BEACH SEDIMENTS: A SOURCE OF DISSOLVED ORGANIC CARBON AND NITROGEN SPECIES TO THE COASTAL OCEAN

Kelly Lynne Taylor

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Approved by

Advisory Committee

Robert F. Whitehead Robert Kieber

G Brooks Avery, Jr.
Chair

Accepted by

_____
Dean, Graduate School

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ABSTRACT

This study presents the first extensive examination of the effect of sandy beach sediments on dissolved organic carbon (DOC), dissolved organic nitrogen (DON), nitrate and ammonium fluxes to the coastal ocean. Through a combination of *in situ* measurements and laboratory sand extraction experiments, it was determined that after exposure of seawater to the sandy beach sediments, concentrations of DOC, DON, nitrate and ammonium were elevated, clearly demonstrating that these sediments are a source of these constituents. On a per meter squared basis, the flux of DOC, DON and nitrate from these sandy sediments was higher than Chesapeake Bay sediments and higher in all constituents than rainwater. In a coastal bay such as Onslow Bay, which has no major riverine input, sandy beach sediments likely supply a significant amount of DOC, DON, and DIN to the coastal zone. The supply of nitrate from these sediments is particularly important accounting for approximately 18% of the standing stock of nitrate in Onslow Bay on an annual basis. Both nitrate and ammonium released from these sediments were rapidly consumed. The nitrate concentrations were correlated to chlorophyll a while DON concentrations remained high indicating that nitrate was driving primary productivity in the coastal waters and that DON was not very bioavailable.

ACKNOWLEDGEMENTS

I would like to first thank Dr. Brooks Avery for propositioning me with such a novel idea for my research. I truly enjoyed working on it both in the lab and in the field. His support and frequent anecdotes helped the discouraging times look a little brighter. I am truly appreciative of his time, knowledge and dedication that he extended me. My thanks also go to Dr. Rob Whitehead. He was the man behind the machine and always willing to offer his expertise when needed. I would also like to thank Dr. Robert Kieber for his insight and suggestions regarding my research and this thesis.

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My sincerest thanks go to Brian Simpson for his physical and emotional support daily. I'm also very grateful for his willingness to teach a girl from Ohio a thing or two about the beach, I couldn't have asked for a more enthusiastic field partner. This experience as a whole would have been lacking without his encouragement and refreshing humor. I'd also like to thank the friends I've met along the way who have offered both their guidance and assistance in times of need.

DEDICATION

This thesis is dedicated to my family. They provided me with a drive towards knowledge and the opportunity of higher education, also physical and emotional support and encouraging words throughout my life. I find strength in each of them.

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INTRODUCTION

Prior to the onset of industrialization in the late 1800's, the atmospheric carbon dioxide (CO_2) concentration was approximately 280 ppm where it had remained for several thousand years (Houghton et al., 2001). Fossil fuel combustion contributed to the steady increase in atmospheric CO_2 concentrations reaching the current value of approximately 378 ppm (WMO Global Atmosphere Watch). The prospect of global warming caused by increases in atmospheric CO_2 concentrations has generated extensive research into the sources and sinks (removal mechanisms) for this greenhouse gas and carbon fluxes in general. Current global carbon budgets (1990-1999) indicate that the major exchange of CO_2 between the atmosphere and earth includes a 120 $GtCyr^{-1}$ sink for terrestrial gross primary productivity that slightly exceeds a 60 $GtCyr^{-1}$ source from plant respiration and 58.6 $GtCyr^{-1}$ for microbial organic matter decomposition in soils and sediments (Houghton et al., 2001). Approximately 90 $GtCyr^{-1}$ are released by the oceans while 92 $GtCyr^{-1}$ are sequestered. Anthropogenic impacts, which are responsible for the increase in atmospheric CO_2 concentrations during the past century, are driven by fossil fuel combustion releasing 6.3 ± 0.4 $GtCyr^{-1}$. This atmospheric CO_2 source represents ¾ of the anthropogenic impact while changes in land-use account for the remainder. The oceans and biosphere act as net sinks for atmospheric CO_2 while anthropogenic emissions are a net source. Currently the net annual increase in atmospheric CO_2 is 3.2 ± 0.1 $GtCyr^{-1}$. However, the pre-mentioned sources and sinks do not explain the observed increase in atmospheric CO_2. Instead, there appears to be a "missing sink" of approximately 2.2 $GtCyr^{-1}$. Therefore particular components of the global carbon cycle are either incorrect or have not been accounted for.

The total oceanic content of carbon (inorganic and organic) is approximately 50 times that found in the atmosphere. Oceanic dissolved organic carbon (DOC), constituting a little under 700 GtC, is the Earth's largest reservoir of actively cycled organic matter (Burshaw et al., 1996 and references therein) and therefore can have a significant impact on atmospheric CO_2. Current imbalances in the global carbon budget may result from uncertainties in these oceanic DOC budgets, therefore it is critical to understand factors that affect both oceanic concentrations of DOC (i.e. sources and sinks) as well as its cycling**.**

All DOC is initially derived from living organisms, with the main source of oceanic DOC resulting from *in situ* production via cell lysis, phytoplankton, and excretory wastes in the surface water (Steele, 2001). In addition to internal production, several external sources of DOC to the oceans also exist, including rainwater (0.43 ± 0.15 $GtCyr^{-1}$) (Willey et al., 2000 and references therein) river water (0.2 $GtCyr^{-1}$) (Avery et al., 2003 and references therein) and coastal and continental margin sediments (0.18 $GtCyr^{-1}$) (Burdige et al., 1999). However, no studies have examined the effect that coastal intertidal sandy beach sediments have on DOC concentrations despite the daily flushing that these sediments experience during tidal inundation. Although their organic carbon content is low, the beach sediments support many biological assemblages and surface algal communities that could either consume or release DOC to the coastal ocean. Changes in DOC due to interactions with these sediments can have important implications for secondary productivity in addition to their impact on oceanic carbon budgets. Therefore, the main purpose of this study was to determine the effect of sandy beach sediments on coastal DOC concentrations.

Whether DOC will represent a long-term storage of organic carbon in the ocean or a source of CO_2 to the atmosphere via microbial respiration depends on the bioavailability of the DOC. The nitrogen content of the DOC has important implications regarding this bioavailability and also reflects the extent of biodegradation. As stated by Carpenter and Capone (1983) 'Nitrogen, an important constituent of DOC, is an essential component of all living materials, and to a large extent its availability, through transfer between various nitrogen reservoirs, can regulate the cycle of organic matter in the world's oceans and estuaries.' During microbial organic matter decomposition, nitrogen is preferentially consumed over carbon. Therefore ratios of carbon to nitrogen (C:N) similar to Redfield ratios (the C:N ratio of living marine planktonic material) indicate fresh, bioavailable organic matter while high C:N ratios indicate biodegradation and therefore refractory organic matter. In addition to the information on DOC cycling that can be obtained from dissolved organic nitrogen (DON) measurements, dissolved inorganic nitrogen (DIN, i.e. nitrate and ammonium) released by biodegradation can be an important nutrient source to the marine environment which is typically nitrogen limited. Despite the potential importance of organic bound nitrogen, little research has focused directly on its bioavailability and oceanic sources. Because of the potential importance of DON to DOC cycling, and the information that DON can provide in terms of the degree of bacterial degradation of DOC, a second goal of this research was to determine the effect of sandy beach sediments on coastal DON and DIN concentrations.

This project utilized a combination of field measurements and laboratory experiments to determine the effect of coastal intertidal sandy beach sediments on DOC, DON and DIN fluxes to the coastal ocean. *In situ* porewater and coastal seawater measurements

were compared to determine whether the beach sediments supplied or consumed DOC, DON, and DIN. Laboratory experiments in which sandy beach sediments were extracted with coastal seawater were also conducted to mimic the effect of tidal flushing on these sediments. Sample sites included four locations along the southeast coast of North Carolina, including both Carolina Beach and Kure Beach. This study presents the first data regarding the impact of coastal intertidal sandy beach sediments on oceanic concentrations of DOC, DON, and DIN.

METHODS

DOC Analysis

Dissolved organic carbon 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 Milli-Q Plus Ultra Pure Water. Both samples and standards were acidified by addition of hydrochloric acid (HCl) and sparged with carbon dioxide free carrier gas for 5 minutes maintaining a flow rate of 125 mL min^{-1} to effectively remove inorganic carbon prior to injection onto a heated catalyst bed (0.5 % Pt on alumina support, 680° C, regular sensitivity). A nondispersive infrared detector measured carbon dioxide gas from the combusted carbon. Each sample was injected three times. The detection limit for this instrument is 5 μM (Avery et al., 2003).

TDN Analysis

Total dissolved nitrogen was analyzed by the method of Alvarez-Salgado et al. (1998). HTCO measurements were performed using a Shimadzu TOC 5050A coupled to an Antek 9000N nitrogen-specific chemiluminescence detector. Nitrate was used as the standard due to its good recovery (Merriam et al., 1996).

Amino Acid Analysis

Amino acid concentrations were determined, as described by Parsons et al. (1984), immediately after collection for porewater samples, extraction samples, and coastal seawater samples by obtaining the fluorescence using a Sequoia Turner Model 450 Fluorometer with 360 nm excitation and 490 nm emission filters. Standards were prepared daily by diluting a 10 mM glycine stock to 100 µM with Milli-Q Plus Ultra Pure Water. The working reagent was prepared weekly using a 0.4 M sodium borate buffer solution, o-Phthalaldehyde solution, and 2-mercaptoethanol. Samples were run in triplicates.

Ammonium Analysis

Ammonium concentrations for porewater samples, extraction samples, and coastal seawater samples were measured immediately after collection by a fluorescence method, as described by Holmes et al. (1999), using a Sequoia Turner Model 450 Fluorometer with 360 nm excitation and 490 nm emission filters. Standards were prepared daily by diluting a 0.5 M NH_4Cl stock solution to 240 µM with Milli-Q Plus Ultra Pure Water.

The working reagent was prepared monthly by addition of sodium sulfite solution, sodium borate buffer solution, and OPA solution. Samples were run in triplicates.

Chlorophyll Analysis

Chlorophyll concentrations were determined for the extracted sand columns by obtaining the fluorescence using a Turner Designs 10-AU Fluorometer. The method was adapted from an approved EPA method (Method 445.0). A 90% acetone solution was allowed to incubate on the extracted sand columns for a duration of 20 hours before being drained. The procedure was carried out in the dark. Samples were stored in the freezer in the dark until analysis.

Nitrate Analysis

Nitrate concentrations were determined for porewater samples, extraction samples, and coastal seawater samples by continuous flow analysis (CFA) with a Bran+Luebbe Auto-Analyzer 3 using an approved EPA method (Method 353.4). Samples were treated with ammonium chloride and passed through a copper-coated cadmium column to convert nitrate to nitrite. The nitrite reacted with sulfanilamide and N-1 napthylethyleneidiamine dihydrochloride to form a pink colored dye. A colorimeter at 540 nm wavelength was used to measure the dye intensity. Nitrate standards were analyzed after every 10 samples for quality assurance. As part of the EPA protocol, 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.

Porewater and Coastal Water Collection

Porewater samples were collected along a beach transect just prior to low tide. The most seaward sample location was 10 feet from the ocean and continued up the beach landward at 10 foot intervals. Porewater samples were retrieved by digging a hole with a small shovel until the sediment appeared wet; digging continued by a gloved (Fisherbrand Disposable Poly Gloves 1.25 mil layered under1.5 mil) hand until the collection hole contained standing water. All glassware in contact with samples was soaked in a 10 % HCl solution for at least two hours and then muffled in an oven of 550°C for at least four hours. Approximately 90 mL of porewater and coastal seawater sample was collected using glass Shimadzu sample vials. Samples were immediately filtered through 0.2 µm acid washed Supor membrane disc filters to remove microorganisms. After transport to the laboratory, samples were stored in the refrigerator until DOC and TDN analysis.

Coastal seawater was also collected in a 350 mL BOD glass bottle and stored in the refrigerator for the sediment extraction experiments. Sandy beach sediments were collected (0 to 5 cm depth) from each site, at the same location as porewater samples. Samples were collected from May 2004 to August 2005.

Sediment DOC and TDN Extraction Experiments

A 100 mL glass column with a fritted glass base was used for extraction experiments. A measured volume (20 to 25 mL) and weight (20 to 40 grams) of the corresponding sandy beach sediment was added to each column. The sediments were then saturated with a measured volume of previously filtered coastal seawater. Additional filtered

coastal seawater equal to the amount needed to saturate the sand (~15 to 20 mL) was added onto each sediment-water column and allowed to incubate for an hour. The sediment column was then drained and the post-extraction seawater was immediately filtered through a 0.2 μm acid washed Supor membrane disc filter. Three extractions were performed, as described above, on each sample. The samples were stored in the refrigerator for later analysis.

Calculations

The flux of DOC, DON and DIN into Onslow Bay was calculated by multiplying the increase in each component after exposure to the sandy beach sediments in laboratory extraction experiments by the volume of water extracted by the beach sand each year. The volume of sand extracted was calculated by multiplying the length of Onslow Bay (160 kilometers) by the approximate width of the beach that undergoes exposure to tidal flushing (20 meters) and the approximate depth of the tidal range (1.0 meter). This resulted in an extracted sand volume of 3.2×10^6 meters^3 or 3.2×10^9 liters. Using the porosity of the beach sand (0.3) and assuming two tides each day yielded a volume of 7.0×10^{11} liters of seawater extracted each year. In order to calculate the flux out of the sediments on a mole meter^{-2} hour^{-1} basis, the flux into Onslow Bay in moles year^{-1} was divided by the surface area of the beach, 3.2×10^6 meters^2 and converted to hours.

