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Nitrogen release from surface sand of a high energy beach along the southeastern coast of North Carolina, USA

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Abstract This study examined changes in dissolved organic nitrogen (DON) and dissolved inorganic nitrogen (DIN) in coastal seawater after exposure to sand along a high energy beach face over an annual cycle between April 2004 and July 2005. Dissolved organic nitrogen, NO_3^-, and NH_4^+ were released from sand to seawater in laboratory incubation experiments clearly demonstrating that they are a potential source of N to underlying groundwater or coastal seawater. DON increases in seawater, after exposure to surface sands in laboratory experiments, were positively correlated with in situ water column DON concentrations measured at the same time as sand collection. Increase in NO_3^- and NH_4^+ were not correlated with their in situ concentrations. This suggests that DON released from beach sands is relatively more recalcitrant while NO_3^- and NH_4^+ are utilized rapidly in the coastal ocean. The release of N was seasonal with carbon to nitrogen ratios indicating that recent primary productivity was responsible for the largest fluxes in summer while more degraded humic material contributed to lower fluxes in winter. Fluxes of total dissolved nitrogen (DON and DIN) from surface sand (2.1×10^{-4} mol m^{-2} h^{-1}) were similar to that of groundwater and more than an order of magnitude larger than rain deposition indicating the potential importance of surface sand derived nitrogen to the coastal zone with a corresponding impact on primary productivity.

Keywords Sandy beach · Dissolved organic nitrogen · Dissolved inorganic nitrogen · Nitrate · Ammonium

Introduction

Studies of biogeochemical sediment processes in coastal ecosystems have focused primarily on organic rich systems due to their rapid rates of remineralization as well as their potential for organic matter accumulation and preservation. These systems are typically characterized by anoxic conditions leading to remineralization processes that result in production and consumption of a variety of biologically and geochemically important constituents including metal species, nutrients, organic compounds, carbon dioxide, and methane (Capone and Kiene 1988). Several studies have examined biogeochemical processes in sandy estuarine sediments (Bowen et al. 2007; Huettel et al. 1998; Kroeger et al. 2007), however, biogeochemical processes occurring in the sand in a high energy beach face have received significantly less attention most likely because of their relatively low organic content and the perception that these systems have less impact on coastal waters relative to organic rich systems.

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The majority of biogeochemical studies that have been conducted in these sandy beach environments have focused on the subsurface interplay between groundwater and tidal pumping of nutrients to the coastal ocean (Boehm et al. 2006; Bowen et al. 2007; Huettel et al. 1998; Kroeger et al. 2007; Maier and Pregnall 1990; Ullman et al. 2003). Although beach sands are low in organic content, they often display complex food web interactions between water column phytoplankton, interstitial fauna, macrobenthos, zooplankton, and fishes. They are also responsible for significant recycling of organic matter deposited at their surface (Brown and McLachlan 1990). Considering the biological assemblages and algal communities occurring near the surface of sand in a high energy beach face, the recycling of organic material in these systems and the daily flushing that they undergo during tidal inundation, these environments could impact N dynamics in the coastal zone. These impacts could be direct, resulting from exchange processes between the sediments and the tidal water, or indirect via transport of N to groundwater beneath the beach that eventually seeps into coastal waters.

