leading to a decrease of benthic primary production (Hopkinson 1985; Sloth et al. 1996; Wainright and Hopkinson 1997; Ståhlberg et al. 2006; Almroth et al. 2009). In the shallow tidal creeks of Darwin Harbour, more or less continuous resuspension caused by the semi-diurnal tides can be found, resulting in a system which is in a constant state of flux. It is therefore likely that the biogeochemical process rates reflect the mean environmental conditions in a continuously changing system.

Implications for tropical estuaries

Ecosystem alteration due to anthropogenic nutrient loading of coastal zones is occurring at a rapid rate in the tropics (Downing et al. 1999). The impact on the ecological functioning of coastal ecosystems varies in intensity and spatial distribution, both locally and globally. This study found that the effect of increased nutrient loads on biogeochemical processes can vary over small spatial scales (i.e. individual tidal creeks), and this is confounded by physical processes, principally residence time. These findings are relevant over larger spatial scales. For example, the importance of denitrification can be assessed on an estuary-wide scale. A whole-of-harbour nitrogen budget for Darwin Harbour found a net import of N to the harbour from the ocean of approximately 15,000 t N $year^{-1}$ (Burford et al. 2008), however, denitrification was not included in this budget but it was suggested it may be an important process. Although the dataset from this study is limited, our calculations confirm that there could be an approximate equivalent export of N from Darwin Harbour as a result of denitrification. Therefore, denitrification represents an important process controlling the amount of N in the harbour as a whole. This is consistent with what has been found throughout the tropics, where microbial denitrification removes biologically available forms of nitrogen from the water column producing substantial deficits relative to other nutrients (Beman et al. 2005). A decrease in DE, as has been observed in BC, can increase the availability of N in the water column and stimulate primary production which has important implications on the health and functioning of the whole ecosystem. Further research is needed to determine the actual contribution of denitrification to the nitrogen budget for Darwin Harbour.

Overall, the impacts of increased nutrient loads from sewage effluent are relatively localized and Darwin Harbour, as with most estuaries in tropical northern Australia, is considered to be relatively pristine. Forecasted increases in population and urbanization of Darwin will increase the nitrogen and phosphorus loads entering the harbour as catchment runoff and STP discharge increase. This will pose mounting pressure on estuarine health on a larger scale. This study has provided measurements of key biogeochemical processes in Darwin Harbour to inform predictive models used by estuarine managers. Additionally, the study of biogeochemical processes in disturbed and relatively pristine tidal creek systems provides important information which will enable comparison with other, more adversely affected tropical estuaries, such as those in southeast Asia.

Conclusions

This study has provided a comparison of rates of multiple biogeochemical processes across three scales of sewage nutrient loading in tropical tidal creeks to identify which processes are most sensitive to increased loading, thereby providing a broad

perspective of the links between nutrient loads and biogeochemical processes. We have shown that both benthic and pelagic biogeochemical processes are significantly affected by increased nutrient loads, particularly under the combined influence of poor tidal flushing. Denitrification, benthic nutrient fluxes and pelagic primary production were identified as the biogeochemical processes most affected by nutrient loading in these tidal creek systems. High levels of oxygen consumption, caused by stimulated primary production and respiration, lead to intermittent hypoxia. This causes an alteration in the key processes controlling nutrient release, resulting in hypereutrophic conditions. The integrated approach used in this study provides relevant information for other tropical estuaries subject to anthropogenic nutrient loading around the world.

Acknowledgments We wish to thank the staff from the Aquatic Health Unit at the Northern Territory Department of Natural Resources, Environment, The Arts and Sport for assistance with boats and logistics, Emily Saeck, Dominic Valdez, Matt Carey and Craig Smith for assistance with field work and laboratory analysis, Janice Trafford (GA) for MIMS analysis, Ed Czobik (NSW DECC) and Frank Krikowa (UC) for nutrient analysis, Liz Webber (GA) for XRF analysis, Rene Diocares (GU) and Rebecca Esmay (CMAR) for isotope analysis, Lesley Clemenston (CMAR) for chlorophyll analysis and Eric Valentine (CDU) for relevant information. We thank Rhys Leeming (CMAR), Alix Post (GA) and 2 anonymous reviewers whose useful comments substantially improved earlier versions of this manuscript.This project was conducted as part of the Tropical Rivers and Coastal Knowledge (TRaCK) program. TRaCK receives major funding for its research through the Australian Government's Commonwealth Environment Research Facilities initiative; the Australian Government's Raising National Water Standards Program; Land and Water Australia; the Fisheries Research and Development Corporation and the Queensland Government's Smart State Innovation Fund.This publication has received permission from the CEO of Geoscience Australia.