Site Variation

In order to examine the results collectively to determine the effect of the sandy beach sediments on the coastal ocean as a system, variations between sites had to be ruled out. Using a one-way analysis of variance (ANOVA) for the five different parameters (DOC,

DON, nitrate, ammonium, and C:N ratios) it was determined that there was no significant difference among the sites. Therefore, all samples were compiled for data interpretation.

RESULTS & DISCUSSION

Dissolved Organic Carbon

Coastal seawater dissolved organic carbon (DOC) concentrations increased during laboratory experiments where coastal seawater was allowed to contact sandy beach sediments for 3 hours (extraction experiments). The largest concentration was measured after the first hour therefore results for all extraction experiments will be reported for the first extraction only. Concentrations of DOC in coastal seawater increased on average 41 ± 32 μM (range: 120 to 2 μM). Prior to extraction, coastal seawater concentrations averaged 113 ± 27 μM, (range: 163 to 73 μM) slightly larger than the value obtained by Guo et al. (1995) of ~75 μM for the surficial open ocean of the Mid Atlantic Bight. Post-extraction seawater DOC concentrations averaged 159 ± 43 μM (range: 242 to 96 μM) representing a 37 ± 33% increase after exposure to beach sand**.**

Coastal seawater DOC concentrations measured at the time of sand collection were positively correlated ($p<0.05$) with post-extraction seawater concentrations of DOC suggesting a direct impact of these sediments on coastal DOC concentrations (Figure 1). During times of high coastal seawater DOC concentrations the amount of DOC extracted from sandy beach sediments in laboratory experiments was greatest. When the coastal seawater DOC concentrations were highest (~160 μM), post-extraction seawater was approximately 90 μM higher (~250 μM). When coastal seawater concentrations were lowest (~100 μM), post-extraction seawater concentrations were similar (~100 μM)

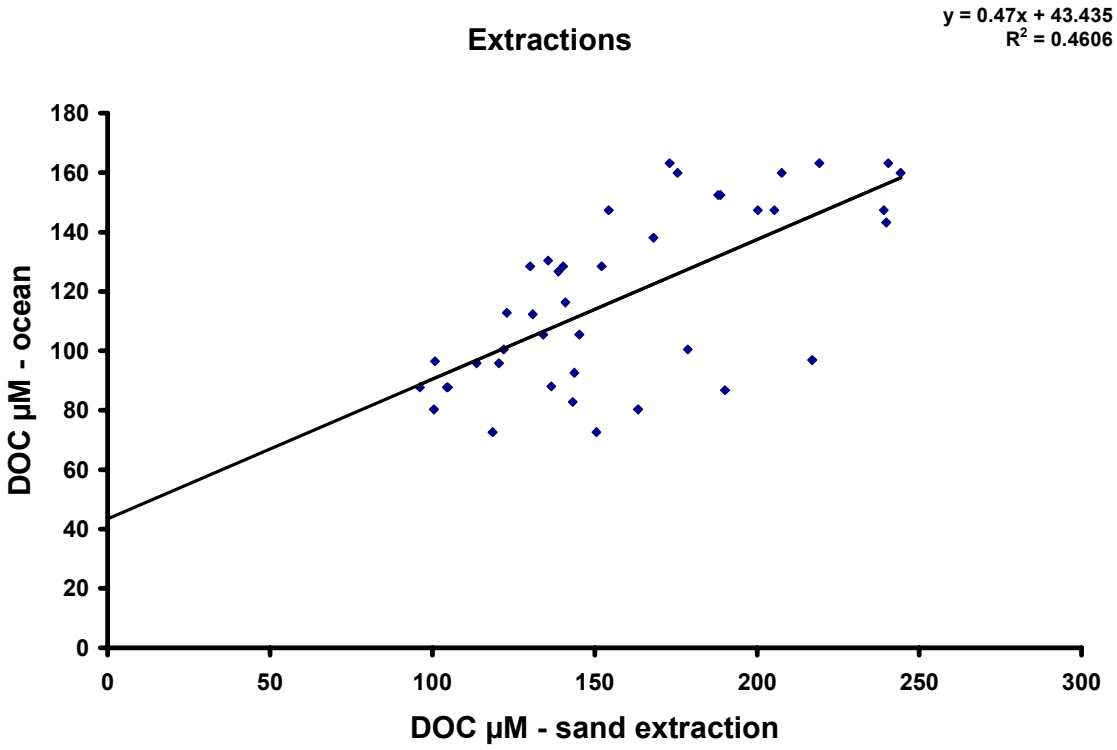

Figure 1. Correlation plot of DOC concentrations for sand extraction samples versus coastal ocean samples. The sand extraction samples were collected as a result of laboratory experiments where coastal seawater was allowed to contact sandy beach sediments for 1 hour. Coastal ocean samples were collected just prior to low tide. All sites were included for extraction experiments and were positively correlated at $p<0.05$, $n=41$.

showing little increase in DOC concentration from exposure to sand. This indicates that when sandy beach sediments are not supplying DOC to the coastal ocean the background DOC concentration is approximately 100 µM and concentrations above that are due to fluxes from sandy beach sediments.

Unlike post-extraction seawater, *in situ* porewater DOC concentrations were not always elevated relative to the coastal seawater measured at the same time. Porewater DOC concentrations ranged from 358 µM higher than the coastal seawater to 73 µM less than the coastal seawater; indicating that *in situ* porewaters did not always reflect the direct extraction of DOC from the sandy beach sediments. The variability with *in situ* porewaters indicates that the DOC concentrations determined in the field may reflect resent removal of DOC via tidal exchange in addition to input of DOC from the sandy beach sediments. Coastal seawater DOC concentrations (125 ± 50 µM, range: 250 to 58 µM) were similar to porewater concentrations (135 ± 91 µM, range: 594 to 56 µM) and positively correlated ($p<0.05$) (Figure 2). The slope of the line for the correlation plot of coastal seawater DOC concentrations versus porewater DOC concentrations was less than 1 indicating that there was significant difference in the DOC concentration found in the porewaters and the coastal seawater. These results indicate that the *in situ* porewater concentrations of DOC were slightly elevated relative to the concentrations in the coastal seawater samples, suggesting that the increase in DOC from sandy beach sediments may be reflected in *in situ* porewater concentrations due to mixing of recently extracted coastal seawater with porewaters. The plot also gives a y-intercept value of 68 µM indicating that theoretically, when porewater concentrations are zero, and the sandy beach sediments are not contributing DOC to the coastal seawater, the concentration

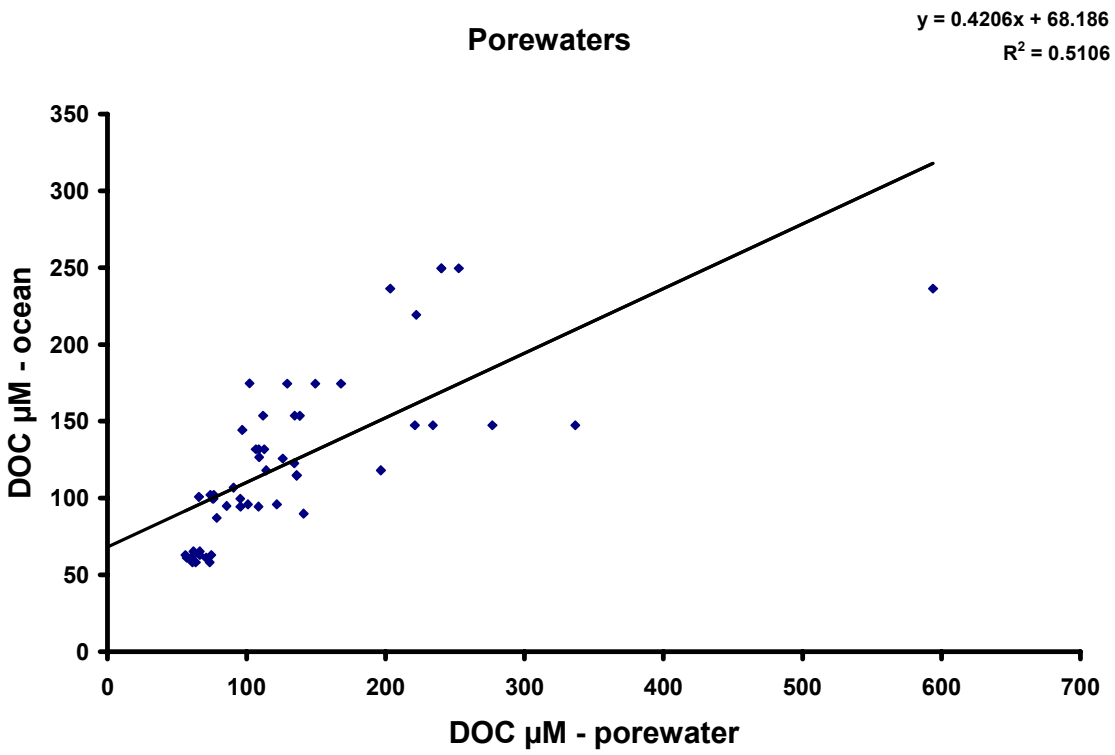

Figure 2. Correlation plot of DOC concentrations for porewater samples versus coastal ocean samples. Porewater samples were collected along a beach transect just prior to low tide. Coastal ocean samples were collected at the same time. All sites were included and were positively correlated at $p<0.05$, $n=53$.

would be approximately 68 µM. This is similar to the value of 100 µM obtained above for the background concentration of DOC when sandy beach sediment fluxes are minimal. These values are both similar to open ocean surface values in the Mid Atlantic Bight of ~75 µM (Guo et al., 1995) which represents little or no recent coastal input supporting the idea that sandy beach sediments are an important source of DOC to the coastal ocean.

Total Dissolved Nitrogen

Total dissolved nitrogen (TDN) values include both dissolved organic nitrogen (DON) and dissolved inorganic nitrogen (DIN); DIN concentrations include ammonium and nitrate. DON concentrations were calculated as the difference between TDN and DIN concentrations. If amino acids were found in the samples the concentration would have increased the DON concentration. Average coastal seawater concentrations of TDN were 11 ± 6 µM (range: 25 to 6 µM) with DON comprising the majority (Figure 3). Concentrations of total dissolved nitrogen (TDN) in coastal seawater increased 15 ± 12 µM (range: 58 to 1µM) as a direct result of exposure to sandy beach sediments in laboratory extraction experiments. This represents a dramatic increase in TDN (135 %) indicating that these sediments are a source of TDN to the coastal ocean during tidal exchange. Concentrations of each component of TDN (DON, nitrate and ammonium) increased after exposure to beach sand and are addressed separately below.

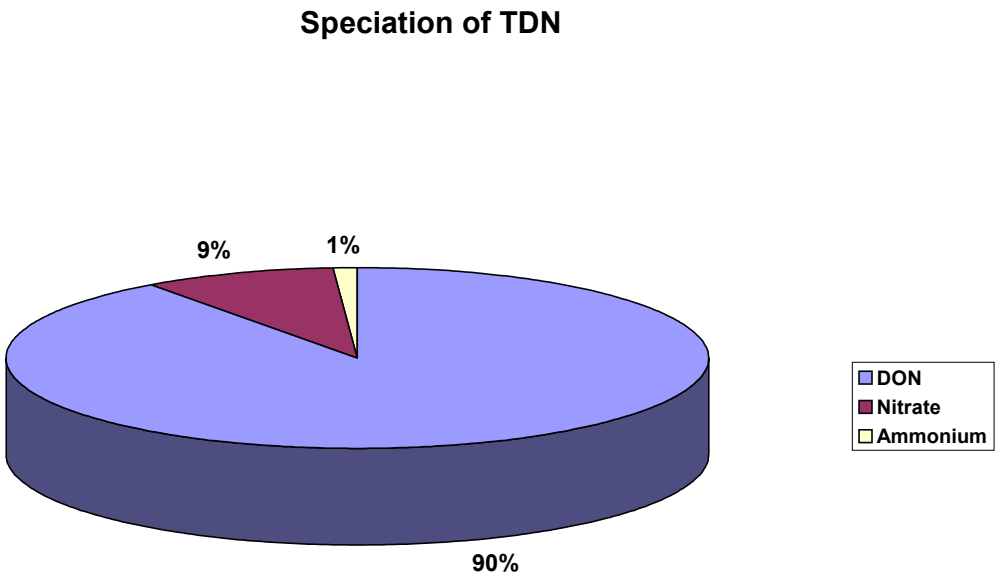

Figure 3. Speciation breakdown of TDN for coastal seawater samples prior to extraction experiments where coastal seawater was allowed to contact sandy beach sediments for 1 hour. Species include average DON, nitrate, and ammonium concentrations.