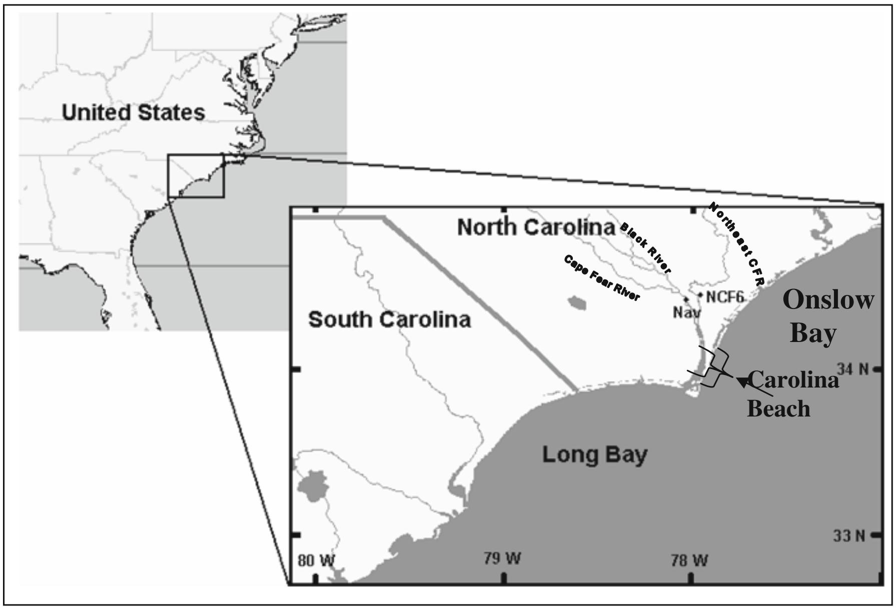
The goal of this research was to determine changes in dissolved organic nitrogen (DON) and dissolved inorganic nitrogen (DIN), including NO_3^- and NH_4^+, in coastal seawater after exposure to beach sand collected along a high energy beach face. This project utilized a combination of field measurements and laboratory experiments to determine the effect of beach sand on N cycling and exchange with coastal waters. Laboratory experiments in which coastal seawater was allowed to incubate in contact with beach sands were conducted to mimic the effect of inundation and flushing by tidal waters. In situ coastal seawater measurements were also made to compare with these laboratory experiments. This study provides new insight into the functioning of surface beach sands in high energy environments and their impact on the biogeochemical cycling of N in the coastal zone.

Methods

Sample sites and sampling

Four separate sites along Carolina Beach, North Carolina were used for this study. The sites were evenly spaced at approximately 2 mile intervals. This high energy beach is typical of exposed sandy beaches along the coast that are directly exposed to swell in a surf zone. Samples were collected from each sampling location on a monthly basis between May 2004 and August 2005. The study site borders the southern end of Onslow Bay and is typical of sandy beach environments along the length of the bay

Fig. 1 Map of study site location. Four sample sites are located on the beach indicated as Carolina Beach



(Fig. 1). The mean tidal range at this beach location is approximately 1 m. Onslow Bay beaches and Onslow Bay geological setting have been described elsewhere (Thieler et al. 2001). There was no significant difference (ANOVA $P > 0.05$) during a given month among the sites for any of the four different parameters discussed in this paper [DON, NO_3^-, NH_4^+ , and carbon to nitrogen ratios (C:N) of dissolved organic matter (DOM)]. Therefore, for simplification, results from all four sites were combined and considered replicates for data interpretation.

Beach sand for laboratory experiments was collected along a transect just prior to low tide. The most seaward sample location was 10 ft from the ocean and continued up the beach landward at 10 ft intervals for a total of four subsites. Approximately 500 ml of sand was collected from the top 10 cm and placed in glass beakers. Coastal seawater was collected using glass bottles for total dissolved nitrogen (TDN) and DIN analysis and sediment extraction experiments. Samples were immediately filtered through 0.2 µm acid washed Supor membrane disc filters to remove microorganisms. Samples were then transported back to the laboratory for analytical analysis or laboratory experiments. All glassware in contact with samples was soaked in 10% HCl for at least 2 h, rinsed with deionized water (Milli-Q plus ultra pure water), covered with aluminum foil, and baked in a muffle furnace at 550°C for at least 4 h to remove organics.

Sediment dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) extraction experiments

Glass columns (100 ml) with a fritted glass base were used for extraction experiments. Two extractions were performed on each sand sample and the results were averaged. A measured volume of sandy beach sediment was added to each column. Previously filtered seawater was added to the sediments until they were saturated. Additional filtered coastal seawater equal to the amount needed to saturate the sand was added onto each sediment–water column and allowed to incubate for 1 h in the dark at 25°C. The sediment column was then drained to the surface of the sand and the seawater was immediately filtered through a 0.2 µm acid washed Supor membrane disc filter.

