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Dissolved Inorganic Nitrogen Dynamics in Swash Zone Sands of Long Bay, SC

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By

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Abstract

A key component affecting the biogeochemistry of the sedimentary environment is pore water between grains of sediments. Sedimentary microorganisms are constantly modifying chemical compounds as part of their life functions which are then exchanged between the sediment column and the overlying water column. Dissolved inorganic nitrogen, a major element for life, takes on several forms including nitrate, nitrite, and ammonium which vary in concentration throughout the sediment and with respect to each other. The relative concentrations of these nitrogen species have been previously briefly explored in sandy columns, where redox gradients that control their relative concentrations can be fairly deep because of high permeability, the ability for fluid to flow through the sediment column. In this study, the dissolved inorganic nitrogen geochemistry is determined in swash zone sandy columns at four sites along the South Carolina Grand Strand, and variations are interpreted based on sediment permeability, phosphate concentrations as they relate to nitrogen through Redfield Richards Ratio stoichiometry, and Chlorophyll *a* concentrations.

Introduction

Sediments play an essential role to coastal marine environments because they are the major site of many biogeochemical processes that alter organic matter (Schulz and Zabel, 2006). Microorganisms beneath the sediment surface are extremely diverse and are responsible for the transformation of many different elements, including macronutrients such as nitrogen. Analysis of pore water at varying depths can often reveal the dominant transformation process at each depth. In sandy sediments that are highly permeable, sedimentary pore water and overlying water mix under the influence of passing currents and waves, exchanging transformed compounds such as nutrients, which are essential to photosynthesizers (Falter and Sansone, 2000).

Dissolved Inorganic Nitrogen

Nitrogen takes on many chemical forms in the oceans. The most significant dissolved inorganic nitrogen (DIN) species are nitrate (NO_3^-), nitrite (NO_2^-), and ammonium (NH_4^+), listed in order of most oxidized to most reduced. These three species follow a pattern in sedimentary pore water with depth that reflects the proximity to the oxic water column. This pattern is most clearly visible with high concentrations of NO_3^- and NO_2^- at the surface layers, and NH_4^+ taking their place in deeper layers (Falter and Sansone, 2000). It is implied that the actual depth at which this transition occurs from oxidized to reduced inorganic nitrogen is controlled by exchange with the oxic water column, and therefore by physical mixing and sedimentary permeability.

Phosphate

In addition to nitrogen species, phosphate (PO_4) is a major component and byproduct in the process of respiration. Phosphate concentrations within pore water and their variation with depth

can indicate microbial activity, transport of phosphate out of the sediments and, when compared with DIN, the metabolic processes behind the microbial activity.

Redfield Richards Ratio

Respiration in the marine environment has been represented as shown in Eq. 1:

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 138O_2 \leftrightarrow 106CO_2 + 16HNO_3 + H_3PO_4 + 122H_2O \qquad \text{Eq. 1}$$
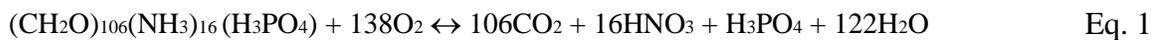
The stoichiometry of the different reactants and products is called the Redfield Richards Ratio (Libes 2009). The Redfield Richards Ratio is the ideal ratio of major elements in phytoplankton, and dictates the ratio of major respiration products/nutrients which should be found within the pore water if respiration of this idealized phytoplanktonic organic matter is taking place. Specifically, the major elements C, N and P participate in a molar ratio of 106:16:1. Whereas nitrate is the main DIN species produced during aerobic respiration, under anaerobic conditions the main DIN species that is produced will be ammonium.

