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Seasonal, daily and diel N₂ effluxes in permeable carbonate sediments

B. D. Eyre, I. R. Santos, and D. T. Maher

Centre for Coastal Biogeochemistry, Southern Cross University, P.O. Box 157, Lismore, NSW 2480, Australia

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Correspondence to: B. D. Eyre (bradley.eyre@scu.edu.au)

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Abstract

Benthic metabolism and inorganic nitrogen and N₂ flux rates (denitrification) were measured in permeable carbonate sands from Heron Island (Great Barrier Reef). Some of the N₂ flux rates were among the highest measured in sediments. All benthic fluxes showed a significant difference between seasons with higher rates in summer and late summer. There was no distinct response of the benthic system to mass coral spawning. Instead, changes in benthic fluxes over 12 days in summer appears to be driven by tidal changes in water depth and associated changes in photosynthetically active radiation reaching the sediments. Dark N₂ fluxes were strongly correlated to benthic oxygen consumption across all sites and seasons ($r^2 = 0.64$; $p < 0.005$; slope = 0.036). However, there were seasonal differences with a steeper slope in summer than winter reflecting either more efficient coupling between respiration and nitrification-denitrification at higher temperatures or different sources of organic matter. Adding data from published studies on carbonate sands revealed two slopes in the dark N₂ flux versus benthic oxygen consumption relationship. The lower slope (0.035) was most likely due to high carbon:nitrogen (C:N) organic matter from coral reefs, but competition by benthic microalgae for nitrogen, N-fixation or inefficient coupling between respiration and nitrification-denitrification can not be excluded. The steeper slope (0.089) was most likely due to respiration being driven by low C:N phyto-detritus. If the different slopes were driven by the sources of organic matter then global estimates of continental shelf denitrification are probably about right. In contrast, global estimates of continental shelf may be over-estimated if the low slope was due to inefficient coupling between respiration and nitrification-denitrification and also due to reduced N₂ effluxes in the light associated with competition by benthic microalgae for nitrogen and N-fixation.

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1 Introduction

Denitrification permanently removes nitrogen from an ecosystem by converting fixed nitrogen to di-nitrogen gas, which can then be lost to the atmosphere. The importance of denitrification, because it may control system production by removing nitrogen that would otherwise be available for primary producers, is demonstrated by the numerous denitrification studies in most types of ecosystems (Seitzinger et al., 2006). Permeable carbonate sands cover large areas of coral reefs, and overall around 40 % of continental shelves (Milliman and Droxler, 1996), but there have been few studies of denitrification in this type of sediment. Of the few measurements of denitrification in carbonate sediments all are in coral reef sediments and all earlier studies were done using the C₂H₂ Blockage technique on ex-situ disturbed slurries (Seitzinger and D'Elia, 1985; Capone et al., 1992; Miyajima et al., 2001). The C₂H₂ Blockage technique underestimates coupled nitrification-denitrification due to inhibition of nitrification (Hynes and Knowles, 1978). More recently direct N₂ fluxes have been measured in the dark using the background removal technique (Nowicki, 1994) in ex-situ chambers in carbonate muds on the Arlington and Sudbury Reefs, Great Barrier Reef (GBR) (Alongi et al., 2006), in carbonate silts to medium sands at inter-reef sites on the northern and central GBR (Alongi et al., 2008) and in carbonate silts to very coarse sands in the Southern GBR (Alongi et al., 2011).

Only one in situ denitrification study has tried to assess the effect of advective pore water flow on rates in permeable carbonate sediments (Eyre et al., 2008). As the advective flow in benthic chambers increased, the N₂ fluxes changed from a diffusive uptake to an increasing efflux (Eyre et al., 2008). Stimulation of denitrification by advection has also been seen in several studies in permeable quartz sediments (Cook et al., 2006; Rao et al., 2007; Gihring et al., 2010; Gao et al., 2012). The quantity and quality (source) of organic matter supply to carbonate sediments was also an important driver of denitrification with a rapid increase N₂ effluxes in response to the episodic deposition of phyto-detritus associated with coral mass spawning (Eyre et al., 2008).

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Measured denitrification rates with advection were also much higher than previously measured rates in carbonate sediments without advection (Eyre et al., 2008). However, Eyre et al. (2008) was limited to dark denitrification rates measured during only one sampling season (early summer) and in only one sediment grain size. The hypothesis of this current study is that denitrification rates in permeable carbonate sands will vary spatially and temporally in response to controlling factors such as carbon and nitrogen supply and temperature. As such, denitrification rates were measured over a diel cycle in very coarse and coarse permeable carbonate sands on seasonal (summer, late summer, winter, spring), daily (12 consecutive days in summer) and episodic (following a coral spawning event) time scales. Benthic metabolism and inorganic nitrogen fluxes were also measured to elucidate the factors controlling N₂ fluxes (denitrification). The implications of this work for coral reef and global nitrogen budgets will also be discussed.

2 Methods

2.1 Study site

Sampling was undertaken on the Heron Island reef flat at the southern end of the Great Barrier Reef about 70 km off the coast of Gladstone, Australia. The reef flat is a mosaic of different coral species and carbonate sands. Overall 85 % of the reef lagoon at Heron Island consists of sand (Glud et al., 2008). The very coarse sand site was about 50 m from the eastern Research Beach shoreline near the site of Glud et al. (2008) and Eyre et al. (2008) and the coarse sand site was in Shark Bay at the southern end of the island near the site of Wild et al. (2004). Both the coarse and very coarse sediments contain < 1 % of silt and clay and have a low organic carbon (< 0.24 %) and nitrogen content (0.042 %) (Wild et al., 2004; Eyre et al., 2008). The coarse sands (Wentworth Scale) had an average grain size of 536 microns, a permeability of $2.1 \times 10^{-10} \text{ m}^2$ and a porosity of 44 % and the very coarse sands had an average

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grainsize of 1160 microns, a permeability of $0.6 \times 10^{-10} \text{ m}^2$ and a porosity of 46 % (Santos et al., 2012a). Average daily water temperature at the study site varied over the study period from 19.1 °C in winter (August) to 27.9 °C in summer (February).

2.2 Chamber measurements and sample analysis

5 A summary of the benthic chamber sampling campaigns is given Table 1. Round benthic chambers with an internal diameter (i.d.) of 190 mm and a height of 330 mm (Huetel and Gust, 1992) were inserted into the permeable sands between outcrops of coral to retain a water column height of 190 to 240 mm. The chambers were deployed between 17:00 and 18:00 on each day and left uncapped for about 3 h to equilibrate. 10 The chambers were stirred at 40 RPM, which induces a sediment percolation rate of approximately $43 \text{ l m}^{-2} \text{ d}^{-1}$ (Glud et al., 2008). Although this is at the low range of advective rates estimated for permeable sediments in the Heron Island reef lagoon (0 to $600 \text{ l m}^{-2} \text{ d}^{-1}$; average $150 \text{ l m}^{-2} \text{ d}^{-1}$; Santos et al., 2010) these higher rates include all advective processes (e.g. tidal pumping) not just the small-scale advective processes in 15 the sediments (e.g. topography induced advection). Most importantly, it was the same stirring rate that was used for most of the benthic metabolism and denitrification measurements from previous studies at the same site (i.e. Glud et al., 2008; Eyre et al., 2008), allowing a direct comparison of measured rates. A range of stirring rates was not used as the effect of different advection rates on benthic metabolism and denitrification in permeable carbonate sands has been well studied (Wild et al., 2004; Glud et al., 2008; Eyre et al., 2008; Santos et al., 2012a). 20

During the summer incubations a HOBO logger was placed on the lid of one chamber and photosynthetically active radiation (PAR) measured every 30 min and water depth every hour. HOBO Lux units were converted to $\mu\text{E m}^{-2} \text{ s}^{-1}$ by multiplying by 0.0165 25 and then calibrated against a Li-Cor-192 light metre. All the benthic incubations were undertaken over a 20 h diel cycle. The chambers were then capped at 21:00, and the first samples from the chambers were collected. Subsequent samples were collected

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at 02:00, 05:00 (dawn), 12:00 and 17:00 (dusk). N₂:Ar samples were only collected at 21:00, 02:00, 05:00 and 08:00, as the formation of bubbles during daytime confounded all gas samples collected after 08:00. Dissolved oxygen concentrations in the 40 RPM chambers typically closely follow dissolved oxygen variations in the water column (Glud et al., 2008; Cyronak et al., 2013). During the summer campaign the chambers were moved between 17:00 and 18:00 within a 100 m² area and again left uncapped for 3 h to equilibrate before re-starting the sampling cycle.