Nitrogen analyses

Total dissolved nitrogen (TDN) was analyzed by high temperature catalytic oxidation (HTCO) (Alvarez-Salgado and Miller 1998). Measurements were performed using a commercial Shimadzu TOC-5050A coupled to an Antek 9000N nitrogen-specific chemiluminescence detector (Antek Instruments, TX). Samples were injected (50 µl injection volume) into the Shimadzu TOC-5050A furnace, filled with a preconditioned Shimadzu catalyst (Al_2O_3 impregnated with 0.5% platinum), at 680°C. The combustion gases from the TOC-5050A furnace were routed to the Antek 9000N detector by pulling with a Vacuubrand MZ 2D diaphragm vacuum pump (ABM, Germany) at the exit of the Antek permeation-tube drier to lower the pressure within the NO_x/O_3 reaction chamber. A high precision controller (Orme Scientific, Manchester, UK) was used to keep a constant vacuum which is critical in maintaining the constant flow through the reaction cell necessary to perform precise measurements. The flow through the Antek 9000N was set to $\sim$75% of the total flow (=150 ml min^{-1}) by means of an extra-fine Nupro (swage-lock) metering valve (Bristol Valve and Fitting, Bristol UK). The detection limit defined as three times the standard deviation of the blank was 0.51 µM with a precision of 2% RSD. A Hansel Laboratory Deep Seawater Reference (Lot # 06-00, Bermuda Biological Station for Research Inc.) was measured to confirm the accuracy of the analysis. Total nitrogen in the reference was 21.3 ± 0.24 µM N ($n = 10$) which was within the accepted values ranging from 20.5 to 21.5 µM N.

Ammonium was determined after returning to the lab using a modified version of a fluorometric method—1.5 ml sample aliquots were pipetted into six 8 ml Nalgene HDPE sample vials to which 5 ml of a working reagent containing orthophthalaldehyde was added and allowed to incubate for 3–8 h in the dark after which the fluorescence was recorded (Holmes et al. 1999). Fluorescence was measured on a Turner Designs Model 450 Fluorometer (Turner Designs, Sunnyvale CA, USA) with 360 nm excitation and 440 nm emission filters. NH_4^+ was quantified in samples by the method of standard additions to eliminate matrix effects. The detection limit defined as three times the standard deviation of the blank is 0.17 µM with a precision of 8% RSD.

Nitrate concentrations were determined by continuous flow analysis (CFA) with a Bran + Luebbe Auto-Analyzer 3 using EPA Method 353.4. Samples were treated with ammonium chloride and passed through a copper-coated cadmium column to convert NO_3^- to NO_2^-. The NO_2^- reacted with sulfanilamide and N-1-napthylethyleneidiamine dihydrochloride to form a pink colored solution. A colorimeter at 540 nm wavelength was used to measure absorbance. Nitrate standards were analyzed after every 10 samples for quality assurance. Reagent water blanks and random samples were spiked with a specific standard and analyzed for additional technique verification. Samples were stored in the freezer until analysis. When NO_3^- is referred to in this study, it actually is the sum of both NO_2^- and NO_3^-; however, NO_2^- concentrations are typically low compared to NO_3^- concentrations in coastal waters (e.g., Kieber et al. 1999).

Dissolved organic nitrogen (DON) was determined as the difference between TDN and DIN where DIN is the sum of both NO_3^- and NH_4^+. Ammonium was reanalyzed in all samples prior to determination of DON to correct for any possible losses due to sample storage.

DOC analysis

Dissolved organic carbon (DOC) was determined in order to calculate C:N ratios of the DOM. DOC was determined by high temperature combustion (HTC) using a Shimadzu TOC-5050A total organic carbon analyzer equipped with an ASI 5000 autosampler (Shimadzu, Kyoto, Japan) (Avery et al. 2003). Standards were prepared using reagent grade potassium hydrogen phthalate (KHP) in deionized water (DIW). Each sample was injected three times. The detection limit for this instrument is 5 μM (Avery et al. 2003). Carbon to nitrogen ratios (C:N) of dissolved organic matter were obtained for seawater samples exposed to sand in laboratory experiments by dividing the concentrations of DOC by DON.

Chlorophyll analysis

Chlorophyll concentrations were determined using a Turner Designs 10-AU Fluorometer (Parsons et al. 1984). A 90% acetone solution was exposed to the extracted sand columns for 20 h in the dark before being drained. The acetone extracts were stored in the freezer until analysis.