Dissolved Organic Nitrogen

Average coastal seawater DON concentrations were 11 ± 7 µM (range: 24 to 5 µM) which are in the upper range of DON values (3 to 10 µM) for coastal waters (Carpenter and Capone, 1983). Post-extraction DON concentrations increased 8 ± 5 µM (range: 17 to 1µM) representing an increase of 86 ± 54 % over coastal seawater as a direct result of exposure to sandy beach sediments, elevating DON concentrations above the range reported by Carpenter and Capone (1983). These elevated concentrations strongly suggest that these sediments act as a source of DON to the coastal ocean and indicate that high values observed in the coastal seawater reflect their proximity to the source. Further evidence for the impact of the sandy beach sediments on DON is shown by the positive correlation ($p<0.05$) between the magnitude of the increase in coastal seawater DON concentrations after exposure to these sediments in extraction experiments and the coastal seawater collected at the same time as the extraction sand (Figure 4). The y-intercept for the correlation plot gives a value of approximately 6 µM. This value is representative of background DON open ocean values when little or no impact is evident from the sandy beach sediments. This value also falls within the range of DON concentrations for coastal waters as reported by Carpenter and Capone (1983). When post-extraction seawater showed a large input of DON, the coastal seawater also had higher DON concentrations.

Nitrate

Average coastal seawater nitrate concentrations in the current study were 0.9 ± 0.6 µM (range: 2.2 to 0.1 µM) . These values are within the range for coastal nitrate (0 to 30

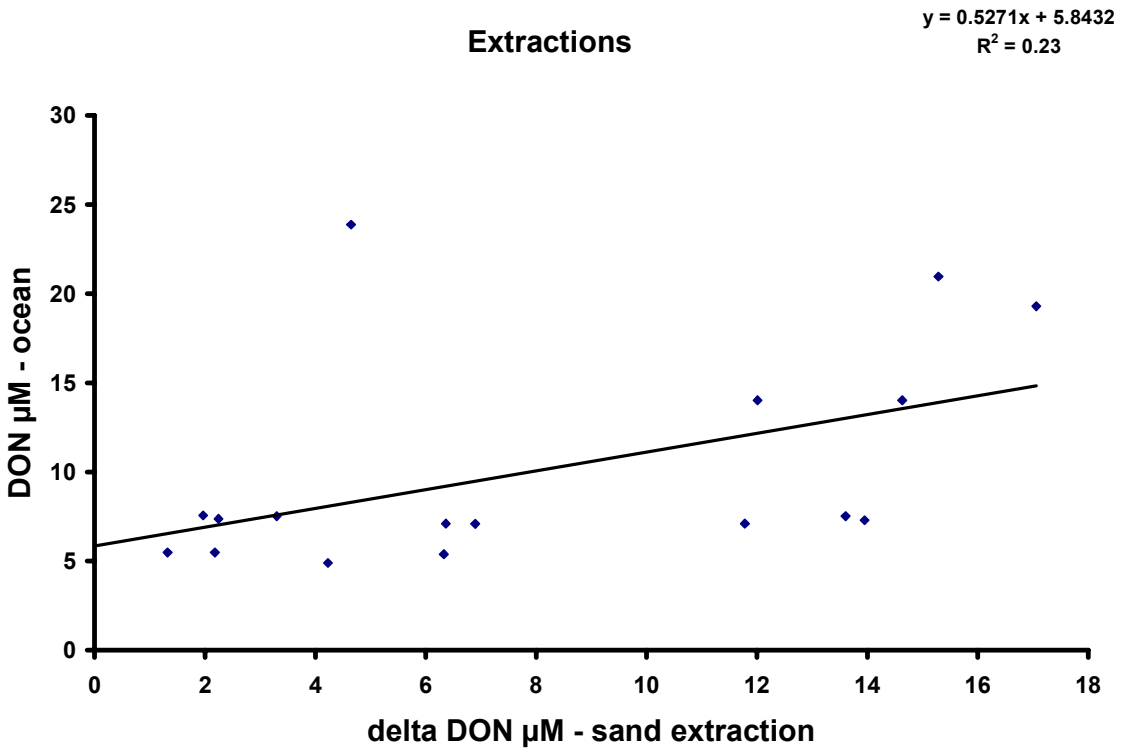

Figure 4. Correlation plot of delta DON concentrations for sand extraction samples versus DON concentrations for coastal ocean samples. The sand extraction samples were collected as a result of laboratory experiments where coastal seawater was allowed to contact sandy beach sediments for 1 hour. Coastal ocean samples were collected just prior to low tide. Delta DON concentrations were obtained by subtracting the DON concentration for the sand extraction sample minus the DON concentration for the coastal ocean sample. All sites were included for extraction experiments and were positively correlated at $p<0.05$, $n=17$.

µM) according to Carpenter and Capone (1983). They are between the values reported 8 km offshore in Onslow Bay (0.11 ± 0.18 µM) and for the Cape Fear River plume (5.5 µM) (Mallin et al., 2005) indicating that they are elevated relative to offshore values but not as high as riverine values. After exposure to sandy beach sediments in laboratory experiments, nitrate concentrations increased 3.9 ± 4.2 µM (range: 16 to 0.2 µM) representing as much as a 600 % increase over coastal seawater concentrations and approached river plume values indicating a significant flux of nitrate from these sediments. However, the similarity between offshore Onslow Bay values and near-shore coastal values of this study suggests that the nitrate supplied by the sandy beach sediment is rapidly consumed after it is deposited in the coastal ocean. Unlike DON, there was no correlation ($p>0.05$) between the addition of nitrate during extraction experiments and coastal seawater (Figure 5) suggesting rapid consumption of the released nitrate. The change in coastal seawater nitrate concentrations as a result of extraction experiments was positively correlated ($p<0.05$) to chlorophyll-a concentrations of the extracted sand column (Figure 6) and suggestive of rapid consumption of nitrate by bacteria and microalgae. Therefore coastal photosynthetic activity likely acts as a sink for the nitrate supplied by sandy beach sediments. The rapid loss of nitrate is not surprising given that nitrogen is usually the limiting nutrient in marine systems. As a result, nitrate does not exist in elevated concentrations in nearshore coastal seawater even though the supply from these sediments is high.

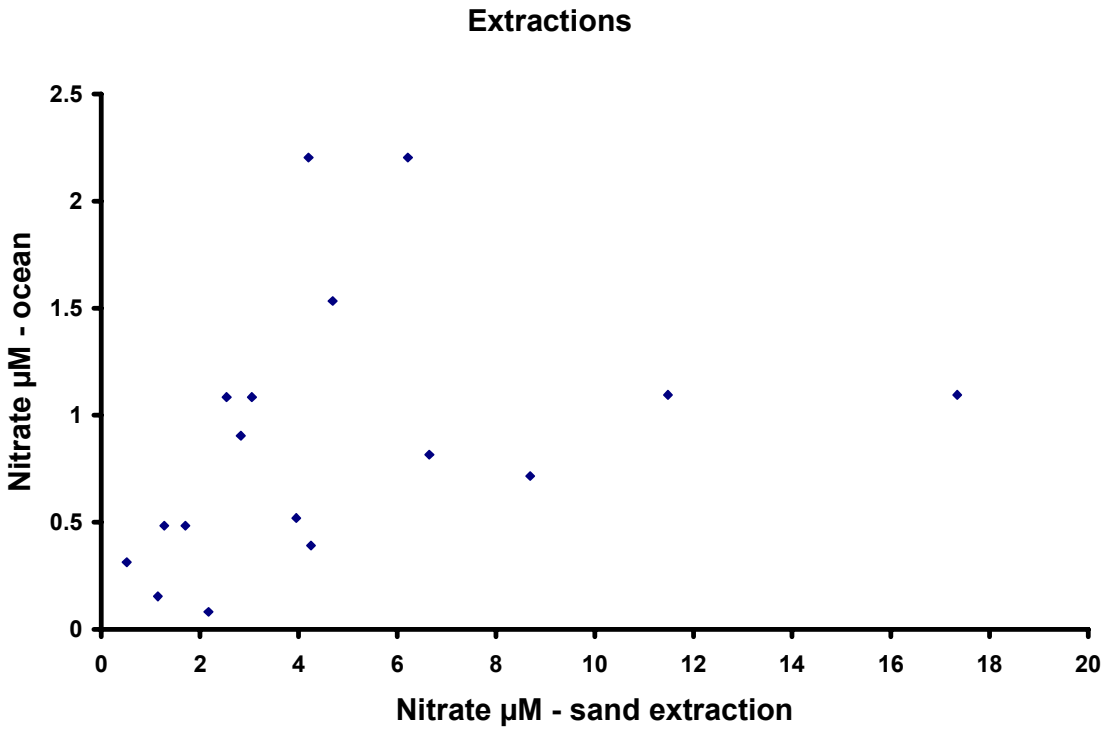

Figure 5. Correlation plot of nitrate concentrations for sand extraction samples versus coastal ocean samples. The sand extraction samples were collected as a result of laboratory experiments where coastal seawater was allowed to contact sandy beach sediments for 1 hour. Coastal ocean samples were collected just prior to low tide. All sites were included for extraction experiments and were not correlated at $p>0.05$, $n=17$.

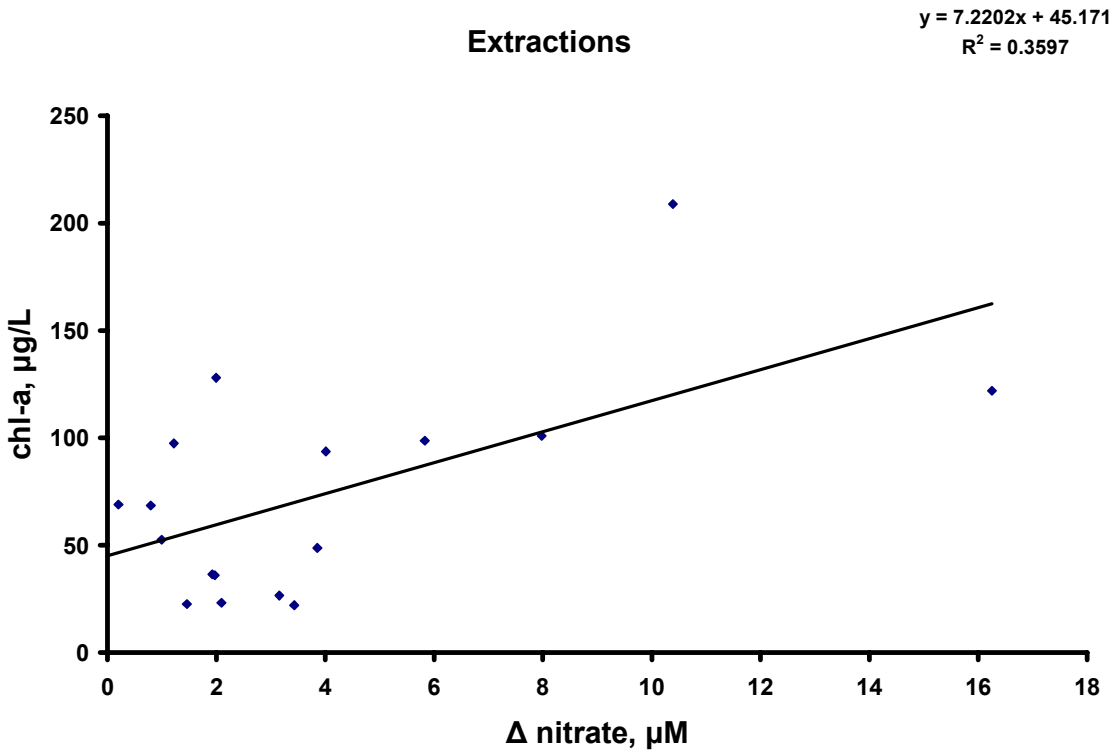

Figure 6. Correlation plot of delta nitrate concentrations for sand extraction samples versus chlorophyll-a concentrations for the sand extraction column. Delta nitrate concentrations were obtained by subtracting the nitrate concentration for the sand extraction sample minus the nitrate concentration for the coastal ocean sample. Chlorophyll a concentrations were obtained from the sand extraction column after the extraction experiments had been run. 90% acetone was allowed to incubate on the sand extraction column for a duration of 20 hours before being drained. All sites were included for extraction experiments and were positively correlated at $p<0.05$, $n=17$.