Chlorophyll a

Primary producers such as phytoplankton and microphytobenthos are responsible for a significant fraction of organic matter in sandy environments. They are especially present in the swash zone where sunlight is readily available and where pore water samples will be taken. Photosynthesis within the marine environment using the Redfield Richards Ratio stoichiometry is shown in Eq. 2 (note that it is essentially the inverse of Eq. 1):

$$106CO_2 + 16HNO_3 + H_3PO_4 + 122H_2O \leftrightarrow (CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 138O_2 \qquad \text{Eq. 2}$$
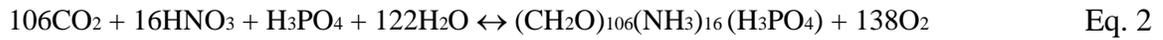
Chlorophyll a is a straight-forward and easily measured tracer of photosynthesizers and photosynthetic activity (MacIntyre et. al, 1996). By measuring both chlorophyll and nutrients that are products of respiration (DIN and phosphate) the dynamic relationship between photosynthesis and respiration within the swash zone environment can be examined.

Hypotheses

Based on the above we formulated several hypotheses tested by this study. As permeability increases, the transformation of nutrients is predicted to occur closer to the sediment surface due to a higher flushing rate of the sediments. As permeability decreases, nutrients are predicted to build up within the sediments because there will be a slower flushing rate. Chlorophyll is predicted to remain in high concentrations at the sediment's surface where sunlight is readily available. The ratio of dissolved inorganic nitrogen to phosphate should remain close to a 16 to 1 ratio in correspondence with the Redfield Richards Ratio, and reflecting that an abundance of respiration is occurring below the sediment's surface.

Methods

Study sites

All study sites are located in Long Bay, South Carolina, along the Grand Strand: Waties Island, Myrtle Beach State Park, Huntington Beach State Park, and Pawley's Island (Figure 1). The biogeochemistry of sand on open ocean-facing beaches at these sites is monitored monthly at Waties Island and on a quarterly basis at the other sites by the Sand Biogeochemistry research program at Coastal Carolina University.
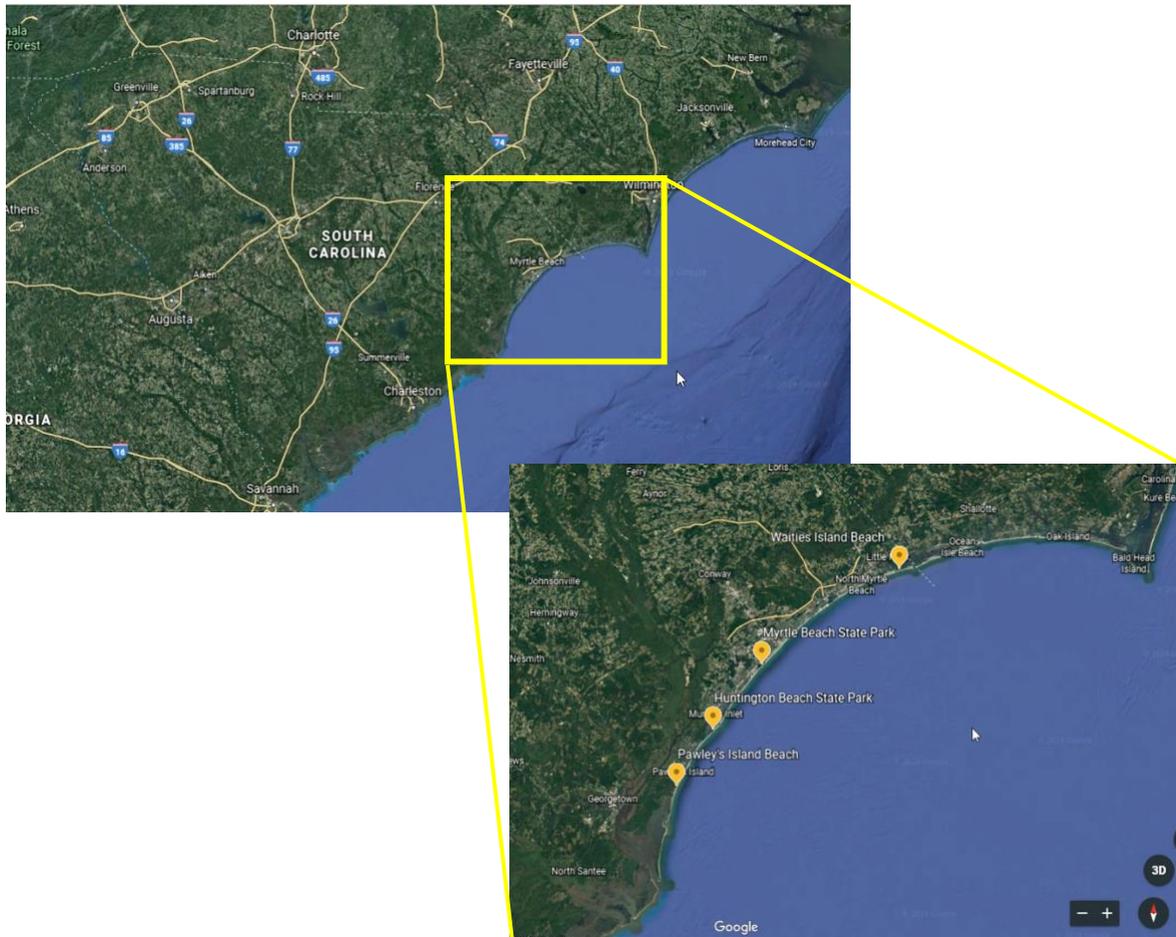