On each sampling occasion two 50 ml pre-soaked (in site water) polypropylene syringes of water were collected from each chamber, and as a sample was withdrawn an equal amount was replaced from the bottom water. Within 10 min of sampling, 20 ml of sample was transferred to a polypropylene vial for dissolved oxygen measurements and 30 ml of sample was immediately filtered through a 0.45 µm cellulose acetate membrane filters (Sartorius) into two 10 ml acid- and sample-rinsed polypropylene vials. To minimise the introduction of bubbles, N₂:Ar samples were collected in triplicate 7 ml gas-tight glass vials with glass stoppers, by adding a piece of gas-tight tubing to the syringe and filling from the bottom of the vial until it overflowed (Eyre et al., 2008). Two vials for nutrient samples were immediately frozen at -20 °C. N₂:Ar samples were poisoned with 20 µl of 5 % HgCl₂ and stored submerged at ambient temperature. Details of the nutrient and N₂:Ar analysis are given in Eyre and Ferguson (2005). Dissolved oxygen measurements ($\pm 0.01 \text{ mg l}^{-1}$) were undertaken using a HACH LDO HQ-10.

2.3 Benthic flux calculations

Fluxes across the sediment-water interface were calculated using the start and end point concentration data, corrected for the addition of replacement water, as a function of incubation time, core water volume, and surface area. Dark flux rates were calculated using concentration data from 21:00 to 05:00 and light flux rates were calculated using concentration data from 05:00 to 17:00. N₂ light fluxes rates were calculated using

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concentration data from 05:00 to 08:00.

Net flux rates = ((hourly dark rates × hours of darkness) + (hourly light rates × hours of daylight))/24 h.

Gross benthic oxygen production (+ve, efflux) =

light O₂ flux (+ve) (net production) – Dark O₂ flux (–ve) (respiration).

Benthic O₂ *p/r* = gross O₂ productivity × daylight hours/dark O₂ flux × 24 h.

Careful consideration was given to the possible effect of bubbles on N₂ fluxes (Eyre et al., 2002). All samples over 96 % O₂ saturated were excluded from N₂ flux calculations because it was clear that these samples were affected by bubbles. As such, many light rates are missing due to samples being over 96 % O₂ saturated by 08:00. In some cases the water column was still saturated (> 96 %) when the first dark sample was taken (21:00) and as such, some dark N₂ rates were calculated using concentration data from 02:00 to 05:00. Bubbles have the effect of reducing the first dark sample N₂ concentration giving much higher dark N₂ flux rates and reducing the last light sample N₂ concentration giving lower light N₂ flux rates or apparent rates of N-fixation. Many net N₂ fluxes are also missing as they could only be calculated when light fluxes were available. Because N₂ fluxes were measured they include both canonical denitrification and anammox. The terms N₂ efflux and denitrification are used interchangeably.

2.4 Statistical analysis

To determine the influence of sediment type (very coarse, coarse) and season (winter, spring, summer and late summer) on benthic fluxes a fixed effects two-level linear mixed model (LMM) was used. The two-level model incorporated sediment type and season as fixed effects. As intra-class correlation is likely within the fixed effects, the LMM procedure was preferred over the commonly used general linear model (GLM) and standard one-way ANOVA models. LMM does not assume independent observations, and allows greater flexibility in fitting and testing heterogeneous covariance

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structures (West et al., 2006). To determine the influence of mass coral spawning on benthic fluxes, a repeated measures ANOVA was carried out over the first 7 days of the summer period for each combination of benthic flux (i.e. NH_4^+ , NO_3^- , O_2 , and N_2) and treatment (i.e. dark, light and net for all fluxes and also Net Primary Production, Gross Primary Production and GPP/respiration (p/r) ratio). Statistical test could only be applied to the first 7 days, as there was no chamber replication for days 8 to 12 (Table 1). Where a significant difference was found among the first 7 days of the summer period, Tukey HSD Post Hoc tests were carried out to determine homogenous subsets. To determine differences between dark and light fluxes paired t -tests were carried out. All analysis was carried out using SPSS v20 with $\alpha = 0.05$.

3 Results

3.1 Benthic fluxes in very coarse and coarse sands, dark versus light and different seasons

None of the fluxes were significantly different between coarse and very coarse sands, except for the NO_3^- fluxes, which were all higher in the very coarse sands (Table 2) (coarse sands data not shown). There were season and sediment type interactions for dark O_2 (respiration), gross benthic primary production (GPP) and dark NO_x (Table 2). In winter respiration and GPP were higher in the very coarse sediments than the coarse sediments, and in late summer respiration and GPP were higher in the coarse sediments than the very coarse sediments (Table 2). Dark NO_x fluxes were smaller in the coarse sediment than the very coarse sediments in late summer (Table 2).

There was a significant difference between all dark and light benthic fluxes (Table 3). The sediments consumed O_2 in the dark (respiration) and produced O_2 in the light (Net Primary Production; NPP) (Fig. 1). NH_4^+ and NO_3^- fluxes generally showed uptakes in the dark and smaller uptakes or effluxes in the light (Figs. 2 and 3). N_2 effluxes were mostly reduced in the light (Fig. 4).

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All benthic fluxes showed a significant difference between seasons, except light NH_4^+ , light NO_3^- and net N_2 fluxes (Table 2). Dark O_2 uptakes (respiration), GPP, NPP and GPP/dark O_2 (p/r) ratios were all higher in late summer and summer than the other seasons (Fig. 1). NH_4^+ and NO_3^- fluxes all showed greater uptakes in summer than the other seasons (Figs. 2 and 3). Dark N_2 effluxes were highest in late summer, but light N_2 effluxes were highest in spring (Fig. 4).

3.2 Daily and episodic variations in benthic fluxes (summer)

Major coral spawning occurred on the night of 7 and 8 December 2010 with *Montipora digitata* and massive corals (e.g. *Platygyra daedalea*) releasing eggs. There was a visible slick of spawning material on the water surface that night, but by the next day little of this material could be seen. There was no large accumulation of spawning material along beaches and in the water column, and only a minor bloom of benthic dinoflagellates (visual observation). Major coral spawning occurred after the benthic chambers were sealed on day 4 in summer and as such, the chamber incubations on days 1 to 4 reflect pre-spawning and days 5 to 12 reflect post-spawning.

The study site experienced a semi-diurnal tide with the average depth of water in the light hours between 08:00 and 16:00 decreasing from day 1 to 7 and then increasing to day 12 (Fig. 5a). The depth of water at 12:00 decreased from a maximum on day 1 of 2.36 m to a minimum of 0.28 m on days 6 and 7 (Fig. 5). Water depth was an important control on PAR measured at the top of the chamber with the highest light levels occurring on days 6 and 7 when the water depth was shallowest (Fig. 5b).

p/r ratios ($p < 0.001$) and dark NH_4 fluxes ($p = 0.006$) were the only benthic fluxes that showed a significant difference between the pre- and post-spawn periods (Figs. 1 and 2). p/r ratios were similar for the first 3 days and then they increased until day 7 and then decreased again to day 12. Dark NH_4 uptakes were greater on days 5–7 (post-spawn) than days 1–4 (pre-spawn). The dark NH_4 uptakes peaked on day 10 and then decreased to day 12.