Ammonium

Average coastal seawater ammonium concentrations in the current study were low (0.1 ± 0.2 µM, range: 0 to 0.2 µM), either because it is the preferred nutrient for phytoplankton or because it is recycled quickly. These values are in the lower range for coastal ammonium (0 to 25 µM) according to Carpenter and Capone (1983). They are also similar to the 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). After coastal seawater was exposed to sandy beach sediments in laboratory experiments, ammonium concentrations increased 0.6 ± 0.7 µM (range: 1.8 to 0.0 µM) exceeding the offshore values for Onslow Bay and approaching approximately 50 % river plume values indicating a significant flux of ammonium from these sediments. However, the similarity between offshore Onslow Bay values and near-shore coastal values of this study suggests that, like nitrate, the ammonium supplied by the sandy beach sediments is rapidly consumed. Similarly to nitrate, there was no correlation ($p>0.05$) between the addition of ammonium during extraction experiments and coastal seawater (Figure 7) adding further evidence to suggest rapid consumption of the released ammonium. Unlike nitrate, there was no correlation ($p>0.05$) between the change in coastal seawater ammonium concentrations as a result of the extraction experiments and chlorophyll-a concentrations of the extracted sand column (Figure 8) suggesting that nitrate and not ammonium is limiting in this system. As ammonium concentrations are depleted by bacteria and microalgae nitrate supplied by the beach sediment will become the preferred nutrient and thus control chlorophyll-a concentrations. This is not surprising given that nitrogen is usually the limiting nutrient in marine systems. As a result, ammonium does not exist in

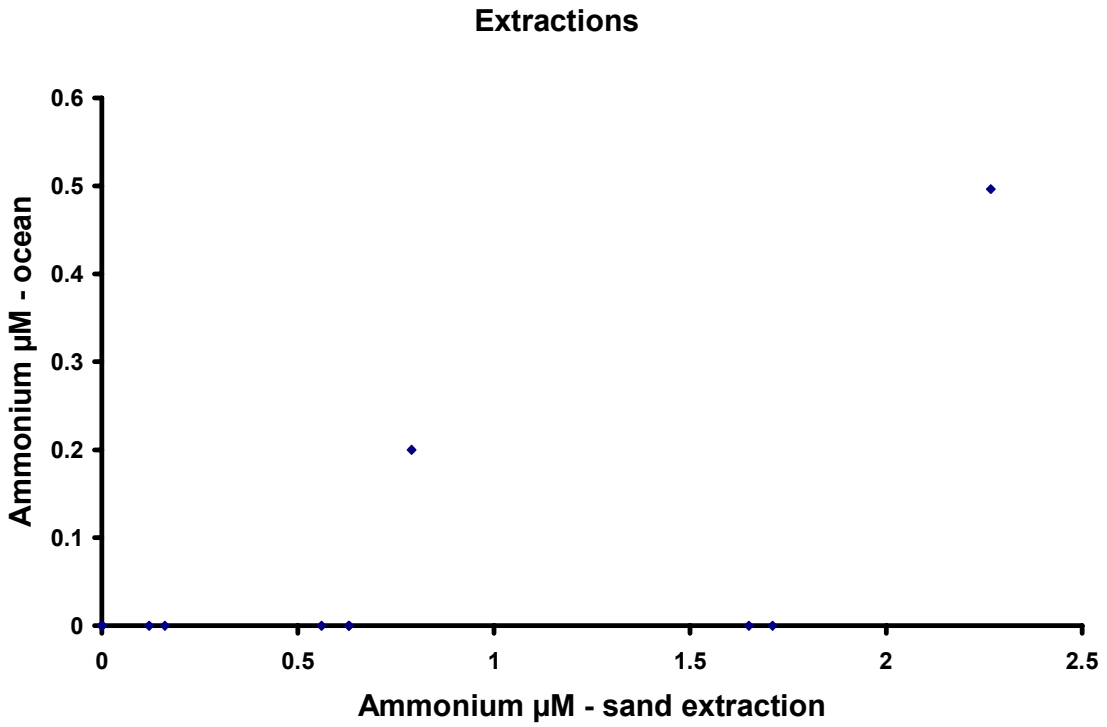

Figure 7. Correlation plot of ammonium concentrations for sand extraction samples versus coastal ocean samples. The sand extraction samples were collected as a result of laboratory experiments where coastal seawater was allowed to contact sandy beach sediments for 1 hour. Coastal ocean samples were collected just prior to low tide. All sites were included for extraction experiments and were not correlated at $p>0.05$, $n=9$.

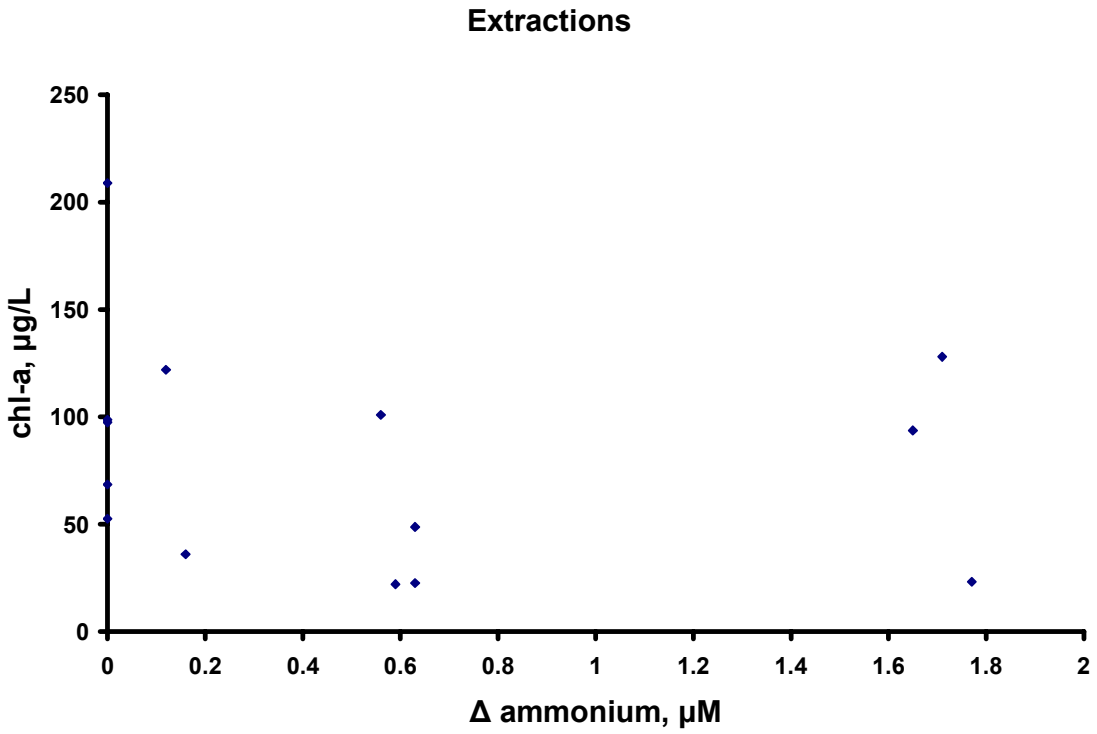

Figure 8. Correlation plot of delta ammonium concentrations for sand extraction samples versus chlorophyll-a concentrations for the sand extraction column. Delta ammonium concentrations were obtained by subtracting the ammonium concentration for the sand extraction sample minus the ammonium concentration for the coastal ocean sample. Chlorophyll a concentrations were obtained from the sand extraction column after the extraction experiments had been run. 90% acetone was allowed to incubate on the sand extraction column for a duration of 20 hours before being drained. All sites were included for extraction experiments and were not correlated at $p>0.05$, $n=14$.

elevated concentrations in nearshore coastal waters even though there is a minimal supply from the sandy sediments.

In contrast to the elevated concentrations of DON, nitrate, and ammonium found in coastal seawater exposed to sandy beach sediments in laboratory experiments, *in situ* porewater concentrations were similar to those found in coastal seawater (Figure 9). Furthermore; *in situ* porewater DON, nitrate, and ammonium concentrations were positively correlated with coastal seawater concentrations ($p<0.05$) (Figures 10, 11, and 12). The slope of the line for the correlation plot of coastal seawater DON and nitrate concentrations versus porewater DON and nitrate concentrations was less than 1 indicating that there was significant difference in the concentrations of these constituents found in the porewaters and the coastal seawater. These results indicate that the *in situ* porewater concentrations of these constituents were slightly elevated relative to the concentrations in the coastal seawater samples. Unlike DOC, DON, and nitrate, the slope of the line for the correlation plot of coastal seawater ammonium concentrations versus porewater ammonium concentrations was equal to 1 indicating that there was no significant difference in the concentrations of the porewaters and the coastal seawater. These results indicate that, as was evident with the DOC concentrations, *in situ* porewaters are not consistently elevated with respect to coastal seawater and would suggest that the increase in DON, nitrate, and ammonium from sandy beach sediments may be reflected in *in situ* porewater concentrations due to mixing of recently extracted coastal seawater with porewaters.

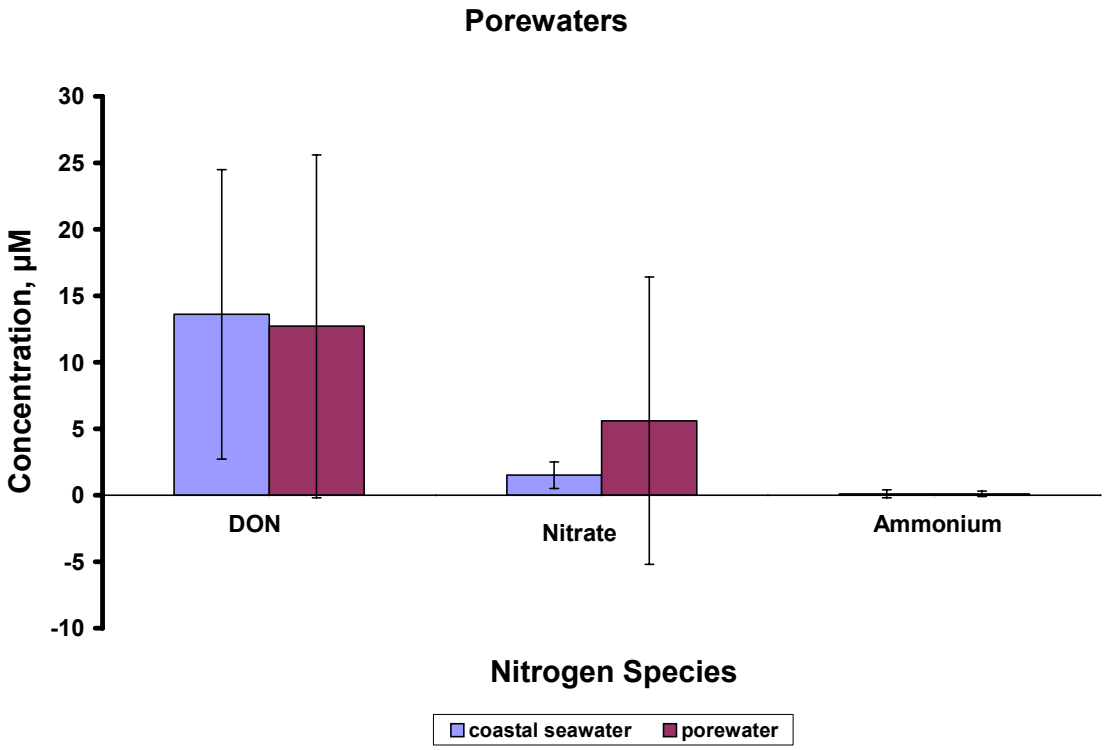

Figure 9. Nitrogen speciation graph for porewater samples and coastal seawater samples. Species include average DON, nitrate and ammonium concentrations. All sites were included.

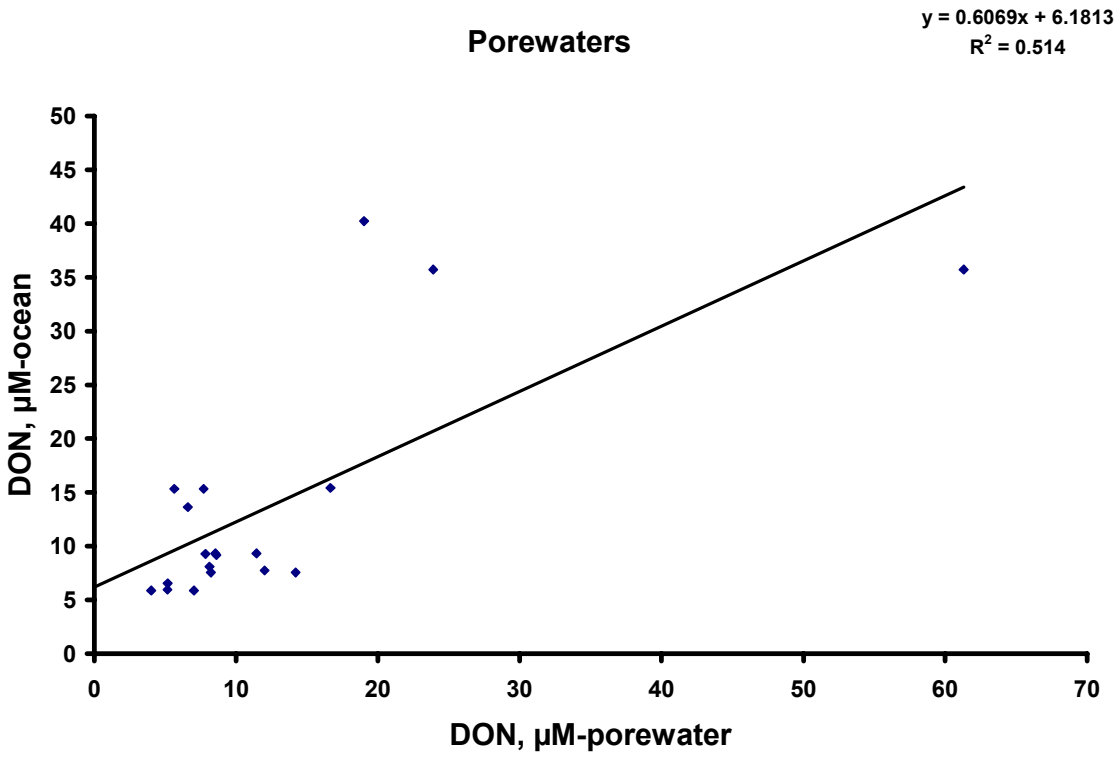

Figure 10. Correlation plot of DON concentrations for porewater samples versus coastal ocean samples. Porewater samples were collected along a beach transect just prior to low tide. Coastal ocean samples were collected at the same time. All sites were included and positively correlated at $p<0.05$, $n=19$.