Figure 1 Location of the study area and the four study sites.

Sampling

Water samples were collected from the swash zone at low tide in February 8-10, 2019. Pore water samples were retrieved in syringes using an MHE PushPoint sampler (MHE Products, East Tawas, Michigan) from four to six depths beneath the sand surface, while overlying water was directly collected in a syringe. All water samples were immediately filtered on site through 0.2 μm inline syringe filters and frozen until analysis. At the same time, sand cores were collected from the same locations using an Icelandic piston corer (Aquatic Research Instruments, Hope, Idaho) and frozen until analysis.

Laboratory analysis

Nitrate was analyzed using an adaptation of the nitrate reduction column protocol (Parsons et al. 1984) where a 1mL syringe is modified using soft tubing and lure-lock pieces. This modified syringe forms a barrel-like cadmium column to which another 1mL syringe may easily be attached on either end to push sample through or collect it. The resulting sample along with an unreduced sample were analyzed to determine nitrate+nitrite and nitrite calorimetrically (Bendschneider and Robinson 1952).

The Sand Biogeochemistry research program protocols were used to determine additional properties with analyses conducted by other members of the research group. Permeability was determined by the constant-head method (Klute and Dirksen, 1986; Rocha et al., 2005). Sedimentary chlorophyll a was measured by fluorescence after extraction in acetone (Hannides et al. 2014). Ammonium (NH_4^+) was analyzed by fluorescence (Holmes et al. 1999), and phosphate was analyzed spectrophotometrically by the molybdenum blue complexation method (Murphy and Riley, 1962; Hansen and Koroleff, 1999).

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Data analysis

Data processing, figure generation and statistical analysis were conducted using MS Excel. Concentration profiles were generated for each nutrient and sedimentary chlorophyll at each sampling site, including the relative contributions of the three DIN species to DIN.

Inventories of nutrients and chlorophyll throughout the top 60 cm of the sediment column were calculated as areal concentrations (in μmol m-2 and mg m-2, respectively) to permit the comparison of standing stocks of these chemicals regardless of profile shapes, minimum values and maximum values. Nutrient inventories (in mmol m-2) were estimated according to Eq. 3:

$$\sum_{Depth\ interval\ i=1}^{Depth\ interval\ i=f} Nutrient = [Nutrient]_i \times \varphi \times z_i \times \frac{L}{10^3\ cm^3} \times \frac{10^4\ cm^2}{m^2} \qquad \text{Eq. 3}$$