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Dark O₂ fluxes (benthic respiration) varied significantly over the summer period ($p < 0.001$) with days 2, 3 and 4 having significantly higher uptake rates than days 1, 5, 6 and 7 (Fig. 1). NPP ($p < 0.001$) varied significantly over the summer period increasing from day 1 to day 6 (Fig. 1). NPP then remained elevated for days 6 to 9 before decreasing again from day 10 to day 12. Dark NO_x uptake rates were significantly different over the summer period ($p < 0.001$) with day 7 having greater uptake rates than the previous 6 days, and day 3 having significantly lower uptake rates than any other day (Fig. 3). There was no significant difference in N₂ fluxes over the first 7 day period ($p = 0.086$), but dark N₂ rates increased greatly on days 11 and 12 (Fig. 4).

4 Discussion

4.1 Comparison of denitrification rates in carbonate sands

There have been few measurements of denitrification in carbonate sediments and these have all been in the dark in coral reef sediments and most of these have been ex-situ (Table 4). In sandy sediments only the previous study of Eyre et al. (2008) simulated the effect of advective pore water flow (Table 4). Denitrification rates measured using C₂H₂ blockage were all much lower than all of the rates of Eyre et al. (2008) and those measured during this study (Table 4). The lower rates measured using C₂H₂ Blockage most likely reflects inhibition of nitrification (Hynes and Knowles, 1978), which would result in rates being underestimated because of the strong nitrification-denitrification coupling (see later discussion). In addition, in the slurries there is no advective pore water flow, which appears to enhance coupled nitrification-denitrification in permeable carbonate sediments (Eyre et al., 2008; Santos et al., 2012a). Upper rates of denitrification measured using the direct N₂ flux technique in carbonate muds and sands without advective flow (Alongi et al., 2006, 2008, 2011), approached the pre-spawning rates of Eyre et al. (2008) and the lower rates of this study, but were still much lower than the higher rates of Eyre et al. (2008) and this study (Table 4). The

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dark summer rates were similar to the 1 to 3 days post-coral spawning rates measured by Eyre et al. (2008) at the same site at the same time of year using exactly the same technique (Table 4), but also lower than the upper rates measured Eyre et al. (2008) 4 to 5 days post-coral spawning. Williams et al. (1985) estimated that denitrification rates of a similar range to those measured in Eyre et al. (2008) and this study (60 to $304 \mu\text{mol N m}^{-2} \text{ h}^{-1}$) must have been occurring to account for the missing nitrogen flux in coral reef sands at St. Croix.

Because of the strong dependence of denitrification rates on advective flow (Cook et al., 2006; Eyre et al., 2008), and because we do not know the in-situ advective pore water flow, the “true” in-situ denitrification rate is unknown. The “true” in-situ rates of denitrification in carbonate sands would probably vary rapidly due to changes in the interaction of organic matter deposition (respiration) and drivers of advective pore water flow such as wave and tidal pumping and flow- and topography-induced advection (see Santos et al., 2012b for review of the drivers of advective flow in permeable sands). Any measured rate would only represent a chamber induced transient state. Overall however, denitrification rates have probably previously been underestimated in carbonate sediments (permeable sands) due to methodological constraints (inhibition of nitrification; no advective pore water flow), and because episodic events that enhance the supply of organic matter to the benthos and stimulate denitrification (e.g. coral spawning, phytoplankton blooms) have only once been previously captured (Eyre et al., 2008). The rates measured in permeable carbonate sands were at the upper end of coupled nitrification-denitrification rates measured in muddy sediments (Fennel et al., 2009), but similar to the range measured in permeable quartz sands (Gao et al., 2012).

4.2 Effect of mass coral spawning on benthic fluxes

There was no distinct response of the benthic system to mass coral spawning as has been previously observed (e.g. Wild et al., 2004; Glud et al., 2008; Eyre et al., 2008). This is consistent with the lack of a large accumulation of spawning material along

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beaches and in the water column, and only a minor bloom of benthic dinoflagellates. In contrast, previous observations of mass coral spawning events at Heron have seen large accumulations of coral spawning material along the beaches and large blooms of benthic dinoflagellates (see Figs. 1c, d in Glud et al., 2008).

Even the significant effects of dark NH_4 uptakes and p/r ratios between pre- and post-spawning are more likely driven by changes in water depth and PAR over the 12 day summer study period. For example, NPP is highly correlated with average hourly PAR received at the top of the chamber ($r^2 = 0.79$; $p = < 0.001$; $n = 26$) and water depth at 13:00 ($r^2 = 0.82$; $p = < 0.001$; $n = 26$), and as expected PAR is highly dependent on water depth ($r^2 = 0.81$; $p = < 0.01$; $n = 26$). Dark NH_4^- uptakes and NPP are positively correlated ($r^2 = 0.55$; $p = < 0.01$; $n = 26$) reflecting the dark uptake of NH_4^- by benthic microalgae. A clear pattern of NH_4^- uptake in the light is not seen because water column NH_4 concentrations are so low during the light (Eyre et al., 2008) that the benthic fluxes are not easily measured (see variability in Fig. 2). It is unknown if the lack of coral spawning material is due to less material being produced by the corals or a physical effect such as wind direction that accumulates spawning material in the lagoon. Inter-annual variations in the response of coral reefs, and in particular the benthic system, to mass coral spawning is an area for further research.

4.3 Organic matter control of denitrification

Dark N_2 fluxes were strongly controlled by benthic respiration (Fig. 6; Table 5), most likely reflecting an increased supply of NH_4 from ammonification for coupled nitrification–denitrification and the availability of electron donors for denitrification. NO_3^- uptakes were not significantly correlated with N_2 fluxes due to the very low water column NO_3^- concentrations ($< 1 \mu\text{mol l}^{-1}$; Eyre et al., 2008) providing further support for a dominance of coupled nitrification-denitrification in these sediments. Benthic respiration and net primary production (NPP) were not correlated ($r^2 = 0.08$) indicating that other sources of organic matter, probably in addition to benthic microalgae, must

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be driving benthic respiration. Possible sources include coral mucus, turf algae, coral spawning material and phytoplankton detritus which have previously been suggested as drivers of benthic respiration and denitrification at this site (Eyre et al., 2008).

The relationship between benthic respiration and dark N₂ efflux is significant if data from all seasons and sites (coarse and very coarse sands) are included (Fig. 6; Table 5). However, there were seasonal differences with a steeper slope in summer than winter (Table 5). The steeper summer slope probably reflects a more efficient coupling between respiration and nitrification-denitrification at higher temperatures or a difference in the source of organic matter driving benthic respiration. Seasonal differences in the relationship between benthic respiration and denitrification were also seen in a shallow temperate coastal system, but steeper slopes occurred in winter and summer compared to spring and fall (Piehler and Smyth, 2011), indicating that temperature was not an important driver of the differences. Despite seasonal differences in the relationship between benthic respiration and dark N₂ efflux, the relationship for a given season appears consistent inter-annually as shown by similar summer slopes in this study and a study at the same site in 2005 (Eyre et al., 2008; Table 5).

Including all the data from tropical carbonate sands improves the strength and significance of the relationship between benthic respiration and dark N₂ efflux (Fig. 7; Table 5). Despite improving the relationship, the inter-reef carbonate sands generally had lower rates of benthic respiration and associated N₂ efflux, which may be due to either, or a combination of, a lack of advective flow during the measurements or the greater depth of the sample sites and therefore less organic matter deposition (Alongi et al., 2008). The slope of the combined data for tropical carbonate sands was similar to that found across some subtropical sub-tidal and inter-tidal muddy habitats (Table 5) and temperate sub-tidal muddy habitats (lowest temperate habitat slope; Table 5). This demonstrates that benthic respiration and associated coupled nitrification-denitrification in carbonate sands can be just as efficient as in some muddy sediments. However, the slope is lower than that found in most muddy temperate and subtropical coastal and continental shelf sediments (Table 5).