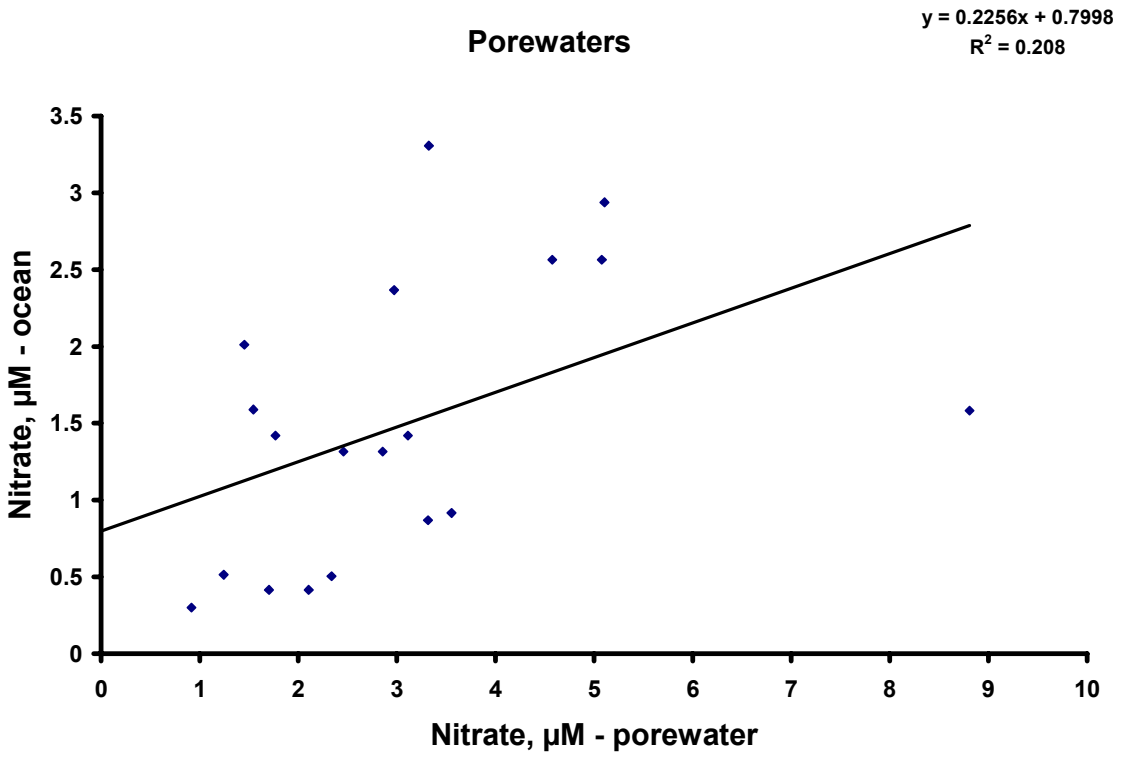

Figure 11. Correlation plot of nitrate concentrations for porewater samples versus coastal ocean samples, an outlier (49.7, 2.0) was removed. Porewater samples were collected along a beach transect just prior to low tide. Coastal ocean samples were collected at the same time. All sites were included and were positively correlated at $p<0.05$, $n=19$.

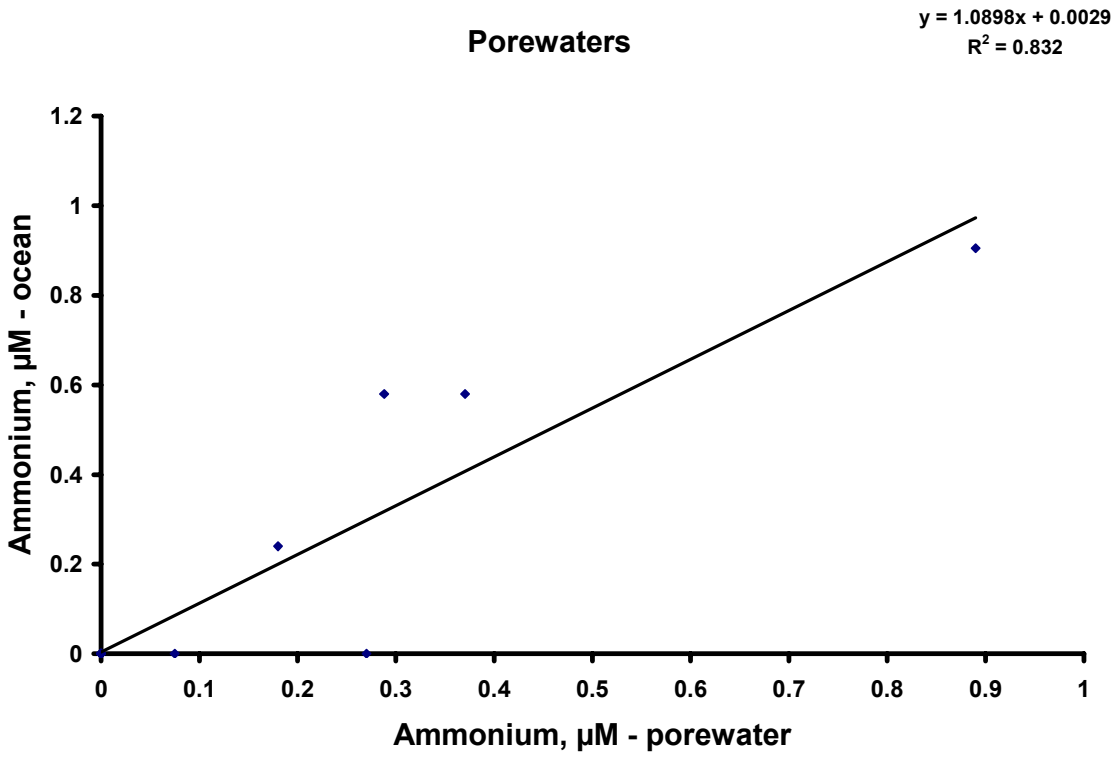

Figure 12. Correlation plot of ammonium concentrations for porewater samples versus coastal ocean samples. Porewater samples were collected along a beach transect just prior to low tide. Coastal ocean samples were collected at the same time. All sites were included and positively correlated at $p<0.05$, $n=7$.

C:N values

Carbon to nitrogen (C:N) values were obtained for coastal seawater samples, post-extraction seawater samples and *in situ* porewater samples by dividing the concentration of DOC by DON. The ratio of C:N in living marine planktonic material known as "Redfield's ratio" is 6.625 C:N. The C:N ratio indicates the degree of organic matter degradation. Nitrogen is typically lost from organic matter more rapidly than carbon, therefore, high C:N ratios indicate organic matter that is more degraded or older while lower C:N ratios are representative of fresher material.

A general trend was observed for the inverse correlation of the C:N ratios with DON concentrations in both extraction experiments and *in situ* porewater samples for all four sites (Figures 13 through 20). High fluxes of DON were evident when the C:N ratios were low, with the smallest C:N value being just at or below Redfield's ratio. This would indicate that when fluxes of DON are the greatest, it is a result of fresh or recently living material. When fluxes of DON were lowest the C:N ratios were high indicating that the organic material is older and probably more degraded. The C:N ratios generally increased to a value of approximately 20:1 which is characteristic of humic materials (Schwarzenbach et al., 1993). These results suggests that *in situ* recent primary productivity is responsible for the high flux of DON during the summer months while remineralization of detrital organic matter likely contributes more to the DON during the winter.

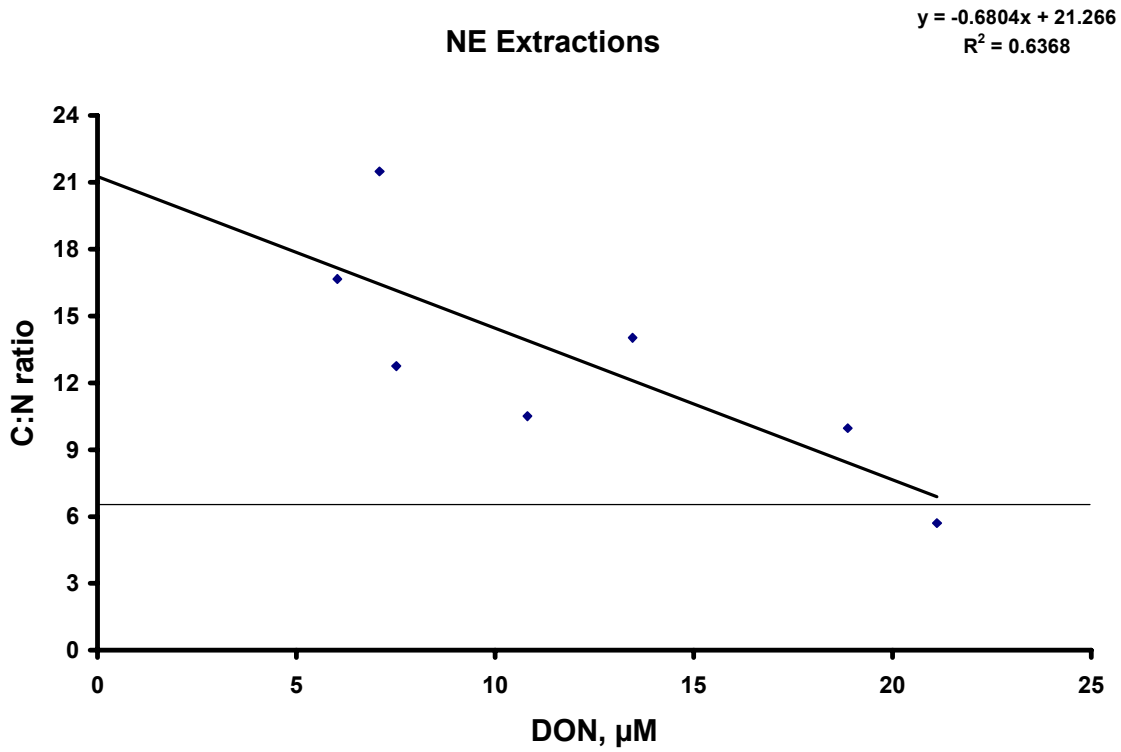

Figure 13. Correlation plot of DON concentrations for sand extraction samples versus C:N ratios obtained for the sand extraction samples at the North End sampling site. Samples include both coastal ocean samples and sand extraction samples and were inversely correlated at $p<0.05$, $n=7$. The sand extraction samples were collected as a result of laboratory experiments where coastal seawater was allowed to contact sandy beach sediments for 1 hour. Coastal ocean samples were collected just prior to low tide. C:N ratios were obtained by dividing the DOC concentration by the DON concentration. The solid line represents Redfield's ratio, 6.625.

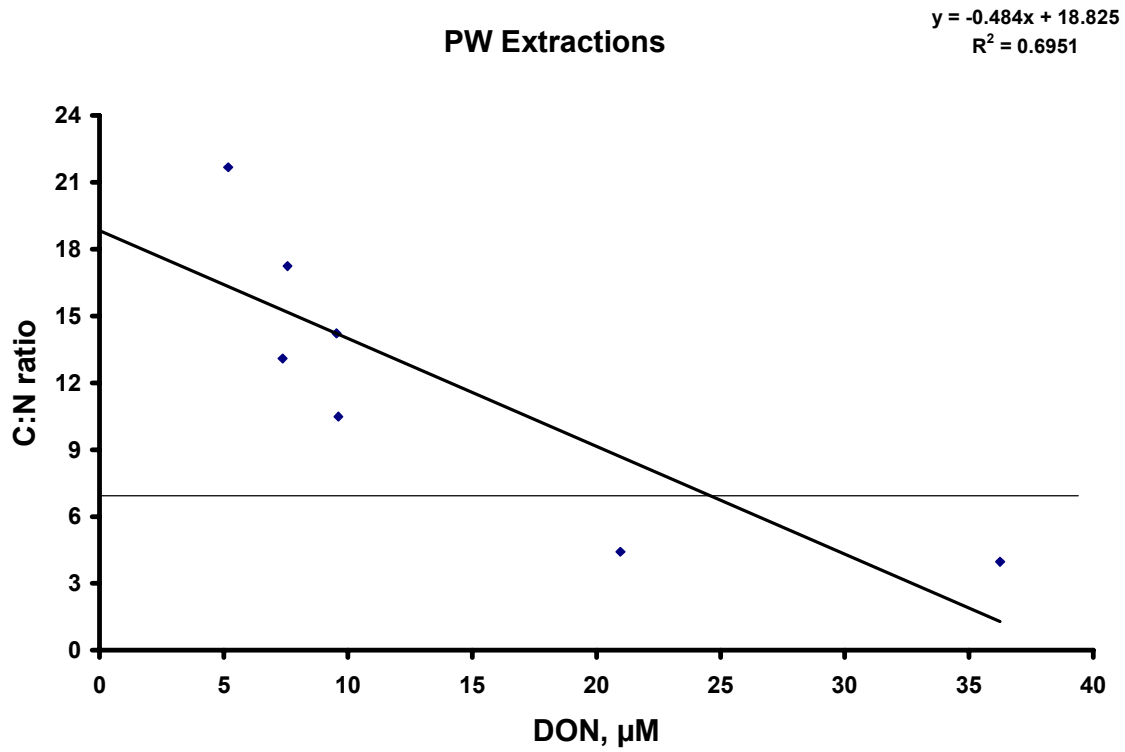

Figure 14. Correlation plot of DON concentrations for sand extraction samples versus C:N ratios obtained for the sand extraction samples at the Pelican Watch sampling site. Samples include both coastal ocean samples and sand extraction samples and were inversely correlated at $p<0.05$, $n=7$. The sand extraction samples were collected as a result of laboratory experiments where coastal seawater was allowed to contact sandy beach sediments for 1 hour. Coastal ocean samples were collected just prior to low tide. C:N ratios were obtained by dividing the DOC concentration by the DON concentration. The solid line represents Redfield's ratio, 6.625.