References

Almroth E, Tengberg A, Andersson JH, Pakhomova S, Hall POJ (2009) Effects of resuspension on benthic fluxes of oxygen, nutrients, dissolved inorganic carbon, iron and manganese in the Gulf of Finland, Baltic Sea. Cont Shelf Res 29:807–818

Alongi DM, Dixon P, Johnston DJ, Van Tien D, Thanh Xuan T (1999a) Pelagic processes in extensive shrimp ponds of the Mekong delta, Vietnam. Aquaculture 175:121–141

Alongi DM, Tirendi F, Dixon P, Trott LA, Brunskill GJ (1999b) Mineralization of Organic Matter in Intertidal Sediments of a Tropical Semi-enclosed Delta. Estuar Coast Shelf Sci 48:451–467

Alongi DM, Wattayakorn G, Pfitzner J, Tirendi F, Zagorskis I, Brunskill GJ, Davidson A, Clough BF (2001) Organic carbon accumulation and metabolic pathways in sediments of mangrove forests in southern Thailand. Mar Geol 179:85–103

Alongi DM, Sasekumar A, Chong VC, Pfitzner J, Trott LA, Tirendi F, Dixon P, Brunskill GJ (2004) Sediment accumulation and organic material flux in a managed mangrove ecosystem: estimates of land-ocean-atmosphere exchange in peninsular Malaysia. Mar Geol 208:383–402

Beman JM, Arrigo KR, Matson PA (2005) Agricultural runoff fuels large phytoplankton blooms in vulnerable areas of the ocean. Nature 434:211–214

Bianchi TS (2007) Biogeochemistry of estuaries. Oxford University Press, New York

Boto KG, Bunt JS (1981) Dissolved oxygen and pH relationships in northern Australian mangrove waterways. Limnol Oceanogr 26:1176–1178

Bouillon S, Connolly RM (2009) Carbon exchange among tropical coastal ecosystems. In: Nagelkerken I (ed) Ecological connectivity among tropical coastal ecosystems. Springer, Dordrecht, pp 45–70

Boynton WR, Kemp WM (1985) Nutrient regeneration and oxygen consumption by sediments along an estuarine salinity gradient. Mar Ecol Prog Ser 23:45–55

Boynton W, Hagy J, Cornwell J, Kemp W, Greene S, Owens M, Baker J, Larsen R (2008) Nutrient budgets and management actions in the Patuxent River Estuary, Maryland. Estuaries Coasts 31:623–651

Burford MA, Longmore AR (2001) High ammonium production from sediments in hypereutrophic shrimp ponds. Mar Ecol Prog Ser 224:187–195

Burford MA, Alongi DM, McKinnon AD, Trott LA (2008) Primary production and nutrients in a tropical macrotidal estuary, Darwin Harbour, Australia. Estuar Coast Shelf Sci 79:440–448

Caffrey J, Murrell M, Wigand C, McKinney R (2007) Effect of nutrient loading on biogeochemical and microbial processes in a New England salt marsh. Biogeochemistry 82:251–264

Clarke AL, Weckström K, Conley DJ, Anderson NJ, Adser F, Andrén E, de Jonge VN, Ellegaard M, Juggins S, Kauppila P, Korhola A, Reuss N, Telford RJ, Vaalgamaa S (2006) Long-term trends in eutrophication and nutrients in the coastal zone. Limnol Oceanogr 51:385–397

Cloern JE (2001) Our evolving conceptual model of the coastal eutrophication problem. Mar Ecol Prog Ser 210:233–253

Conley D, Carstensen J, Vaquer-Sunyer R, Duarte C (2009) Ecosystem thresholds with hypoxia. Hydrobiologia 629: 21–29