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The lower slope of the relationship between benthic respiration and dark N₂ efflux in tropical carbonate sediments may be due to either, or a combination of, competition with benthic microalgae for nitrogen, enhanced N-fixation, less efficient coupled respiration-nitrification-denitrification in sands, or the composition of organic matter driving respiration and associated assimilation of nitrogen by heterotrophic bacteria. Support for a reduction in N₂ efflux due to competition from benthic microalgae is given by the negative correlation between dark N₂ efflux and dark NH₄ ($r^2 = 0.34$, $p = 0.05$, $n = 29$) and NO_x ($r^2 = 0.24$, not significant, $n = 29$) uptakes, and dark N₂ efflux and benthic productivity/respiration (p/r) ($r^2 = 0.56$, $p < 0.01$, $n = 29$). In addition, N₂ effluxes are generally greatly reduced in the light (although note the one exception in Spring; Fig. 4). N₂ effluxes are a measure of denitrification minus N-fixation and as such, increased N-fixation will result in a reduced N₂ efflux. The reduced N₂ effluxes in the light could also be due to increased N-fixation. In tropical oligotrophic coral reef environments competition for nitrogen by benthic microalgae that are typically nitrogen limited (Dizon and Yap, 1999; Clavier et al., 2005) and N-fixation may be more important than in temperate coastal systems, resulting in the lower slope of the relationship between benthic respiration and dark N₂ efflux.

Phytoplankton production is also typically low in oligotrophic coral reef environments (Furnas et al., 2005) highlighting the possible role of other sources of organic matter, such as coral mucus, turf algae, macrophytes and coral spawning material, in driving benthic respiration. These sources of organic matter have higher carbon : nitrogen (C : N) ratios than phyto-detritus resulting in less nitrogen being released as N₂ for a given amount of respiration due to competition for nitrogen by heterotrophic bacteria (Oakes et al., 2011). N-limitation of the microbial decomposition of high C : N organic material results in the uptake and accumulation of nitrogen by bacteria (Tupas and Koike, 1991; van Duyl et al., 1993; Lomstein et al., 1998). Several types of bacteria can assimilate NH₄⁺, including sulphate reducers and fermentative bacteria (Koike and Sumi, 1989). C : N ratios of sediment trap material at the Heron Island reef lagoon study site ranged from 10.5 to 17.2 (Eyre et al., 2008) and sediment C : N ratios at

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the inter-reef channel sites ranged from 8.1 to 16.8 (Alongi et al., 2008). Remineralisation ratios (O_2 respiration/ $(N-N_2+NH_4+NO_x)$) of the data in Fig. 7 (excluding outliers) ranged from 15 to 65 and averaged 37 demonstrating that high C:N organic matter was being respired. The remineralisation ratios were always higher than the organic matter substrate, which is consistent with assimilation of nitrogen by heterotrophic bacteria. High C:N organic matter may also favour anammox over denitrification due to denitrification not proceeding all the way to N_2 and associated leakage of NO_2 that fuels anammox (Trimmer and Nicholls, 2009; Erler et al., 2012). Anammox was found at some of the inter-reef sites (Erler et al., 2012) but not in the Heron Island reef lagoon (Eyre et al., 2008). However, if anammox was quantitatively important the end result would be more N_2 production for a given benthic respiration not less (i.e. lower slope).

Further support for the low slope of the relationship between benthic respiration and dark N_2 efflux being driven by high C:N organic material is given by the outliers in each of the three data sets used to develop the relationship in tropical carbonate sands (Fig. 7). The outliers fell outside the upper 95 % confidence limit for the regressions of the 3 data sets (Alongi et al., 2008, 2011; Eyre et al., 2008; this study). The slope of the outliers is significantly different from the lower slope (Student t -test; $p < 0.05$) and is similar to the slopes for most of the non-tropical carbonate sand sediments (Table 5). The outliers from Eyre et al. (2008) were due to the deposition of phyto-detritus suggesting the higher slope of the outliers data and the non-tropical carbonate sand sediments are driven by the deposition of nitrogen rich phyto-detritus. The remineralisation ratios (O_2 respiration/ $(N-N_2+NH_4+NO_x)$) of the outliers ranged from 5.0 to 14.2 and averaged 7.0, which is very close to that expected for phyto-detritus, and no heterotrophic assimilation of nitrogen due to low C:N. In addition, flow-through reactor experiments using permeable carbonate sands from the same site as this study, and seawater with phytoplankton as the organic matter source, had a benthic respiration versus dark N_2 efflux slope of 0.114 (Santos et al., 2012a), which is also similar to the outliers slope (Table 5).

Modelling and flume studies have suggested that permeable quartz sands have a low respiration-nitrification-denitrification efficiency with a maximum loss of about 15 % or less as N_2 of the remineralised nitrogen for Redfield organic matter (Cardenas et al., 2008; Kessler et al., 2012). Using the benthic respiration versus dark N_2 slope of 0.035 for tropical carbonate sands gives losses of 23, 42 and 71 % as N_2 of the remineralised nitrogen for organic matter C:N ratios of Redfield (6.6), coral mucus (12.0; Wild et al., 2004) and coral spawning material (20.3; Eyre et al., 2008), respectively, which are all higher than the modelling and flume studies. Similarly, using the higher slope (0.088) and Redfield organic matters give a loss of 58 % as N_2 . At a carbon mineralisation rate of $1133 \mu\text{mol m}^{-2} \text{h}^{-1}$ the permeable quartz sands model estimated a maximum denitrification rate of $30 \mu\text{mol N m}^{-2} \text{h}^{-1}$ (Cardenas et al., 2008), which is also lower than the denitrification rate of $40 \mu\text{mol N m}^{-2} \text{h}^{-1}$ estimated using the 0.035 slope and $100 \mu\text{mol N m}^{-2} \text{h}^{-1}$ using the 0.088 slope. The difference between the modelled and measured respiration-nitrification-denitrification efficiencies and denitrification rates may be due to the unique interaction of advection and biogeochemistry in permeable carbonate sands (see Santos et al., 2012a) not captured in the model, or that the model simply under-estimates denitrification rates in permeable sediments (see high rates in Gao et al., 2012).

Permeable carbonate sands appear to be just as efficient as muds in coupling between respiration and nitrification-denitrification with rates of denitrification controlled by the quantity and quality of organic matter driving respiration (Fig. 7). Most importantly, a high denitrification efficiency ($\%N_2\text{-N}/(N_2\text{-N}+\text{DIN})$ efflux) is maintained even at high respiration rates ($> 5000 \mu\text{mol m}^{-2} \text{h}^{-1}$). In contrast, the denitrification efficiency of muds decreases rapidly above respiration rates of around $1500 \mu\text{mol m}^{-2} \text{h}^{-1}$ (Eyre and Ferguson, 2009). Recent flow-through reactor experiments with permeable carbonate sediments give some insight into the possible drivers of this high efficiency (Santos et al., 2012a). Three-dimensional microenvironments within the porous carbonate grains may enhance the area, compared to quartz grains, where microbial communities grow and biogeochemical reactions can occur. The increase in coupled

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nitrification-denitrification as advection increases (Eyre et al., 2008) is due to partial flushing of the sands with oxygenated pore water and the development of sharp oxic-anoxic gradients between the inner and outer parts of the carbonate grains. The FTRs showed a decrease in coupled nitrification-denitrification at high advective flows, that was not seen in the benthic chambers at the advective flows used (Eyre et al., 2008), due to complete flushing of the sands with oxygenated porewater that prevented the development of oxygen-depleted microenvironments within grains (Santos et al., 2012a).