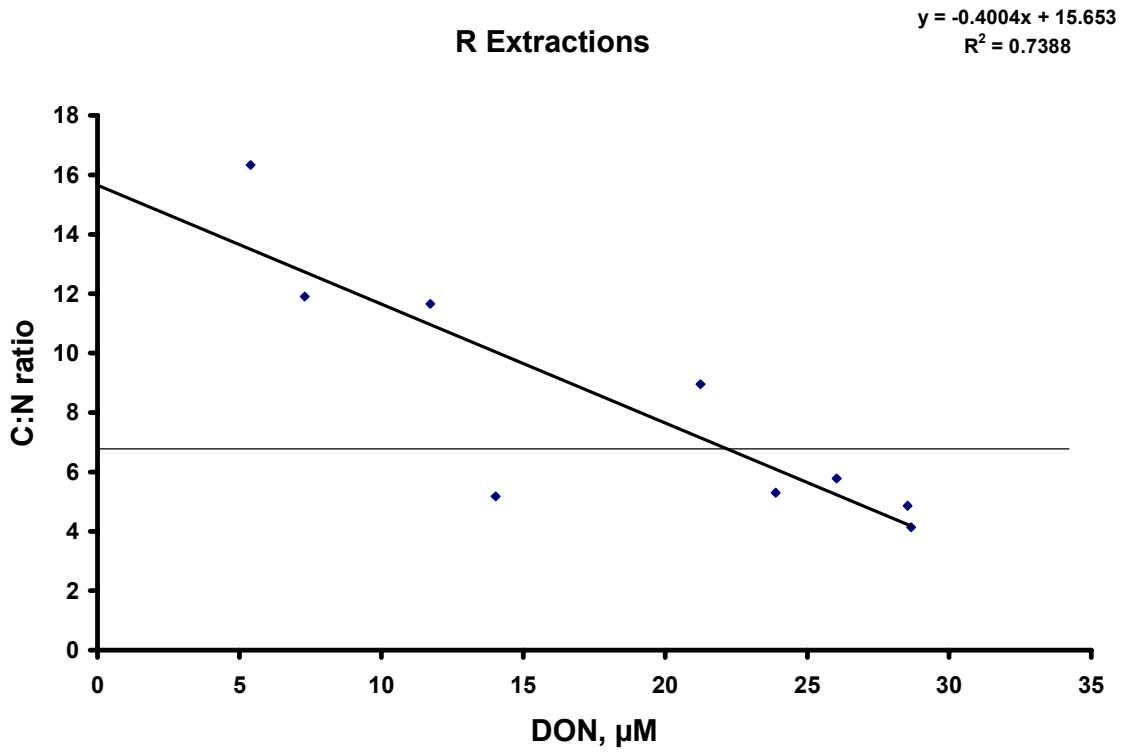

Figure 15. Correlation plot of DON concentrations for sand extraction samples versus C:N ratios obtained for the sand extraction samples at the Riggings sampling site. Samples include both coastal ocean samples and sand extraction samples and were inversely correlated at $p<0.05$, $n=9$. The sand extraction samples were collected as a result of laboratory experiments where coastal seawater was allowed to contact sandy beach sediments for 1 hour. Coastal ocean samples were collected just prior to low tide. C:N ratios were obtained by dividing the DOC concentration by the DON concentration. The solid line represents Redfield's ratio, 6.625.

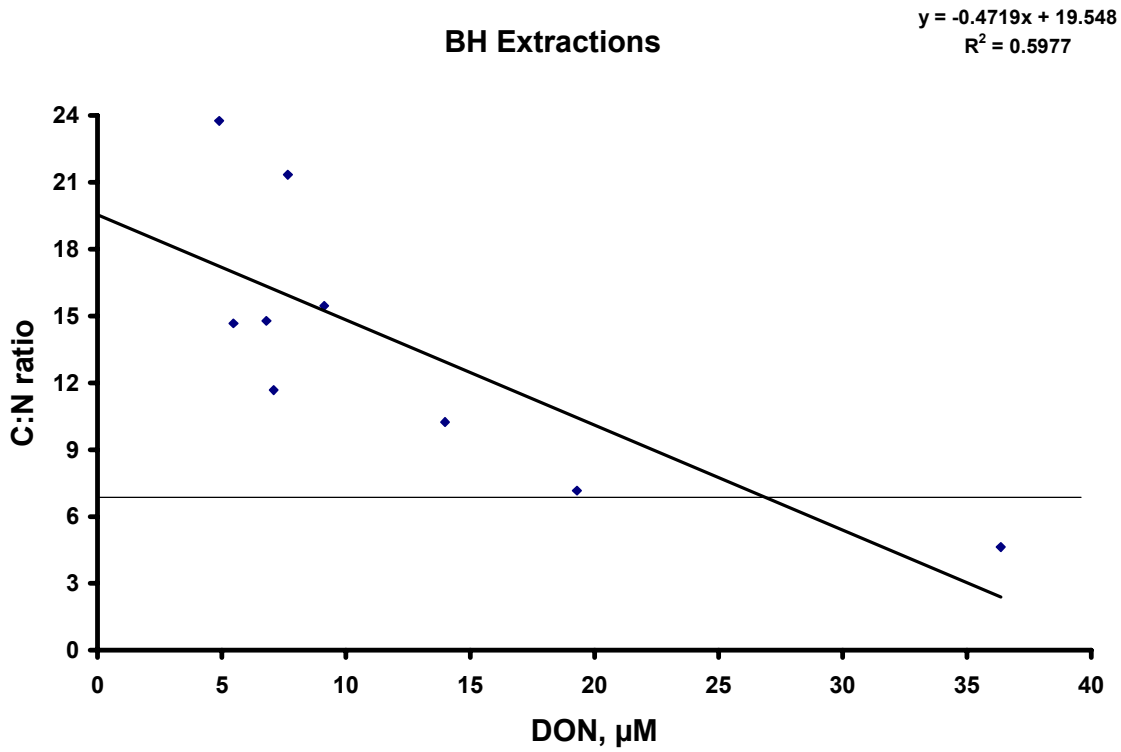

Figure 16. Correlation plot of DON concentrations for sand extraction samples versus C:N ratios obtained for the sand extraction samples at the Bathhouses sampling site. Samples include both coastal ocean samples and sand extraction samples and were inversely correlated at $p<0.05$, $n=9$. The sand extraction samples were collected as a result of laboratory experiments where coastal seawater was allowed to contact sandy beach sediments for 1 hour. Coastal ocean samples were collected just prior to low tide. C:N ratios were obtained by dividing the DOC concentration by the DON concentration. The solid line represents Redfield's ratio, 6.625.

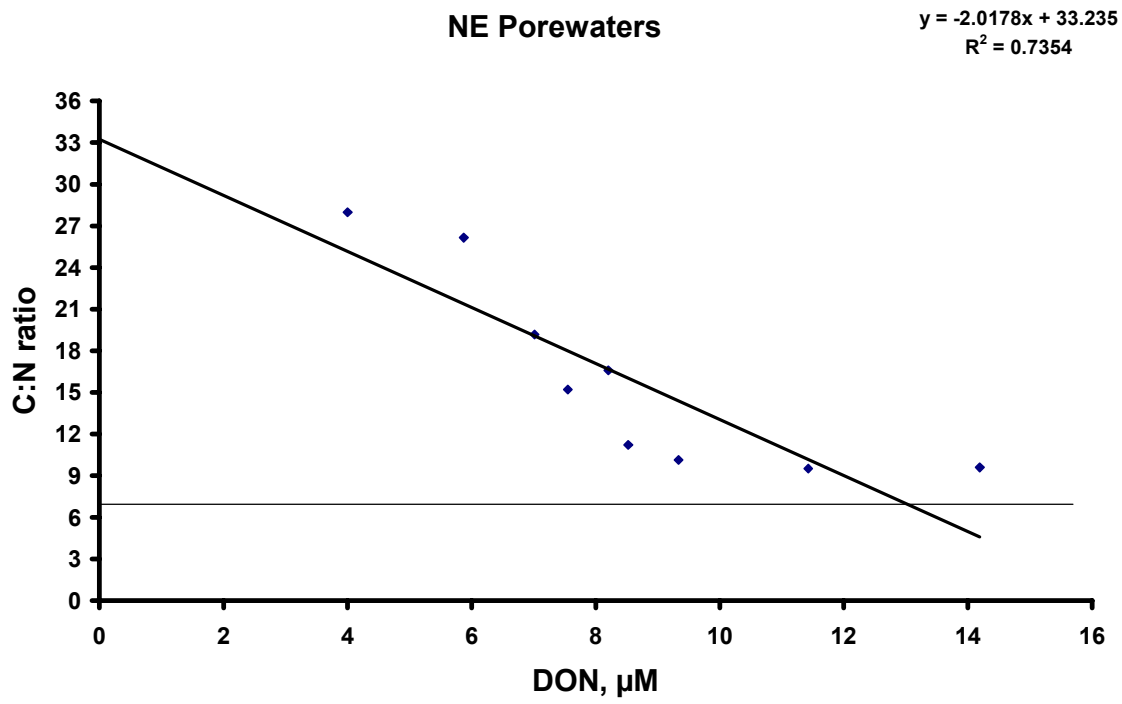

Figure 17. Correlation plot of DON concentrations for porewater samples versus C:N ratios obtained for porewater samples at the North End sampling site. Samples include both coastal ocean samples and porewater samples and were inversely correlated at $p<0.05$, $n=9$. Porewater samples were collected along a beach transect just prior to low tide. Coastal ocean samples were collected at the same time. C:N ratios were obtained by dividing the DOC concentration by the DON concentration. The solid line represents Redfield's ratio, 6.625.

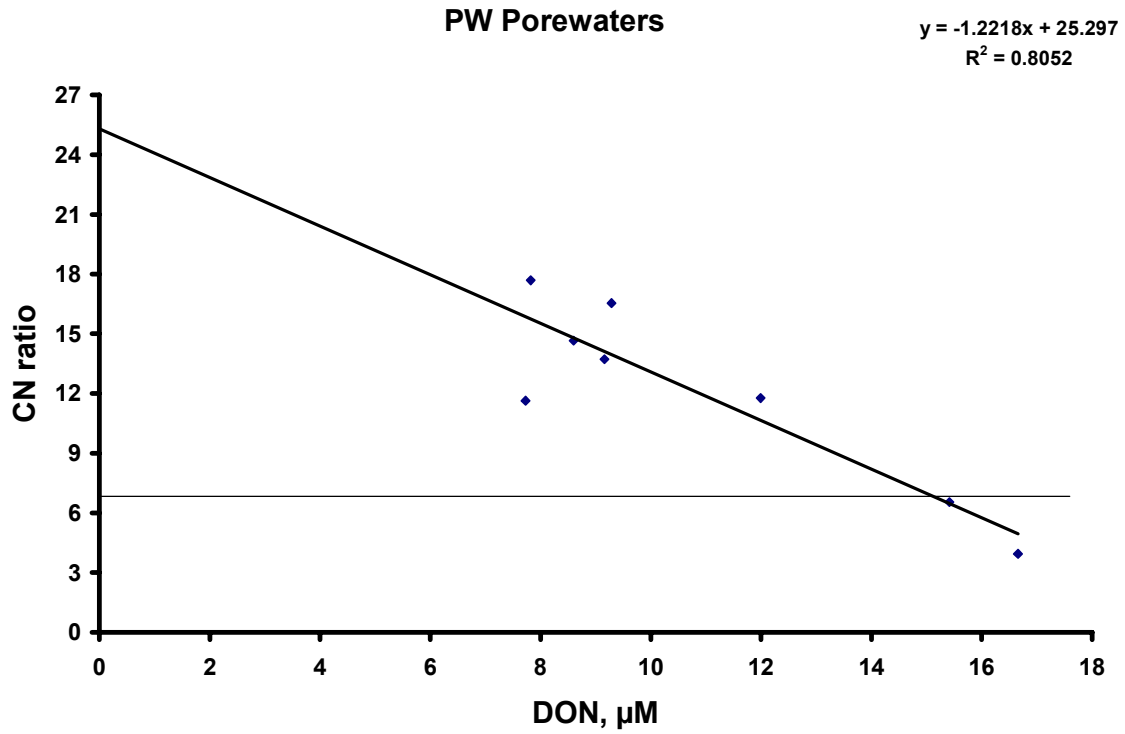

Figure 18. Correlation plot of DON concentrations for porewater samples versus C:N ratios obtained for porewater samples at the Pelican Watch sampling site. Samples include both coastal ocean samples and porewater samples and were inversely correlated at $p<0.05$, $n=8$. Porewater samples were collected along a beach transect just prior to low tide. Coastal ocean samples were collected at the same time. C:N ratios were obtained by dividing the DOC concentration by the DON concentration. The solid line represents Redfield's ratio, 6.625.