Calculations

The annual flux of DON and DIN into Onslow Bay for beach sand was calculated by multiplying the increase in each component after exposure to sandy beach sediments in laboratory extraction experiments by the volume of water exposed to the beach sand each year. The volume of beach sand was estimated by multiplying the length of Onslow Bay (160 km) by the approximate width of beach undergoing exposure to tidal flushing (20 m) and the approximate depth of the tidal range (1.0 m). This resulted in an extracted sand volume of 3.2×10^6 m^3 or 3.2×10^9 l. Using the porosity of beach sand (0.3) and assuming two tides each day yielded a volume of 7.0×10^{11} l of seawater extracted each year. The flux into Onslow Bay in moles per year was divided by the surface area of the beach, 3.2×10^6 m^2 and converted to h resulting in a flux out of sediments on a mol m^{-2} h^{-1} basis. Fluxes per meter of beach were calculated by multiplying the fluxes in m^2 by the length of the tidal range perpendicular to the beach (20 m).

Results and discussion

Total dissolved nitrogen (TDN)

The average TDN concentration of coastal water collected during this study was 11 ± 6 μM (range: 6–25 μM). The majority of TDN was DON with the remaining fraction DIN (approximately 10% nitrate and 1% ammonium). The concentration of TDN in coastal seawater increased 15 ± 12 μM (range: 1–58 μM) as a direct result of exposure to beach sand during laboratory extractions. This increase in TDN (135%) is important because it implies that these sands may be a significant source of TDN to the coastal ocean during tidal exchange or to groundwater beneath the beach. Increases in coastal seawater TDN concentrations after exposure to beach sand in laboratory experiments displayed a marked seasonality. The highest TDN input from beach sand occurred in late summer while the lowest occurred during winter months (Fig. 2). This seasonal trend suggests increased primary production and/or remineralization

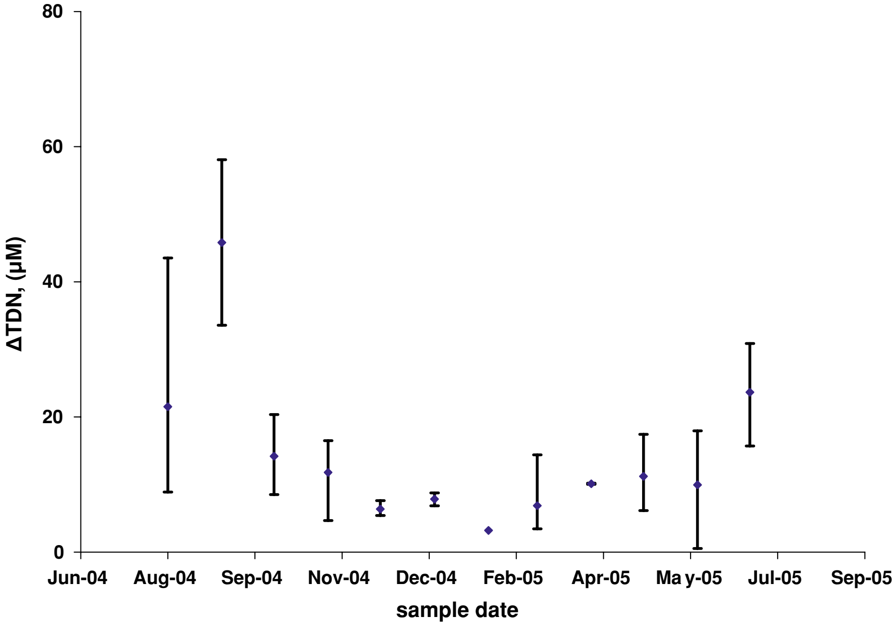


Fig. 2 Increase in TDN in seawater upon exposure to beach sand in laboratory experiments versus sample date. Diamonds are the averages; error bars represent ranges

of organic material during periods of warmer weather increases TDN extracted from beach sands.

Dissolved organic nitrogen

Average coastal seawater DON concentrations were 11 ± 7 μM (range: 5–24 μM) some of which are higher than values for central shelf water (5.06 ± 1.97 μM) and shelf break water (5.75 ± 1.73 μM) (Sharp et al. 2002). After exposure to surface beach sand in laboratory experiments, DON concentrations increased 8 ± 5 μM (range: 1–17 μM) representing an increase of 86% over coastal seawater as a direct result of exposure to beach sand. The higher DON values were approximately 38% of groundwater values entering estuaries [e.g., 44 ± 39 μM, (Bowen et al. 2007)]. The release of significant amounts of DON from beach sands strongly suggests that these sediments are a source of DON to the coastal ocean.