4.4 Missing nitrogen on the reef

Although easily explained by the high respiration rates in the shallow productive environment, denitrification rates in the coral reef carbonate sands were very high for such a nitrogen poor environment. Carbonate sands cover about 85% of the Heron Island lagoon (Glud et al., 2008). With such a large loss of nitrogen via denitrification, combined with net autotrophic production in the sediments ($p/r > 1$), the question has to be asked “from where does the nitrogen that supports denitrification and benthic production come”? Possible sources include cross-reef advection of large volumes of water (Atkinson, 1992), N-fixation by coral symbionts (Lesser et al., 2007) and particles from the ocean catchment (Wyatt et al., 2010). Another process that could account for the large nitrogen input required to balance the large nitrogen losses via benthic denitrification is unmeasured N-fixation in the sediments.

The few measurements of light N_2 fluxes are generally much lower than dark N_2 effluxes probably due to N-fixation, although competition for nitrogen with benthic microalgae can not be excluded. The resultant net N_2 fluxes would result in far less nitrogen loss from the system then would be estimated using dark N_2 effluxes. It also needs to be noted that these rates are only for the first few hours of the day. However, if these rates were measured over the full light cycle we suspect that the sediments would be net N_2 sinks with N-fixation in the light exceeding denitrification in the dark, but this can not be determined using the N_2/Ar method. Unfortunately, bubbles are produced during the light in the highly productive sediments, which reduces the N_2/Ar ratio (see

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Discussion in Eyre et al., 2002) giving a psuedo-rate of N-fixation. As such, most of the light N_2/Ar data in this study, and all of the light N_2/Ar data in the previous study at this site (Eyre et al., 2008), had to be excluded. Measured N-fixation rates in coral reef sediments are low (e.g. Capone et al., 1992), including at this site (Eyre et al., 2008), but these have all been measured using slurries and exclude advection and diel cycles, which may be important drivers of N-fixation; earlier measurements of denitrification that excluded advection and diel cycles were also much lower (Table 4). Further work is required to better measure N-fixation in permeable coral reef carbonate sands over diel cycles with advection.

4.5 Global nitrogen budgets

Continental shelves account for a third to half of the global denitrification (Middelburg et al., 1996; Seitzinger et al., 2006). Seventy percent of continental shelves are covered by permeable sediments (Emery, 1968), and around 40 % of the shelves are covered by carbonate sediments (Milliman and Droxler, 1996). There has been some debate over the role of these permeable sediments in global rates of denitrification on the continental shelf. Based on modelling of permeable quartz sands Cardenas et al. (2008) argue that global rates of continental shelf denitrification are over-estimated by a factor of 2 to 7. In contrast, Gao et al. (2012) suggest that global rates of continental shelf denitrification may be under-estimated due to high rates of denitrification measured in permeable quartz sands. The findings from this study suggest that global rates of continental shelf denitrification may be either over-estimated or about right, but not under-estimated.

A recent estimate of denitrification in shelf sediments of 250 Tg N yr^{-1} (Seitzinger et al., 2006) was based on a slope of 0.116 for benthic respiration and dark N_2 (Table 5; Seitzinger and Giblin, 1996) and is within the range of previous estimates ($214\text{--}300 \text{ Tg N yr}^{-1}$; reviewed in Seitzinger et al., 2006). If the lower slope (0.035) for benthic respiration and dark N_2 (Fig. 7; Table 5) is due to less efficient coupled respiration and nitrification-denitrification in permeable carbonate sediments it would result in a

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reduction in global shelf denitrification rates of around 20 %, and if the lower slope applied to all permeable sediments than it would result in a reduction of around 50 %. The latter decrease is consistent with the smallest of Cardenas et al. (2008) estimates of reduced shelf denitrification (i.e. 2 times reduction). However, if the 0.035 slope is due to high C : N organic matter associated with the coral reef environments, and the higher outliers slope of 0.088 is applicable to most continental shelves that are dominated by phytoplankton production, then permeable carbonate sediments should not greatly influence previous estimates of shelf denitrification.

All estimates of global continental shelf denitrification are based on denitrification rates measured in the dark (Seitzinger et al., 2006). Although Laursen and Seitzinger (2002) measured denitrification in continental shelf sediments over a diel cycle too few samples ($n = 3$) were taken to see an effect in the light. However, N_2 effluxes might be reduced in the light due to competition with benthic microalgae and N-fixation (Fig. 4). Because light reaches 33 % of the global shelf area (Gattuso et al., 2006), estimates of global continental shelf denitrification based on dark rates of denitrification may be over-estimated. Future work should be directed at better characterising the relationship between benthic respiration and dark and light (net) N_2 efflux for permeable carbonate and quartz sands. In particular, the interaction between diel cycles in benthic metabolism and denitrification, N-fixation and net N_2 effluxes and advective porewater flow.

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Table 1. Summary of benthic chamber sampling campaigns.

Sample campaign	Sediment type	Chamber incubation length	Chamber replication
Winter (Aug 2009)	Very coarse and coarse sands	One 21 h diurnal cycle	Triplicate
Summer (Dec 2009)	Very coarse sands	Twelve consecutive 21 h diurnal cycles	Triplicate on days 1 to 7 Single on days 8 to 12
Late Summer (Feb 2010)	Very coarse and coarse sands	One 21 h diurnal cycle	Duplicate
Spring (Oct 2010)	Very coarse sands	One 21 h diurnal cycle	Duplicate

Table 2. Results from linear mixed model analysis of the effect of season and sediment type on benthic fluxes.

	Season	Sediment type	Season × sediment type
Dark NH ₄	$F = 4.593_{3,62} p = 0.006$ (summer < winter, late summer, spring)	$F = 0.011_{1,62} p = 0.911$	$F = 0.079_{1,62} p = 0.780$
Light NH ₄	$F = 1.558_{3,63} p = 0.208$	$F = 0.730_{1,63} p = 0.396$	$F = 0.707_{1,63} p = 0.404$
Net NH ₄	$F = 6.996_{3,62} p < 0.001$ (summer < winter, late summer, spring)	$F = 0.366_{1,62} p = 0.547$	$F = 1.606_{1,62} p = 0.210$
Dark NO _x	$F = 39.202_{3,62} p < 0.001$ (summer < late summer < spring, winter)	$F = 10.654_{1,62} p = 0.002$ (coarse < very coarse)	$F = 4.296_{1,62} p = 0.042$ (late summer coarse < very coarse)
Light NO _x	$F = 4.040_{3,64} p = 0.011$ (spring < winter)	$F = 10.293_{1,64} p = 0.002$ (coarse < very coarse)	$F = 1.000_{1,64} p = 0.321$
Net NO _x	$F = 20.076_{3,64} p < 0.001$ (summer < late summer, spring < winter)	$F = 20.540_{1,64} p < 0.001$ (coarse < very coarse)	$F = 2.792_{1,64} p = 0.100$
Dark DO	$F = 18.408_{3,62} p < 0.001$ (summer, late summer < spring, winter)	$F = 0.005_{1,62} p = 0.944$	$F = 9.922_{1,62} p = 0.003$ (winter very coarse < coarse; late summer coarse < very coarse)
Light DO	$F = 68.988_{3,63} p < 0.001$ (spring < winter < summer, late summer)	$F = 0.444_{1,63} p = 0.508$	$F = 3.917_{1,63} p = 0.052$
Net DO	$F = 57.036_{3,63} p < 0.001$ (spring, winter < summer, late summer)	$F = 1.145_{1,63} p = 0.289$	$F = 0.267_{1,63} p = 0.607$
GPP DO	$F = 57.030_{3,63} p < 0.001$ (spring, winter < summer, late summer)	$F = 0.629_{1,63} p = 0.431$	$F = 5.373_{1,63} p < 0.024$ (winter very coarse < coarse; late summer coarse < very coarse)
p/r DO	$F = 22.276_{3,62} p < 0.001$ (spring, winter < summer, late summer)	$F = 2.042_{1,62} p = 0.158$	$F = 1.242_{2,62} p = 0.296$
Dark N ₂	$F = 6.164_{3,55} p = 0.001$ (winter, spring, summer < late summer)	$F = 1.692_{1,55} p = 0.199$	$F = 0.414_{1,55} p = 0.523$
Light N ₂	$F = 3.108_{3,23} p = 0.046$ (summer, winter, late summer < spring)	$F = 0.299_{1,23} p = 0.590$	–
Net N ₂	$F = 2.157_{3,19} p = 0.127$	$F = 0.000_{1,19} p = 0.986$	–

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Table 3. Results from paired *t*-test to determine differences in dark and light fluxes.