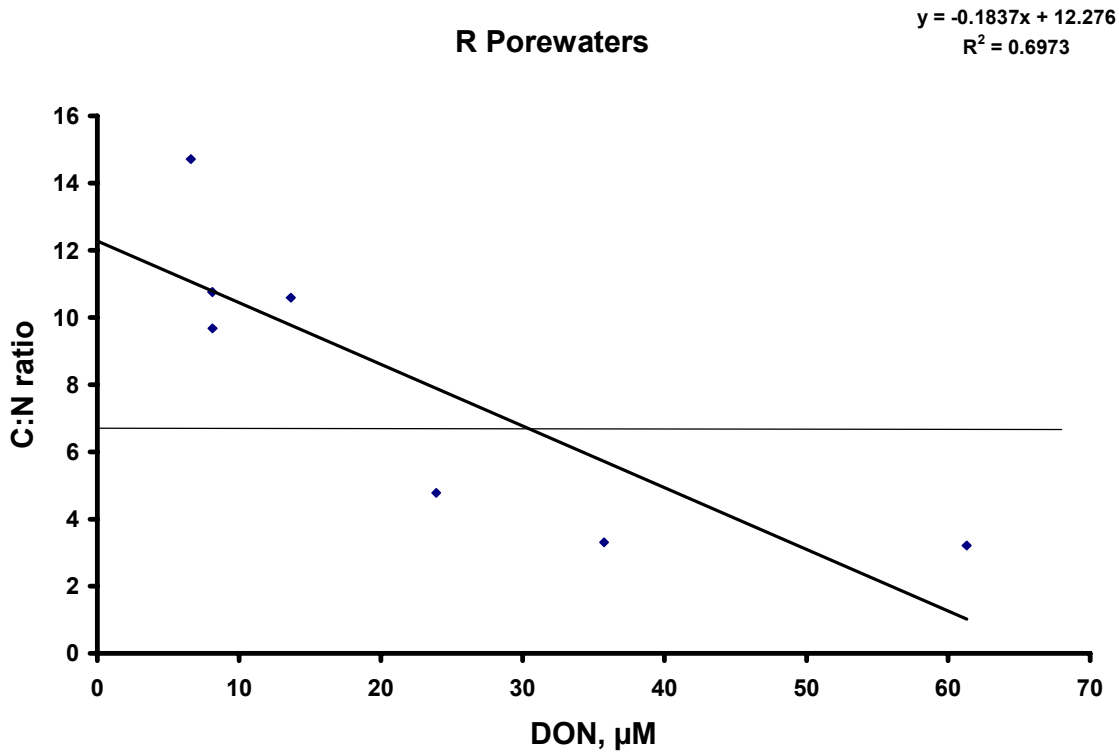

Figure 19. Correlation plot of DON concentrations for porewater samples versus C:N ratios obtained for porewater samples at the Riggings sampling site. Samples include both coastal ocean samples and porewater samples and were inversely correlated at $p<0.05$, $n=7$. Porewater samples were collected along a beach transect just prior to low tide. Coastal ocean samples were collected at the same time. C:N ratios were obtained by dividing the DOC concentration by the DON concentration. The solid line represents Redfield's ratio, 6.625.

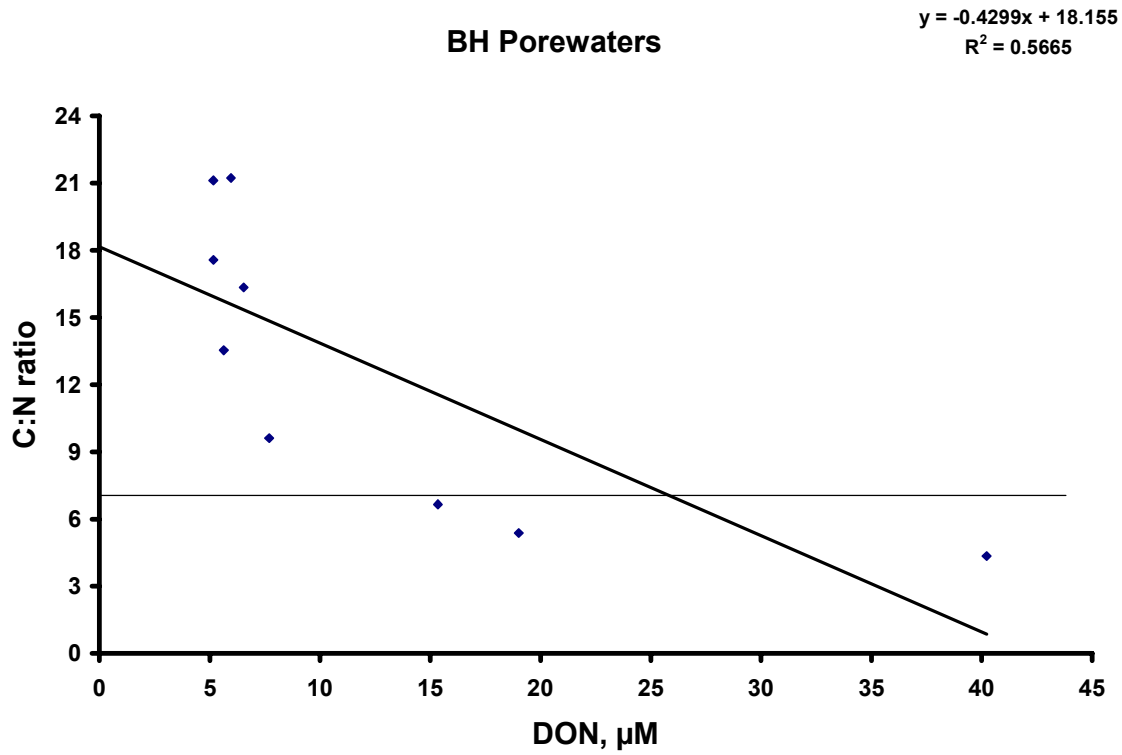

Figure 20. Correlation plot of DON concentrations for porewater samples versus C:N ratios obtained for porewater samples at the Bathhouses sampling site. Samples include both coastal ocean samples and porewater samples and were inversely correlated at $p<0.05$, $n=9$. Porewater samples were collected along a beach transect just prior to low tide. Coastal ocean samples were collected at the same time. C:N ratios were obtained by dividing the DOC concentration by the DON concentration. The solid line represents Redfield's ratio, 6.625.

Seasonality

Increases in coastal seawater DOC and TDN concentrations after exposure to sandy beach sediments in extraction experiments appear to display seasonality, with the highest DOC and TDN input from the sandy beach sediments in late summer and lowest during the winter months (Figures 21 and 23). This seasonal trend is consistent with increased primary production during periods of warmer weather including longer days, the presence of more sunlight and increased sea surface temperatures. Seasonality in the summer months was not as evident with porewaters (Figures 22 and 24) although there still appear to be higher concentrations during warmer months. The pattern is likely not as clear because of the complexity of what the porewater concentrations reflect as described above.

Implications

There is a significant flux (moles $meter^{-2}$ $hour^{-1}$) of DOC, DON, and nitrate from these sandy beach sediments to the coastal ocean (Table 1). In comparison with estuarine sediments from the Chesapeake Bay (Burdige & Zheng, 1998), the sediment fluxes of these three constituents in the present study were larger by several orders of magnitude (Figure 25 & Table 1). These results are surprising given that the Chesapeake Bay contains fine-grained, organic rich estuarine sediments (Burdige & Zheng, 1998) that would be expected to have a large flux out of the sediments. The flux of ammonium found in this study (0.1×10^{-4} moles m^{-2} hr^{-1}) was an order of magnitude less than the flux observed from the Chesapeake Bay sediments (1.5×10^{-4} moles m^{-2} hr^{-1}) consistent with the remineralization rates observed in these well oxygenated sediments. The

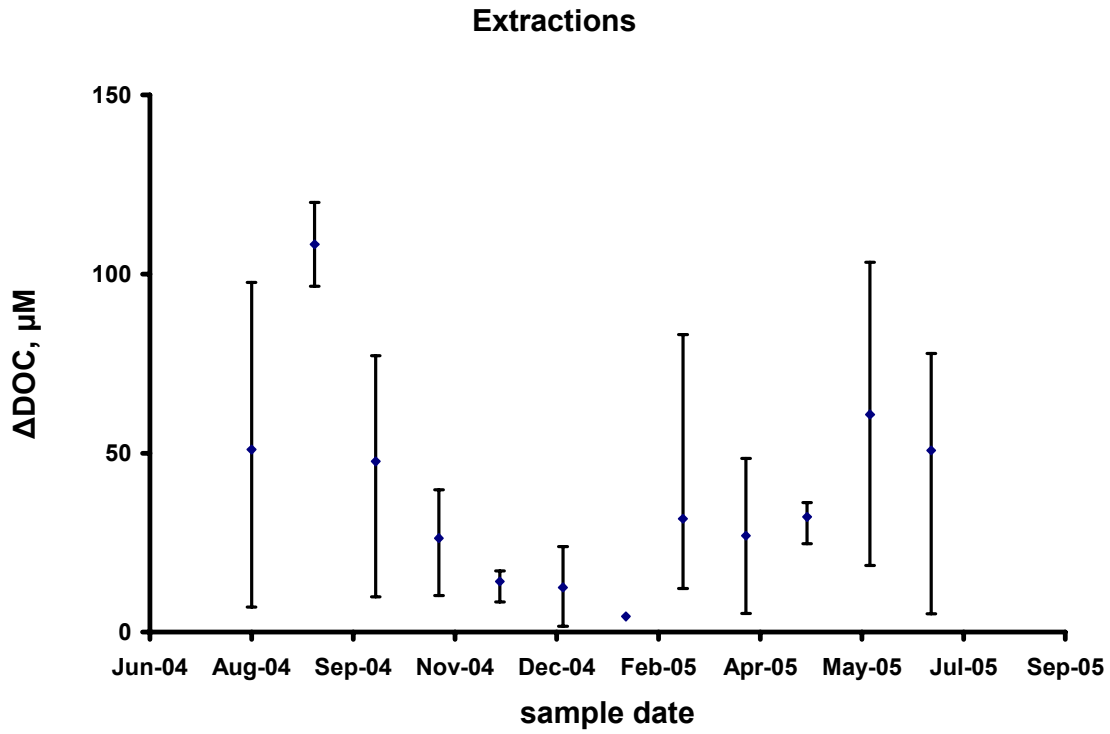

Figure 21. Seasonal pattern for delta DOC concentrations for sand extraction experiments. Delta DOC concentrations were obtained by subtracting the DOC concentration for the sand extraction sample minus the DOC concentration for the coastal ocean sample. Average concentrations are represented by the dot with the range represented by error bars. All sites were included.

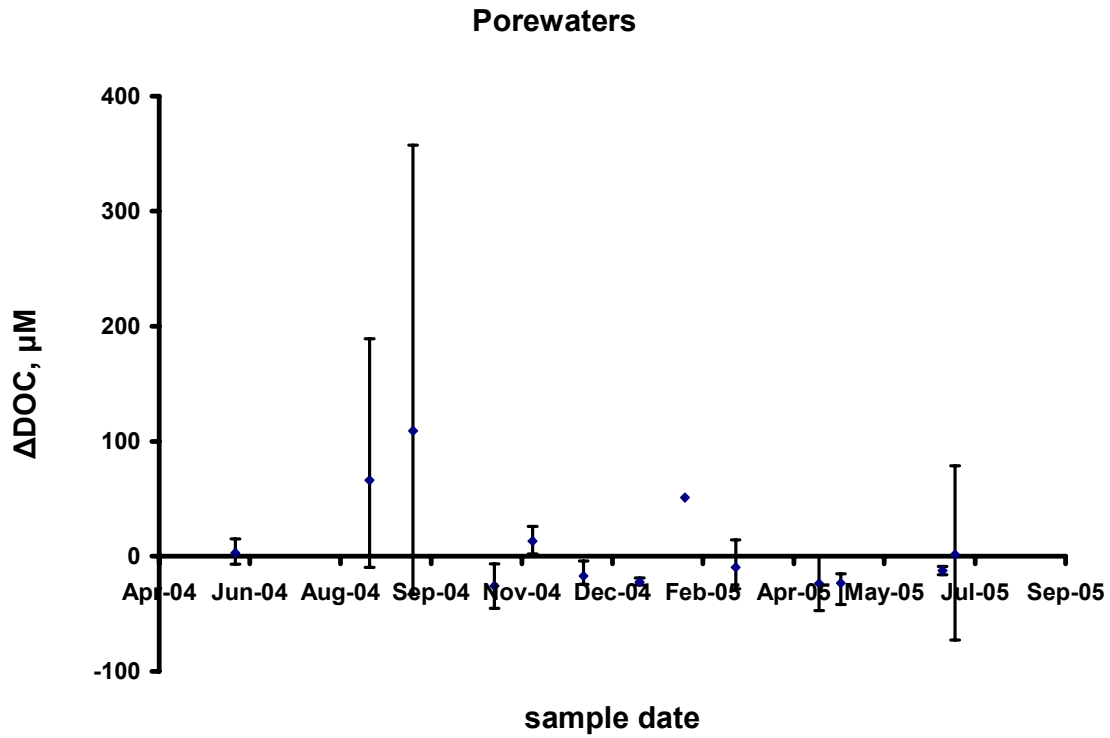

Figure 22. Seasonal pattern for delta DOC concentrations for porewater samples. Delta DOC concentrations were obtained by subtracting the DOC concentration for the porewater sample minus the DOC concentration for the coastal ocean sample. Average concentrations are represented by the dot with the range represented by error bars. All sites were included.