Further evidence for beach sand source of DON to coastal seawater is shown by the positive correlation ($P < 0.05$, $n = 17$) between the increase in coastal seawater DON concentrations upon exposure to beach sand in laboratory experiments (ΔDON) and DON concentrations in coastal seawater collected at the same time as the sand (Fig. 3). This correlation suggests that DON from beach sands is not rapidly consumed as its impact can be seen in higher coastal seawater concentrations. If the DON were consumed rapidly within the beach sand or in the coastal seawater its concentrations would not be elevated relative to shelf water (5.06 ± 1.97 μM) during times of high DON release from beach sands. The y-intercept in Fig. 3 (5.8 μM) represents a background coastal seawater concentration when the contribution of DON from sand along the beach face is zero. This is similar to the value for offshore shelf water (ca. 5 μM) reported by Sharp et al. (2002) and suggests that beach sands may be an important source of DON

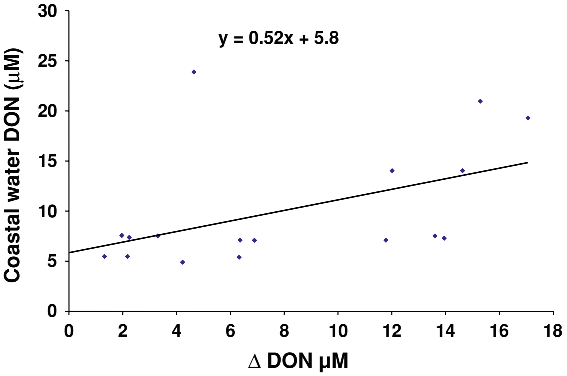


Fig. 3 Coastal water DON concentration measured at the time of sand collection for laboratory exposure experiments versus increase in DON during exposure experiments. Correlation is significant ($P < 0.05$, $n = 17$, $r^2 = 0.23$). Inorganic nitrogen species were determined on 17 coastal water samples throughout the year to obtain DON values from TDN concentrations for correlation analysis with ΔDON

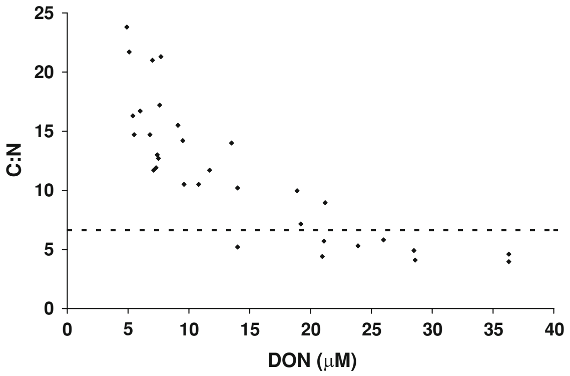


Fig. 4 Carbon to nitrogen ratio versus DON concentration of coastal seawater after exposure to beach sand in laboratory experiments. Broken line indicates Redfield ratio

when coastal ocean concentrations are elevated above this shelf water background.

Carbon to nitrogen ratios (C:N) of dissolved organic matter were inversely correlated to DON concentrations ($P < 0.05$, $n = 32$, $r^2 = 0.23$; Fig. 4). High release of DON from the sand in the laboratory experiments was evident when the C:N ratios were low while low DON release was observed when C:N ratios were high. The smallest C:N values were at or below Redfield ratio and the highest C:N were approximately 20. The ratio of C:N in living marine planktonic material known as "Redfield ratio" is 6.625 C:N and represents fresh or recent living material while older or degraded organic material such as humics have a C:N of approximately 20 (Schwarzenbach et al. 1993). The C:N ratio can therefore be used to indicate the degree of organic matter degradation. The higher C:N for more degraded material is a result of nitrogen being lost from organic matter preferentially to carbon during microbial remineralization [(Hopkinson and Vallino 2005) and references therein]. The results shown in Fig. 4 indicate that when release of DON in laboratory experiments is greatest, it is the result of an input of fresh or recently living material as evidenced by the low C:N ratio of the extracted organic material. When release of DON was lowest the C:N ratios were high suggesting that the organic material was more degraded. The high TDN release observed in summer (Fig. 2) in conjunction with the low C:N ratio of the DON (Fig. 4) suggests recent primary productivity may be responsible for the high release of TDN during summer months while remineralization of detrital organic matter contributes more to TDN during winter.