	NH ₄	NO _x	DO	N ₂
<i>t</i>	3.605	9.057	32.173	11.961
<i>p</i>	0.001	< 0.001	< 0.001	0.007
Difference	dark < light	dark < light	dark < light	light < dark

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Table 4. Denitrification rates in carbonate sediments.

Rate $\mu\text{mol N}_2\text{-N m}^{-2} \text{ h}^{-1}$	System	Season	Method	Source
19 (dark)	Sands, Bahamas		Dark, C_2H_2 , slurry	Seitzinger and D'Elia (1985)
0.12 to 0.45 (dark)	Sands, Hopkinson Reef, GBR		Dark, C_2H_2 , slurry	Capone et al. (1992)
0.2 to 13.3 (dark)	Sands, Bowl Reef, GBR		Dark, C_2H_2 , slurry	Capone et al. (1992)
1.7 to 6.5 (dark)	Sands, Ishigaki Island		Dark, C_2H_2 , slurry	Miyajima et al. (2001)
17 to 37 (dark)	Carbonate muds, Arlington Reef, GBR		Dark, direct N_2 , ex-situ chamber, no advective flow	Alongi et al. (2006)
7 to 83 (dark)	Carbonate muds, Sudbury Reef, GBR		Dark, direct N_2 , ex-situ chamber, no advective flow	Alongi et al. (2006)
3 to 67 (dark)	Fine to medium inter-reef channel sands	Winter	Dark, direct N_2 , ex-situ chamber, no advective flow	Alongi et al. (2008)
61 to 94 (dark)	Fine to medium inter-reef channel sands	Summer	Dark, direct N_2 , ex-situ chamber, no advective flow	Alongi et al. (2008)
60 to 85 (dark)	Very coarse outer reef channel sands	Spring	Dark, direct N_2 , ex-situ chamber, no advective flow	Alongi et al. (2011)
19 to 65 (dark)	Very coarse outer reef channel sands	Summer	Dark, direct N_2 , ex-situ chamber, no advective flow	Alongi et al. (2011)

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Table 4. Continued.

Rate $\mu\text{mol N}_2\text{-N m}^{-2} \text{h}^{-1}$	System	Season	Method	Source
34 to 92 (dark)	Pre-spawning, very coarse permeable sands, Heron Island, GBR	Summer	Dark, N ₂ :Ar, in-situ chamber, advective flow, 40 rpm	Eyre et al. (2008)
96 to 152 (dark)	1–3 days post-spawning, very coarse permeable sands, Heron Island, GBR	Summer	Dark, N ₂ :Ar, in-situ chamber, advective flow, 40 rpm	Eyre et al. (2008)
400 to 480 (dark)	4–5 days post-spawning, very coarse permeable sands, Heron Island, GBR	Summer	Dark, N ₂ :Ar, in-situ chamber, advective flow, 40 rpm	Eyre et al. (2008)
54 (dark) 66 (light) 60 (net)	Very coarse permeable sands, Heron Island, GBR	Winter	Dark, light, N ₂ : Ar, in-situ chamber, advective flow, 40 rpm	This study
80–214 (dark) 2–14 (light) 7–70 (net)	Very coarse permeable sands, Heron Island, GBR	Summer	Dark, light, N ₂ :Ar, in-situ chamber, advective flow, 40 rpm	This study
234 (dark) 52 (light) 128 (net)	Very coarse permeable sands, Heron Island, GBR	Late Summer	Dark, light, N ₂ :Ar, in-situ chamber, advective flow, 40 rpm	This study
82 (dark) 344 (light) 234 (net)	Very coarse sands, Heron Island, GBR	Spring	Dark, light, N ₂ :Ar, in-situ chamber, advective flow, 40 rpm	This study

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Table 5. Slope of the relationship between benthic oxygen respiration ($\mu\text{mol O}_2 \text{ m}^{-2} \text{ h}^{-1}$) and dark N₂ efflux ($\mu\text{mol N}_2\text{-N m}^{-2} \text{ h}^{-1}$). Regressions were forced through zero as there would be no N₂ efflux when respiration equals zero and to allow comparisons with previous studies. Outliers were removed from all regressions (see Sect. 4).

Season	Sediment type	Slope	r^2	p	Source
All	Coarse and very coarse permeable carbonate sands	0.036	0.64	< 0.005	This study
Winter	Coarse and very coarse permeable carbonate sands	0.019	0.62	Not Sig.	This study
Summer	Very coarse permeable carbonate sands	0.036	0.42	< 0.05	This study
Late summer	Coarse and very coarse permeable carbonate sands	0.047	0.43	Not Sig.	This study
Summer	Very coarse permeable carbonate sands	0.033 ¹	0.54	< 0.05	Eyre et al. (2008)
Winter (Jul)	Fine to medium carbonate sands	0.021 ²	0.89	< 0.05	Alongi et al. (2008)
All seasons	Fine to very coarse carbonate sands	0.025 ³	0.44	Not Sig.	Alongi et al. (2008, 2011)
All seasons above	All sands above	0.035	0.71	< 0.005	This study; Eyre et al. (2008); Alongi et al. (2008, 2011)
Outliers, all seasons above (see Fig. 7)	Outliers, all sands above (see Fig. 7)	0.089	0.81	< 0.01	This study; Eyre et al. (2008); Alongi et al. (2008, 2011)
Summer	Subtropical muds, range of habitats from subtidal shoals to seagrass	0.036 ⁴	0.90 ⁴	< 0.01	Eyre et al. (2011)
Range	Subtropical to temperate continental shelf muds	0.116	0.64	< 0.001	Seitzinger and Giblin (1996)
Range	Subtropical to temperate muds and sands	0.086	0.30	< 0.01	Fennel et al. (2009)
Range	Temperate muds, range of habitats from subtidal shoals to seagrass	0.036 to 0.107 0.063 (average)	0.67 to 0.94	< 0.001	Piehl and Smyth (2011)

¹ Data from Fig. 4 in Glud et al. (2008) and Fig. 3 in Eyre et al. (2008).

² Data from sites KR, PR, MR, OB and IR in Tables 4 and 8 in Alongi et al. (2008).

³ Alongi et al. (2008) and data from site PRC4 and OS1B in Table 3 and Fig. 8 in Alongi et al. (2011).

⁴ Data from Fig. 6 in Eyre et al. (2011), r^2 is slightly less than in Eyre et al. (2011) due to forcing through zero.