Cook PLM, Revill AT, Clementson LA, Volkman JK (2004) Carbon and nitrogen cycling on intertidal mudflats of a temperate Australian estuary III. Sources of organic matter. Mar Ecol Prog Ser 280:55–72

Diaz RJ, Rosenberg R (2008) Spreading dead zones and consequences for marine ecosystems. Science 321:926–929

Dittmar T, Hertkom N, Kattner G, Lara RJ (2006) Mangroves, a major source of dissolved organic carbon to the oceans. Glob Biogeochem Cycles 20:GB1012

Downing JA, McClain M, Twilley R, Melack JM, Elser J, Rabalais NN, Lewis WM, Turner RE, Corredor J, Soto D, Yanez-Arancibia A, Kopaska JA, Howarth RW (1999) The impact of accelerating land-use change on the N-cycle of tropical aquatic ecosystems: current conditions and projected changes. Biogeochemistry 46: 109–148

Eyre BD, Ferguson AJP (2002) Comparison of carbon production and decomposition, benthic nutrient fluxes and denitrification in seagrass, phytoplankton, benthic microalgae- and macroalgae-dominated warm-temperate Australian lagoons. Mar Ecol Prog Ser 229:43–59

Eyre BD, Ferguson AJP (2009) Denitrification efficiency for defining critical loads of carbon in shallow coastal ecosystems. Hydrobiologia 629:137–146

Ferrón S, Alonso-Pérez F, Anfuso E, Murillo FJ, Ortega T, Castro CG, Forja JM (2009) Benthic nutrient recycling on the northeastern shelf of the Gulf of Cádiz (SW Iberian Peninsula). Mar Ecol Prog Ser 390:79–95

Froelich PN (1988) Kinetic control of dissolved phosphate in natural rivers and estuaries: a primer on the phosphate buffer mechanism. Limnol Oceanogr 33:649–668

Haese RR, Murray EJ, Smith CS, Smith J, Clementson L, Heggie DT (2007) Diatoms control nutrient cycles in a temperate, wave-dominated estuary (southeast Australia). Limnol Oceanogr 52:2686–2711

Halpern BS, Walbridge S, Selkoe KA, Kappel CV, Micheli F, D'Agrosa C, Bruno JF, Casey KS, Ebert C, Fox HE, Fujita R, Heinemann D, Lenihan HS, Madin EMP, Perry MT, Selig ER, Spalding M, Steneck R, Watson R (2008) A global map of human impact on marine ecosystems. Science 319:948–952

Herbert RA (1999) Nitrogen cycling in coastal marine ecosystems. FEMS Microbiol Rev 23:563–590

Hopkinson CS Jr (1985) Shallow-water benthic and pelagic metabolism. Mar Biol 87:19–32

Howarth R, Sharpley A, Walker D (2002) Sources of nutrient pollution to coastal waters in the United States: implications for achieving coastal water quality goals. Estuaries Coasts 25:656–676

Jennerjahn TC, Ittekkot V, Klopper S, Adi S, Purwo Nugroho S, Sudiana N, Yusmal A, Prihartanto, Gaye-Haake B (2004) Biogeochemistry of a tropical river affected by human activities in its catchment: Brantas River estuary and coastal waters of Madura Strait, Java, Indonesia. Estuar Coast Shelf Sci 60:503–514

Jickells TD (1998) Nutrient biogeochemistry in the coastal zone. Science 281:217–222

Jones AB, O'Donohue MJ, Udy J, Dennison WC (2001) Assessing ecological impacts of shrimp and sewage effluent: biological indicators with standard water quality analyses. Estuar Coast Shelf Sci 52:91–109

Kana TM, Darkangelo C, Hunt MD, Oldham JB, Bennett GE, Cornwell JC (1994) Membrane inlet mass spectrometer for rapid high-precision determination of N_2, O_2, and Ar in environmental water samples. Anal Chem 66:4166–4170

Kemp WM, Sampou P, Caffrey J, Mayer M, Henriksen K, Boynton WR (1990) Ammonium recycling versus denitrification in Chesapeake Bay sediments. Limnol Oceanogr 35:1545–1563