Nitrate

Average coastal seawater NO_3^- concentrations in the current study were 0.9 ± 0.6 μM (range: 0.1–2.2 μM). These coastal water NO_3^- concentrations are slightly elevated relative to concentrations 8 km offshore of our study site in Onslow Bay (0.11 ± 0.18 μM) (Mallin et al. 2005) but not as high as values reported for the Cape Fear plume (5.5 μM) which flows into Long Bay just south of our study site (Fig. 1). After exposure to beach sand in laboratory extractions, coastal seawater NO_3^- concentrations increased 3.9 ± 4.2 μM (range: 0.2–16 μM) representing as much as a 600% increase over in situ coastal seawater concentrations. After contact with the surface sand, concentrations approached river plume values indicating a significant release of NO_3^-.

Unlike DON, there was no correlation between the increase in NO_3^- during exposure of seawater to sand and the concentration of nitrate in coastal seawater measured at the time of sand collection. Furthermore, coastal seawater NO_3^- concentrations were similar to offshore Onslow Bay values suggesting the NO_3^- supplied by beach sand was rapidly consumed soon after release. The most likely fate of this NO_3^- is consumption via primary productivity either within the beach sand or in the coastal zone. Beach sand chlorophyll-a content was positively correlated ($P < 0.05$) with increases in NO_3^- concentrations in laboratory experiments supporting the suggestion that coastal photosynthetic activity acts as a rapid sink for NO_3^- supplied by the beach sand. Dissolved organic nitrogen, in contrast, did not correlate with chlorophyll-a in these experiments supporting the assertion that this pool of N is relatively recalcitrant and is more easily exported to the coastal ocean after extraction from the surface sand environment.

Ammonium

The average coastal seawater NH_4^+ concentration in the current study was 0.1 ± 0.2 μM (range: non detectable to 0.2 μM) which is similar to values reported 8 km offshore in Onslow Bay (0.33 ± 0.30 μM) and lower than those for the Cape Fear River plume (2.3 μM) (Mallin et al. 2005). Seawater NH_4^+ concentrations increased 0.6 ± 0.7 μM (range: 0–1.8 μM) after exposure to beach sand, exceeding the offshore concentration for Onslow Bay and approaching 50% of Cape Fear River plume values. This indicates that there is a significant release of NH_4^+ from beach sands after exposure to coastal seawater. The similarity between offshore Onslow Bay values and near-shore coastal values of this study suggests that, like NO_3^-, NH_4^+ supplied by sandy beach sediments is rapidly consumed by primary productivity before it elevates concentrations in the surrounding coastal watershed. There was no correlation between NH_4^+ addition resulting from extraction and coastal seawater concentrations again suggesting rapid consumption of released NH_4^+ .

Unlike NO_3^-, there was no correlation between the NH_4^+ increase upon exposure to beach sand and chlorophyll-a concentrations of the extracted sand column. This suggests that primary productivity on the beach sands and nearby coastal waters is driven primarily by NO_3^- and not NH_4^+ . Ammonium may be rapidly depleted by bacteria and microalgae resulting in NO_3^- becoming the preferred nutrient thereby controlling chlorophyll-a concentrations.

Implications

The results of this study indicate that there are significant releases of DIN and DON off surface beach sands during tidal exchange. This suggests these high energy environments may be important to coastal primary productivity and secondary productivity along the immediate coast since N is typically the limiting nutrient in these systems. The potential significance of surface beach sand to the biogeochemical cycling of N in the surrounding coastal ocean is best addressed by comparison to other potentially important N inputs including rain, groundwater, and estuaries.