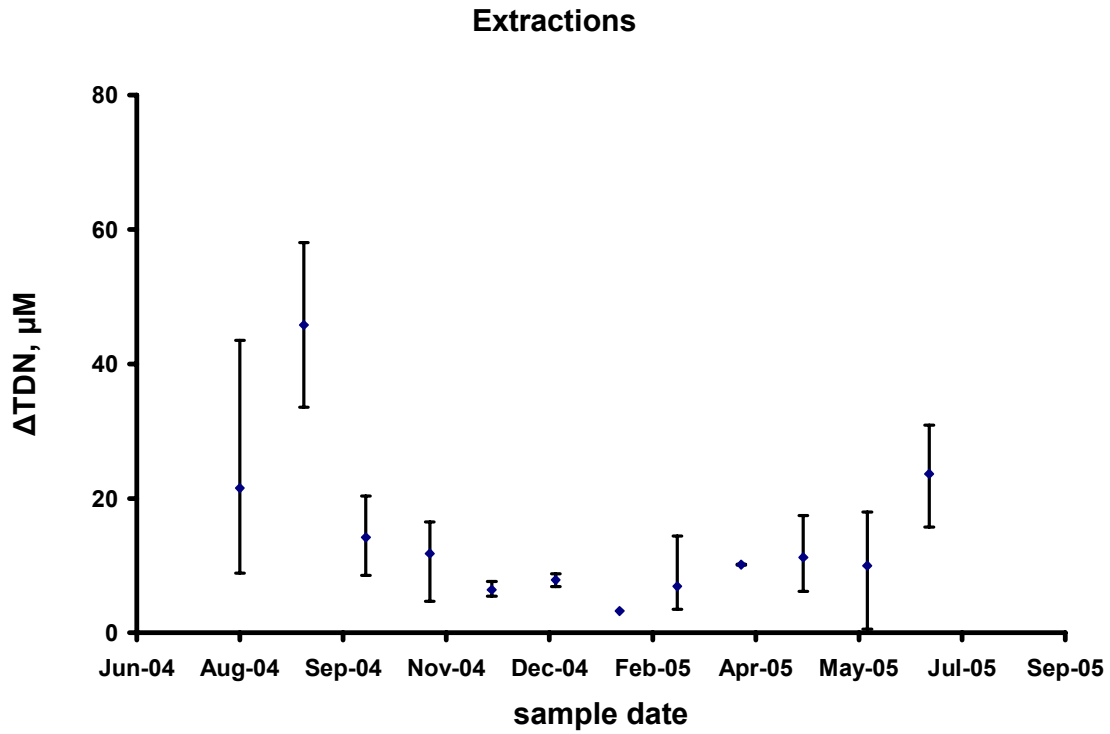

Figure 23. Seasonal pattern for delta TDN concentrations for sand extraction experiments. Delta TDN concentrations were obtained by subtracting the TDN concentration for the sand extraction sample minus the TDN concentration for the coastal ocean sample. Average concentrations are represented by the dot with the range represented by error bars. All sites were included.

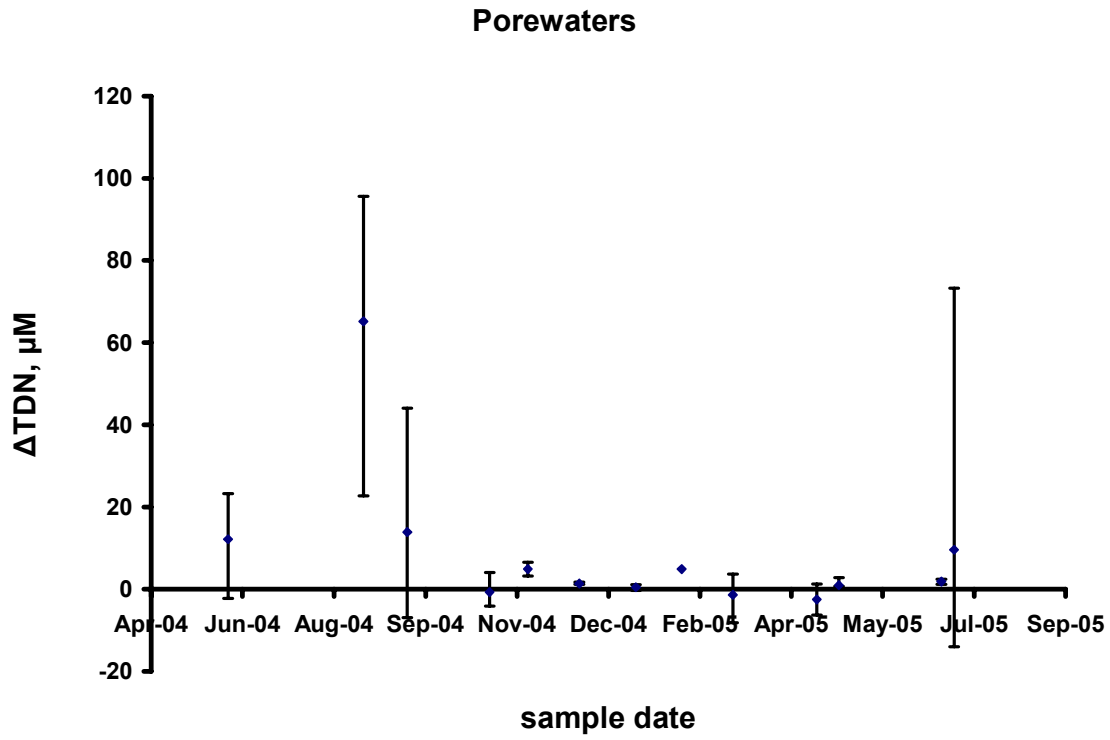

Figure 24. Seasonal pattern for delta TDN concentrations for porewater samples. Delta TDN concentrations were obtained by subtracting the TDN concentration for the porewater sample minus the TDN concentration for the coastal ocean sample. Average concentrations are represented by the dot with the range represented by error bars. All sites were included.

	DOC	DON	Nitrate	Ammonium	Reference
Sandy Beach Sediments	10	2	1	0.1	This Study
Chesapeake Bay Sediments	0.2	0.04	0.01	1.5	Burdige & Zheng 1998
Rain Deposition*	0.2	0.007	0.02	0.02	Long 2003
North Carolina Continental Slope Sediments	.0032				Alperin et al, 1999

Table 1. Flux of DOC, DON, nitrate and ammonium in 10^{-4} moles meter^{-2} hour^{-1}. Includes results for sandy beach sediments for this study, Chesapeake Bay estuarine sediments, wet particle rain deposition, and North Carolina continental slope sediments.
*Collected between September 1, 2002 and August 31, 2003

sediment fluxes of DOC, DON, nitrate and ammonium for this study were also at least an order of magnitude larger than those reported by Long 2003 for direct wet deposition by rain (Figure 25 & Table 1). These significant flux results suggest that the sandy beach sediments are a previously undescribed source of DOC, DON, and nitrate to the nearshore coastal ocean that may play an important role in the net primary productivity of coastal bays.

The annual flux (moles $year^{-1}$) of DOC, DON, and ammonium from sandy beach sediments make up only a small fraction of the standing stock of these constituents into Onslow Bay on the southeast coast of the United States. In contrast, approximately 18% of the standing stock of nitrate in Onslow Bay is supported by the flux out of these sandy beach sediments. The flux of DOC, DON, nitrate and ammonium associated with rain deposition is significantly larger than the flux of these constituents associated with tidal flushing of sandy beach sediments (Table 2). It is important to note that the flux from rain is episodic and seasonal in conjunction with hurricanes. The surface area encompassed for the rain deposition calculation is also much larger than that for sandy beach sediments. However, in a coastal bay where no riverine input is present and there's been no recent rainfall, the sandy beach sediments likely supply a significant fraction of DOC and dissolved nitrogen species to the coastal ocean.

CONCLUSIONS

This study presents the first extensive examination of the impact of coastal intertidal sandy beach sediments on oceanic concentrations of DOC, DON, and DIN. This project included *in situ* porewater measurements as well as laboratory experiments where sandy

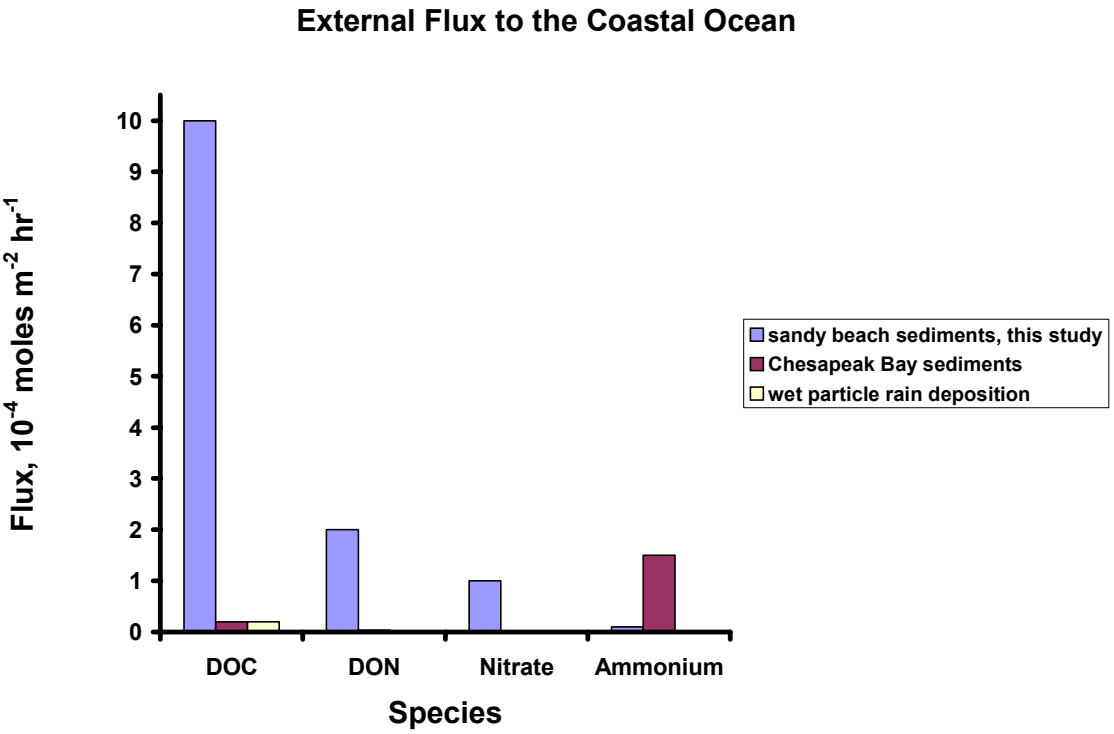

Figure 25. Flux of DOC, DON, nitrate and ammonium in 10^{-4} moles meter^{-2} hour^{-1}. Includes results for sandy beach sediments for this study, Chesapeake Bay estuarine sediments and wet particle rain deposition.

	DOC	DON	Nitrate	Ammonium	Reference
Sandy Beach Sediments	2.8	0.56	0.28	0.04	This Study
Rain Deposition	112	3.8	11.6	10.5	Long 2003

Table 2. Annual flux of DOC, DON, nitrate and ammonium in10^7 moles $year^{-1}$ into Onslow Bay. Includes results for sandy beach sediments for this study and Chesapeake Bay estuarine sediments.

beach sediments were extracted with coastal seawater. These beach sediments were shown to be a source of DOC, DON and nitrate. The flux (moles m^{-2} hr^{-1}) of these constituents from sandy beach sediments was several orders of magnitude higher than Chesapeake Bay sediments and rainwater. In a coastal bay such as Onslow Bay, which has no major riverine input, sandy beach sediments supply a significant amount of DOC, DON, and DIN. The supply of nitrate from these sediments is particularly important supplying approximately 18% of the standing stock of nitrate on an annual basis. DOC and DON concentrations were elevated in the coastal seawater during times when extracted amounts of these constituents from the sediment were largest showing a direct impact of these beach sediments on their concentrations. However, the same was not true for nitrate and ammonium likely reflecting their rapid consumption in coastal waters after they were exported from the beach. A positive correlation between nitrate extracted and chlorophyll a in the extracted sand column suggests that nitrate from these beach sediments may be driving productivity in the coastal waters. The lack of rapid consumption of DON observed in this study, and the lack of correlation between DON and chlorophyll a indicates that the DON released from these beach sediments is probably not very bioavailable. By quantifying the fluxes of DOC, DON and DIN from these sandy beach sediments, this study will be useful in refining budgets for both organic carbon and nitrogen species in the coastal ocean.

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