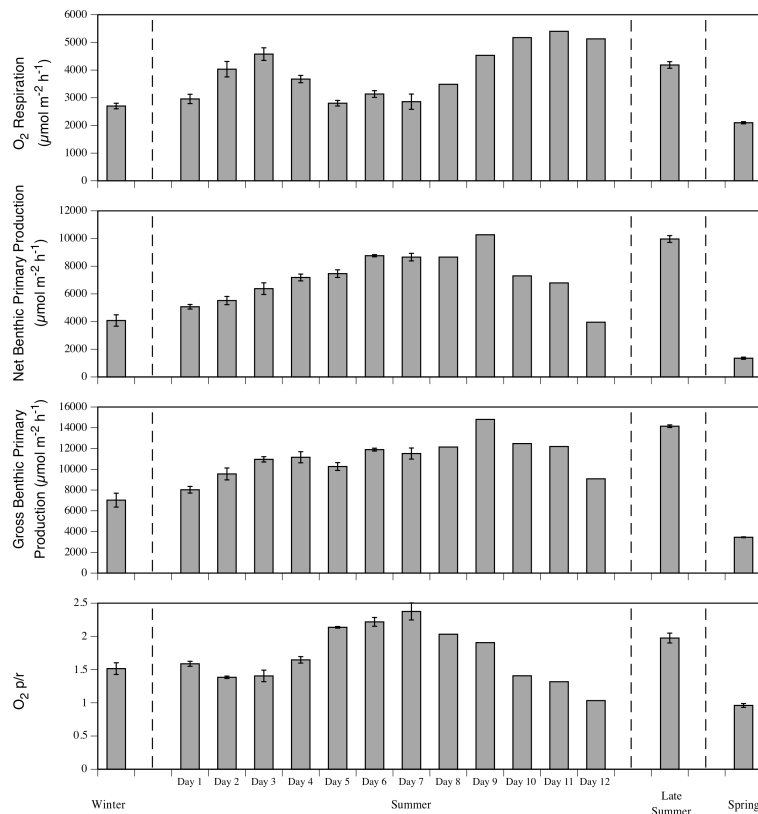


Fig. 1. Benthic dark O₂ consumption (respiration), light O₂ fluxes (net primary production (NPP), gross primary production (GPP) and GPP) respiration (p/r) (mean \pm SE where replicated see Table 1).

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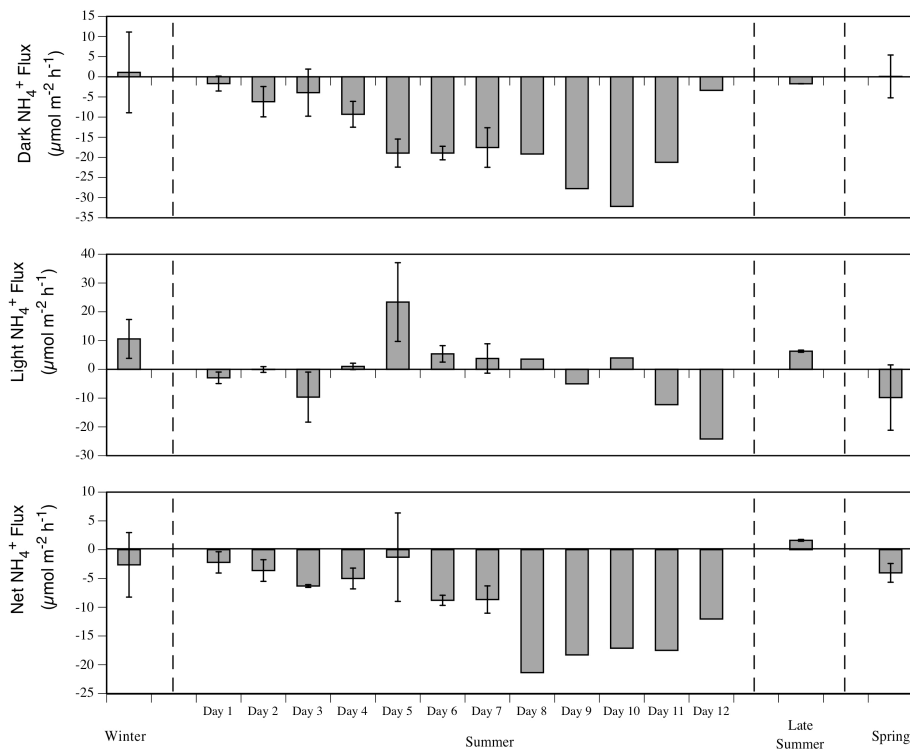


Fig. 2. Benthic dark, light, and net ammonium (NH_4^+) fluxes (mean \pm SE where replicated see Table 1).

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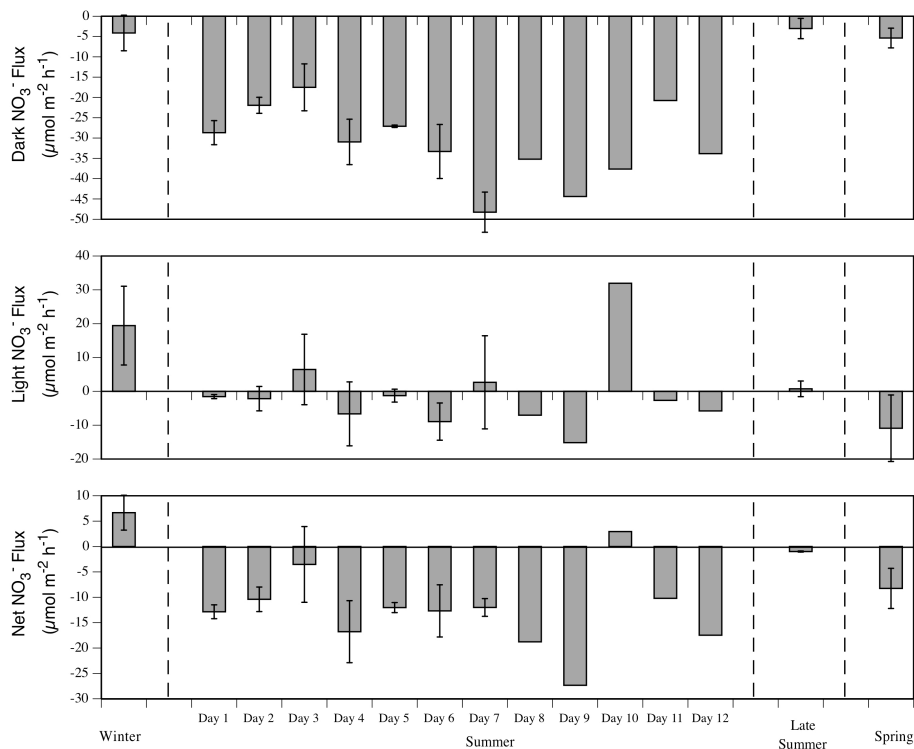


Fig. 3. Benthic dark, light, and net nitrate (NO_3^-) fluxes (mean \pm SE where replicated see Table 1).

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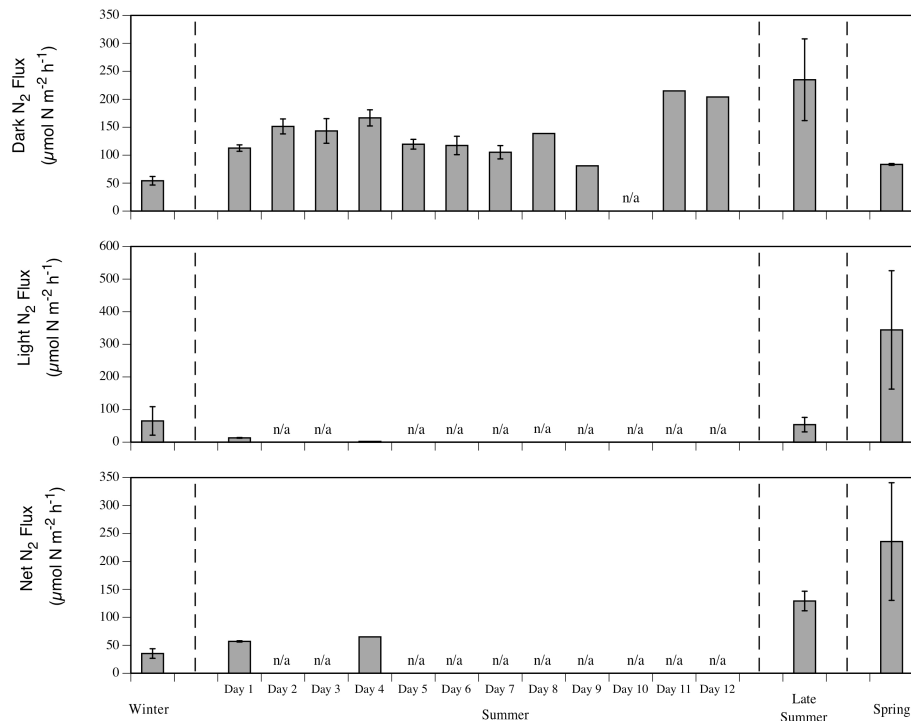


Fig. 4. Benthic dark, light, and net di-nitrogen gas (N₂) fluxes (mean ± SE where replicated see Table 1). n/a = no data available due to oxygen saturation of the chamber water (see Sect. 2).