For depth intervals 1 to f, where [Nutrient]$_i$ is the average nutrient concentration of depth layer i in mmol L-1, φ is the porosity, and z_i is the thickness of depth layer i in cm. Chlorophyll *a* inventories (in mg m-2) were similarly estimated according to Eq. 4:

$$\sum_{Depth\ interval\ i=1}^{Depth\ interval\ i=f} Chl\ a = [Chl\ a]_i \times (1 - \varphi) \times \rho_g \times z_i \times \frac{10^4\ cm^2}{m^2} \qquad \text{Eq. 4}$$

Where [Chl a]$_i$ is the average chlorophyll concentration of depth layer i in mg g-1 dry sediment and ρ_g is the density of dry sediment (2.65 g cm-3; Breitzke 2006). Nutrient and chlorophyll inventories at each site were contrasted to sand permeabilities to elucidate the presence of patterns influenced by permeability-driven physical exchange.

Results

Permeability

Permeability across the four sites ranged from 1.1E-11 ± 2.4E-13 m_2 (WIB) to 1.6E-11 ± 3.6E-13 m_2 (PIB). Waities Island beach had the smallest permeability followed by Huntington Beach State Park, Myrtle Beach State Park, and finally Pawley's Island Beach with the largest permeability (Figure 2).

Dissolved Inorganic Nitrogen

Dissolved inorganic nitrogen in overlying water is similar along all sampling sites but with depth the profiles range drastically (Figure 3). Waities Island Beach and Myrtle Beach State Park have fairly low and steady DIN throughout the profile but both Huntington Beach State Park and Pawley's Island Beach have large spikes in DIN at depth. A breakdown of total DIN into its three major species, nitrate (NO_3^-), nitrite (NO_2^-), and ammonium (NH_4^+), reflects this expectation (
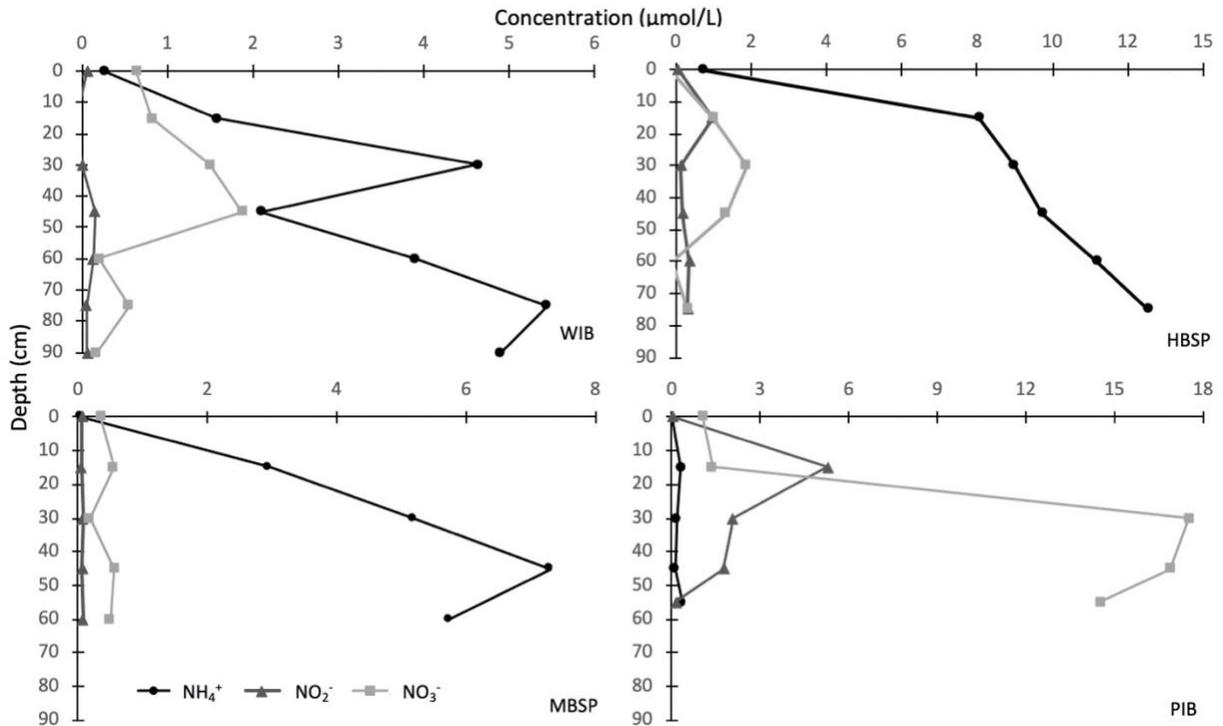