An earlier review of nutrient dynamics in a high energy sandy beach environment in South Africa contains what is probably the most comprehensive study of N dynamics in these systems to date (Cockcroft and McLachlan 1993). The authors estimated net export of DIN and DON + POC (particulate organic carbon) by subtracting phytoplankton demand from inputs and recycled N in the beach and surf zone. Inputs included groundwater, rain, and estuarine N while recycled N included interstitial fauna, macrobenthos, zooplankton, fishes and the microbial loop. Their results were reported as net N fluxes across 1 m of beach face to the ocean (Table 1).

It is interesting, considering the widely different locations for the two beaches sampled, that the fluxes in the current study containing one component of the sandy beach ecosystem are approximately 20% of the net ecosystem flux reported by Cockcroft and McLachlan (1993). Furthermore, the ratio of DON to DIN flux for the current study (1.8) was very similar to the DON to DIN flux ratio (1.5) for the South African beach suggesting some consistency in the N cycling and flux from sandy beach systems.

Groundwater discharge of DIN under sandy beach environments has been quantified in earlier studies conducted in coastal North America (Table 1). These fluxes are thought to be important to coastal productivity and in some cases are significant sources of N to macrophytes growing close to sandy beaches (Maier and Pregnall 1990). Surface sand DIN fluxes from the current study are similar to groundwater flux values reported from a variety of sandy beach environments (Table 1) indicating the potential importance of these surface processes to groundwater and coastal primary productivity.

Table 1 Flux of DON, and DIN (nitrate and ammonium) in mmol m^{-1} h^{-1}

Study	Study site	Flux type	DIN ($mM\ m^{-1}\ h^{-1}$)	DON ($mM\ m^{-1}\ h^{-1}$)
Current study	Pleasure Island, NC, USA	Surface sand	2.2	4.0
Cockcroft and McLachlan (1993)	Sundays River Beach, South Africa	Beach and surf zone	13.0	20.0
Boehm et al. (2006)	Huntington Beach, California, USA	Ground water	4.8	
Maier and Pregnall (1990)	Shore Lab and Great Harbor, Woods Hole, MA, USA	Ground water	−0.32–8.6[a]	
Ulman et al. (2003)	Cape Henlopen, Delaware, USA	Ground water	4.2–25.0	

[a] Calculated flux assumes 4 m wide beach

Table 2 Annual flux of DON, nitrate and ammonium in 10^7 mol year^{-1} into Onslow Bay

	DIN	Nitrate	Ammonium	DON	Reference
Sandy beach sediments	0.32	0.28	0.04	0.56	This study
Rain deposition	22.1	11.6	10.5	3.8	Long (2003)
Cape Fear River estuary[a]	5.6	3.6	2.0	35	Bradshaw (2005)

Rain deposition was calculated by multiplying the deposition of nitrogen species m^2 from Long 2003 by the area of Onslow Bay (40 km × 160 km)

[a] Flux calculated for Long Bay

Table 3 Flux of DON, nitrate and ammonium in 10^{-4} mol m^{-2} h^{-1}

	DON	DIN	Nitrate	Ammonium	Reference
Sandy beach sediments	2	1.1	1	0.1	This study
Rain deposition[a]	0.007	0.04	0.02	0.02	Long (2003)

[a] Collected between 1 September 2002 and 31 August 2003

Rain and riverine fluxes of N species are best compared to sandy beach fluxes of N on a basin-wide basis as an input to Onslow Bay. Although there are no major river systems discharging directly into Onslow Bay, the Cape Fear River, which flows into Long Bay south of Onslow Bay (Fig. 1), can be used to compare the potential impact of a river relative to a sandy beach. The majority of DIN entering Onslow Bay is from rainwater deposition while a riverine input such as the Cape Fear River would be the dominant source of DON (Table 2). Sandy beach sediment fluxes of DON, NO_3^- and NH_4^+ (mol m^{-2} h^{-1}) were more than an order of magnitude larger than rainwater deposition (Long 2003) (Table 3). This suggests that cycling of N in beach sands is a significant source of N locally producing elevated concentrations which could play an important role in net primary productivity along the immediate coast. Furthermore, because rainwater addition is episodic while tidal flushing of high energy beach sands occurs daily, in a coastal bay with no riverine input and no recent rainfall, processes occurring on the beach face may account for a significant fraction of the TDN to the surrounding waters during these periods.

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