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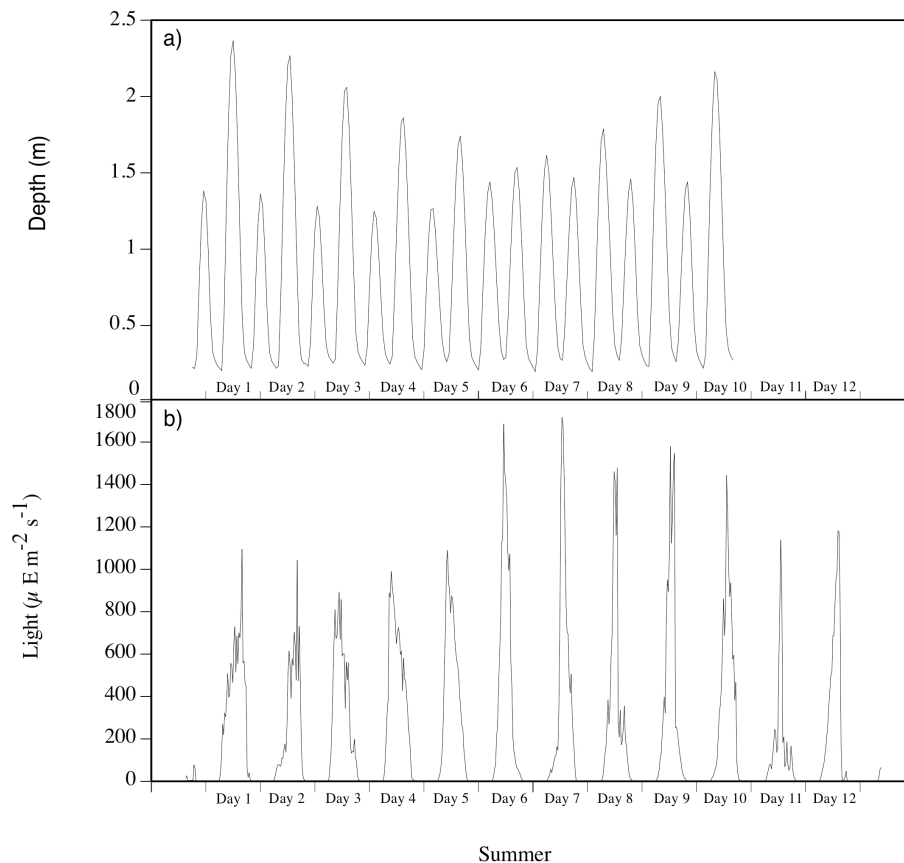


Fig. 5. (a) Depth and (b) photosynthetically active radiation (PAR), over the 12 day summer sampling period.

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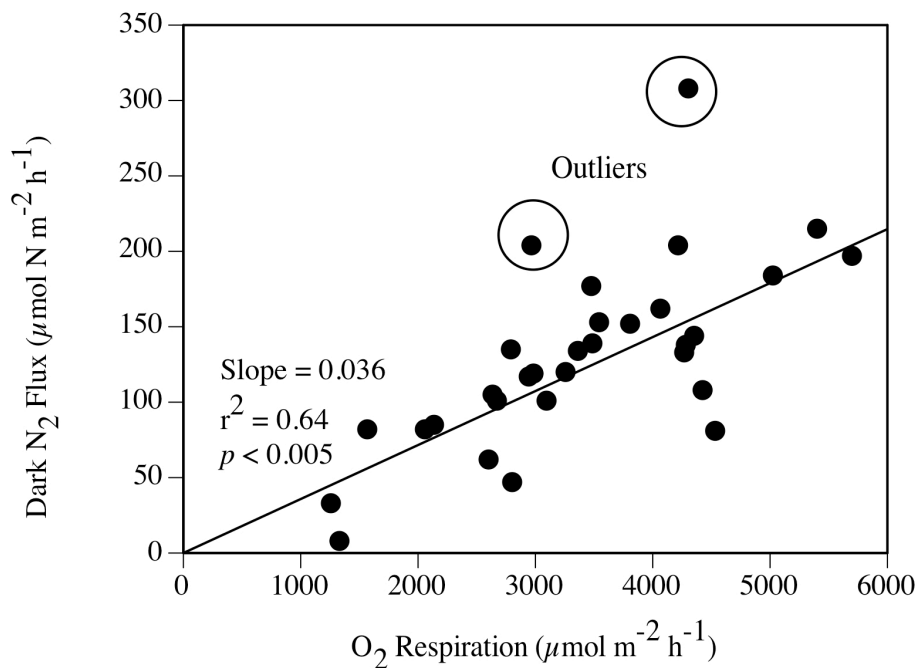


Fig. 6. Dark N₂ effluxes versus benthic respiration for all seasons in very coarse and coarse sands (individual chambers).

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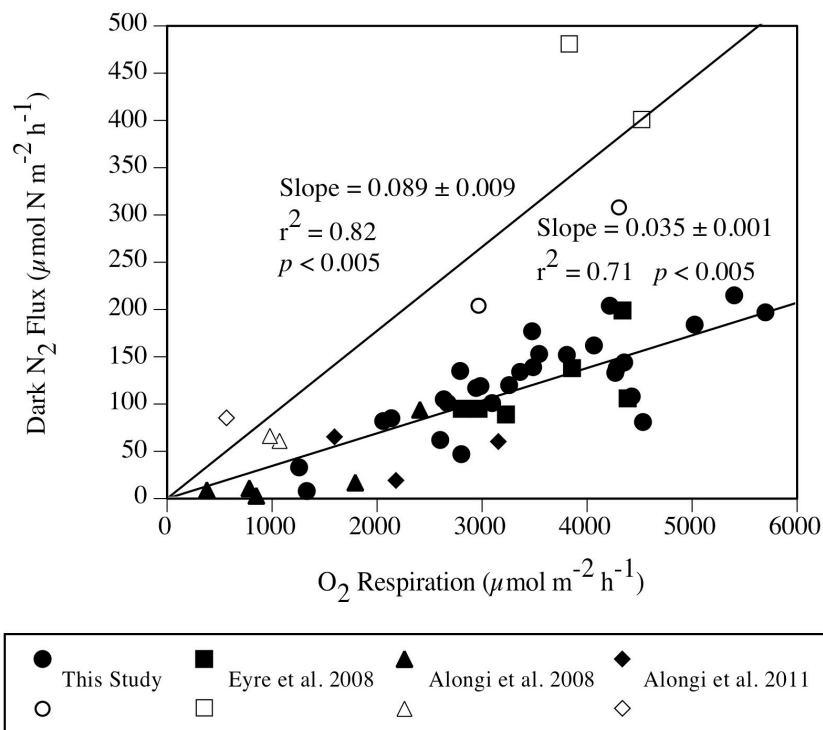


Fig. 7. Dark N₂ effluxes versus benthic respiration for carbonate sands from this study (individual chambers), Eyre et al. (2008) (individual chambers) and Alongi et al. (2008, 2011). See Table 4 for sites used from Alongi et al. (2008, 2011). Open symbols are outliers that fall above the upper 95 % confidence interval of the regressions of the 3 data sets above (see Sect. 4).

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