Figure 4). When DIN values were averaged or taken inventory and plotted against each site's respective permeability there was a slight positive correlation but the Waities Island Beach data point was an outlier (Figure 5).
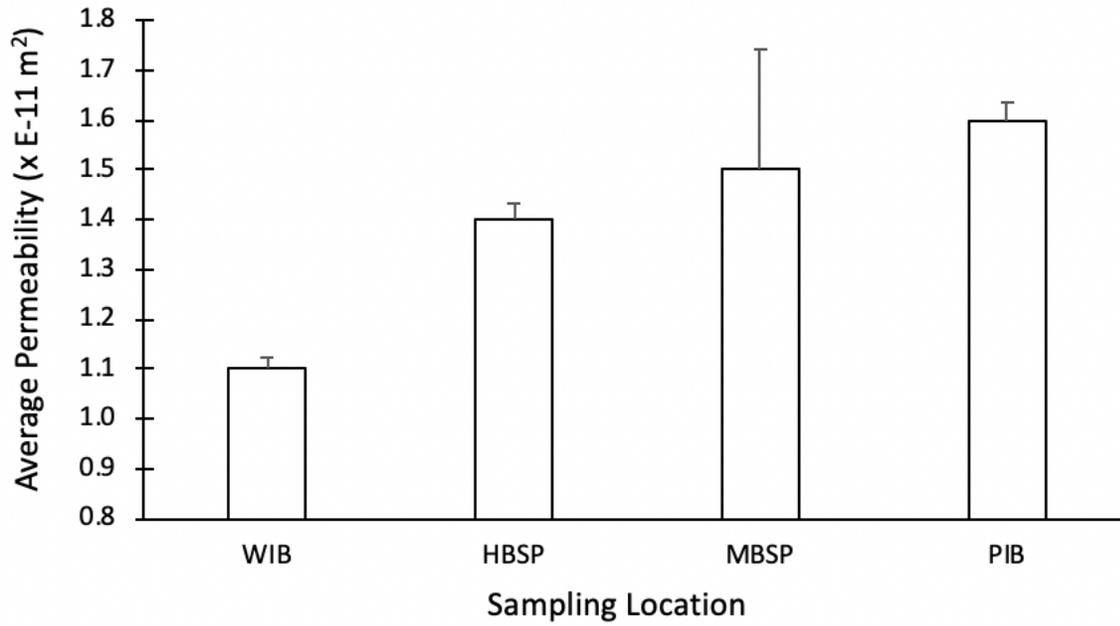
Figure 2 Permeability (m2) at the four study sites along the South Carolina Grand Strand: WIB: Waities Island Beach, HBSP: Huntington Beach State Park, MBSP: Myrtle Beach State Park, and PIB: Pawley's Island Beach. Error bars indicate one standard deviation.
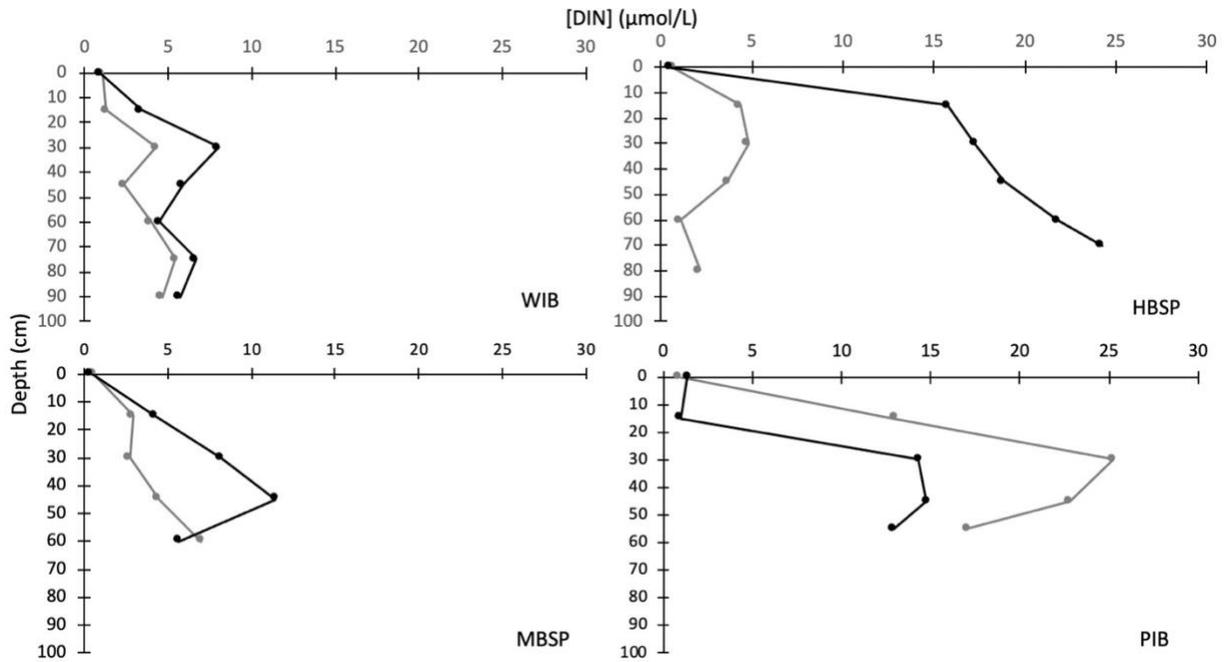
Figure 3 Duplicate Dissolved Inorganic Nitrogen concentration (µmol/L) profiles with depth (cm) in February 2019 at the four study sites along the South Carolina Grand Strand: WIB: Waities Island Beach, HBSP: Huntington Beach State Park, MBSP: Myrtle Beach State Park, and PIB: Pawley's Island Beach.
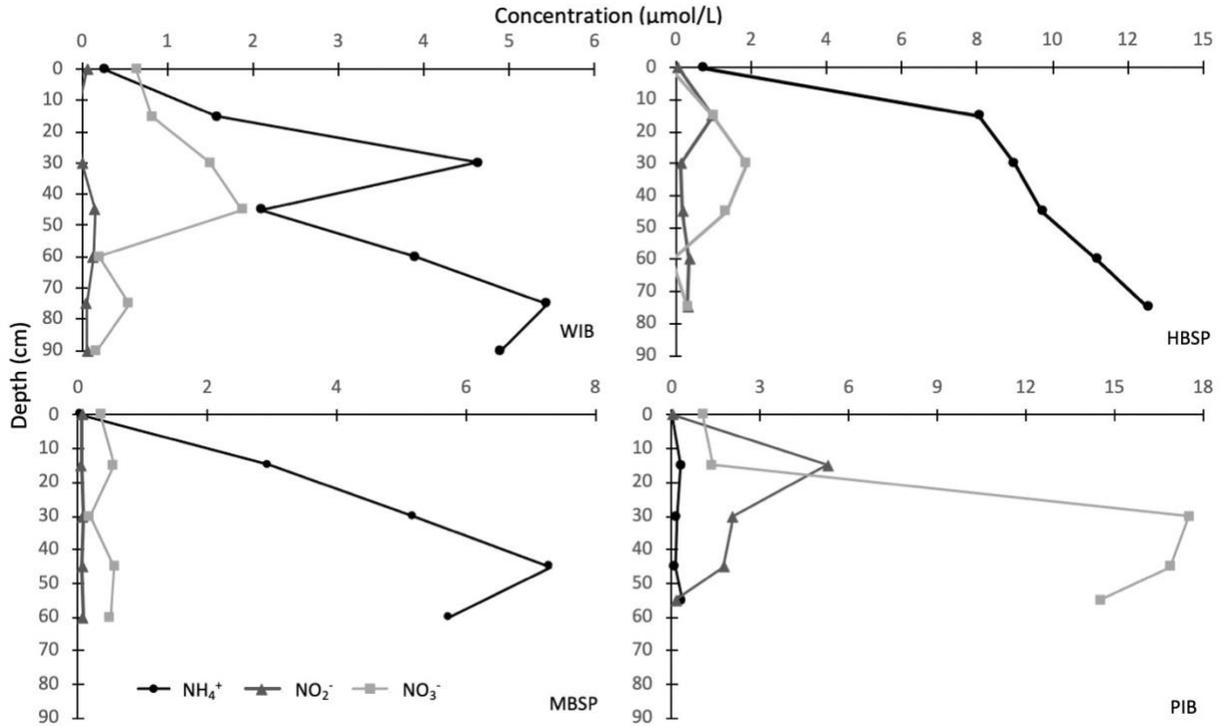