Kemp WM, Boynton WR, Adolf JE, Boesch DF, Boicourt WC, Brush G, Cornwell JC, Fisher TR, Glibert PM, Hagy JD, Harding LW, Houde ED, Kimmel DG, Miller WD, Newell RIE, Roman MR, Smith EM, Stevenson JC (2005) Eutrophication of Chesapeake Bay: historical trends and ecological interactions. Mar Ecol Prog Ser 303:1–29

Koné YJ-M, Borges AV (2008) Dissolved inorganic carbon dynamics in the waters surrounding forested mangroves of the Ca Mau Province (Vietnam). Estuar Coast Shelf Sci 77:409–421

Kristensen E, Andersen FØ, Holmboe N, Holmer M, Thongtham N (2000) Carbon and nitrogen mineralization in sediments of the Bangrong mangrove area, Phuket, Thailand. Aquat Microb Ecol 22:199–213

Kristensen E, Flindt MR, Ulomi S, Borges AV, Abril G, Bouillon S (2008) Emission of CO_2 and CH_4 to the atmosphere by sediments and open waters in two Tanzanian mangrove forests. Mar Ecol Prog Ser 370:53–67

Mackenzie FT, Ver LM, Lerman A (2002) Century-scale nitrogen and phosphorus controls of the carbon cycle. Chem Geol 190:13–32

McGlathery KJ, Sundbäck K, Anderson IC (2004) The importance of primary producers for benthic nitrogen and phosphorus cycling. In: Nielsen SL, Banta GT, Pedersen MF (eds) Estuarine nutrient cycling: the influence of primary producers. Kluwer, Dordrecht, pp 231–261

McKinnon AD, Smit N, Townsend S, Duggan S (2006) Darwin Harbour: water quality and ecosystem structure in a tropical harbour in the early stages of urban development. In: Wolanski E (ed) The environment in Asia Pacific Harbours. Springer, Dordrecht, pp 433–459

McKinnon AD, Carleton JH, Duggan S (2007) Pelagic production and respiration in the Gulf of Papua during May 2004. Cont Shelf Res 27:1643–1655

McKinnon AD, Trott LA, Brinkman R, Duggan S, Castine S, O'Leary RA, Alongi DM (2010) Seacage aquaculture in a World Heritage Area: the environmental footprint of a Barramundi farm in tropical Australia. Mar Poll Bull 60:1489–1501

Nixon SW (1995) Coastal marine eutrophication: a definition, social causes, and future concerns. Ophelia 41:199–219

Nixon S, Ammerman J, Atkinson L, Berounsky V, Billen G, Boicourt W, Boynton W, Church T, Ditoro D, Elmgren R, Garber J, Giblin A, Jahnke R, Owens N, Pilson M, Seitzinger S (1996) The fate of nitrogen and phosphorus at the land-sea margin of the North Atlantic Ocean. Biogeochemistry 35:141–180

Norrish K, Hutton JT (1969) An accurate X-ray spectrographic method for the analysis of a wide range of geological samples. Geochim Cosmochim Acta 33:431–453

Nowicki BL (1994) The effect of temperature, oxygen, salinity, and nutrient enrichment on estuarine denitrification rates measured with a modified nitrogen gas flux technique. Estuar Coast Shelf Sci 38:137–156

Patrick WH Jr, Khalid RA (1974) Phosphate release and sorption by soils and sediments: effect of aerobic and anaerobic conditions. Science 186:53–55

Pratihary AK, Naqvi SWA, Naik H, Thorat BR, Narvenkar G, Manjunatha BR, Rao VP (2009) Benthic fluxes in a tropical estuary and their role in the ecosystem. Estuar Coast Shelf Sci 85:387–398

Ram ASP, Nair S, Chandramohan D (2003) Seasonal shift in net ecosystem production in a tropical estuary. Limnol Oceanogr 48:1601–1607

Richardson K, Jørgensen BB (1996) Eutrophication: definition, history and effects. In: Jørgensen BB, Richardson K (eds) Eutrophication in coastal marine systems. American Geophysical Union, Washington, pp 1–19

Rivera-Monroy V, Madden C, Day J, Twilley R, Vera-Herrera F, Alvarez-Guillén H (1998) Seasonal coupling of a tropical mangrove forest and an estuarine water column: enhancement of aquatic primary productivity. Hydrobiologia 379:41–53

Robertson AI, Daniel PA, Dixon P, Alongi DM (1993) Pelagic biological processes along a salinity gradient in the Fly delta and adjacent river plume (Papua New Guinea). Cont Shelf Res 13:205–224

Rysgaard S, Christensen PB, Nielsen LP (1995) Seasonal variation in nitrification and denitrification in estuarine sediment colonized by benthic microalgae and bioturbating infauna. Mar Ecol Prog Ser 126:111–121

Sarma VVSS, Gupta SNM, Babu PVR, Acharya T, Harikrishnachari N, Vishnuvardhan K, Rao NS, Reddy NPC, Sarma VV, Sadhuram Y, Murty TVR, Kumar MD (2009) Influence of river discharge on plankton metabolic rates in the tropical monsoon driven Godavari estuary, India. Estuar Coast Shelf Sci 85:515–524

Seabergh WC (2006) Hydrodynamics of tidal inlets. In: Vincent L, Demirbilek Z (eds) Coastal Engineering manual, Part II, Coastal hydrodynamics, chap 6, Engineer manual 1110-2-110. U.S. Army Corps of Engineers, Washington

Seitzinger SP (1988) Denitrification in freshwater and coastal marine ecosystems: ecological and geochemical significance. Limnol Oceanogr 33:702–724

Sloth NP, Blackburn H, Hansen LS, Risgaard-Petersen N, Lomstein BA (1995) Nitrogen cycling in sediments with different organic loading. Mar Ecol Prog Ser 116: 163–170

Sloth NP, Riemann B, Nielsen LP, Blackburn T (1996) Resilience of pelagic and benthic microbial communities to sediment resuspension in a coastal ecosystem, Knebel Vig, Denmark. Estuar Coast Shelf Sci 42:405–415

Soetaert K, Middelburg J (2009) Modeling eutrophication and oligotrophication of shallow-water marine systems: the importance of sediments under stratified and well-mixed conditions. Hydrobiologia 629:239–254

Sokal RR, Rohlf FJ (1995) Biometry, 3rd edn. WH Freeman and Company, New York

Ståhlberg C, Bastviken D, Svensson BH, Rahm L (2006) Mineralisation of organic matter in coastal sediments at different frequency and duration of resuspension. Estuar Coast Shelf Sci 70:317–325

Trott LA, Alongi DM (1999) Variability in surface water chemistry and phytoplankton biomass in two tropical, tidally dominated mangrove creeks. Mar Freshw Res 50:451–457

Trott LA, McKinnon AD, Alongi DM, Davidson A, Burford MA (2004) Carbon and nitrogen processes in a mangrove creek receiving shrimp farm effluent. Estuar Coast Shelf Sci 59:197–207

Wainright SC, Hopkinson CS (1997) Effects of sediment resuspension on organic matter processing in coastal environments: a simulation model. J Mar Syst 11:353–368

Webster IT, Harris GP (2004) Anthropogenic impacts on the ecosystems of coastal lagoons: modelling fundamental biogeochemical processes and management implications. Mar Freshw Res 55:67–78

Williams D, Wolanski E, Spagnol S (2006) Hydrodynamics of Darwin Harbour. In: Wolanski E (ed) The environment in Asia Pacific Harbours. Springer, Dordrecht, pp 461–476

Wolanski E, Jones M, Bunt JS (1980) Hydrodynamics of a tidal creek-mangrove swamp system. Mar Freshw Res 31: 431–450

Wolanski E, Mazda Y, Ridd P (1992) Mangrove hydrodynamics. In: Robertson AI, Alongi DM (eds) Tropical mangrove ecosystems. American Geophysical Union, Washington, pp 43–62

Wolanski E, Spagnol S, Thomas S, Moore K, Alongi DM, Trott L, Davidson A (2000) Modelling and visualizing the fate of shrimp pond effluent in a mangrove-fringed tidal creek. Estuar Coast Shelf Sci 50:85–97

Woodroffe CD, Bardsley KN, Ward PJ, Hanley JR (1988) Production of mangrove litter in a macrotidal embayment, Darwin Harbour, N.T., Australia. Estuar Coast Shelf Sci 26:581–598

Zar JH (1999) Biostatistical analysis, 4th edn. Prentice Hall, Upper Saddle River