Figure 4 Profiles of nitrate (NO_3^-), nitrite (NO_2^-), and ammonium (NH_4^+) concentrations (µmol/L) with depth (cm) in February 2019 at the four study sites along the South Carolina Grand Strand: WIB: Waities Island Beach, HBSP: Huntington Beach State Park, MBSP: Myrtle Beach State Park, and PIB: Pawley's Island Beach.
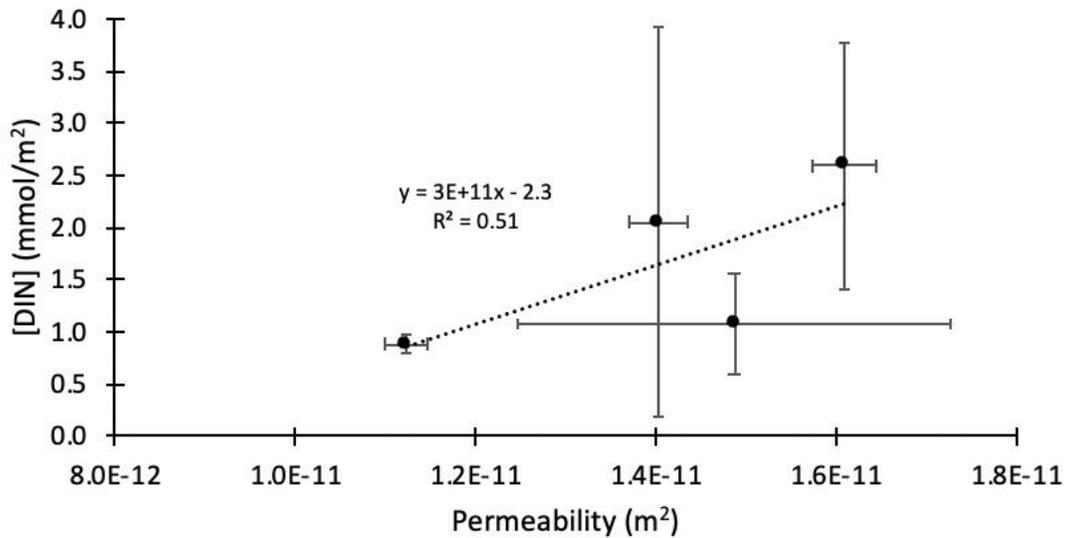
Figure 5 Dissolved Inorganic Nitrogen (mmol/m2) inventory values vs permeability (m2) in February 2019 at the four study sites along the South Carolina Grand Strand. Error bars indicate 1 standard deviation. The dotted line and associated statistics represent a line-of-best-fit generated by linear regression.

Phosphate

Phosphate, like DIN, was found at very low concentrations at the surface across all. At depth, phosphate concentrations at Waties, Myrtle Beach, and Pawley's Island stay below 2 μmol/L of phosphate but at Huntington Beach are higher, up to 5 μmol/L (Figure 6).
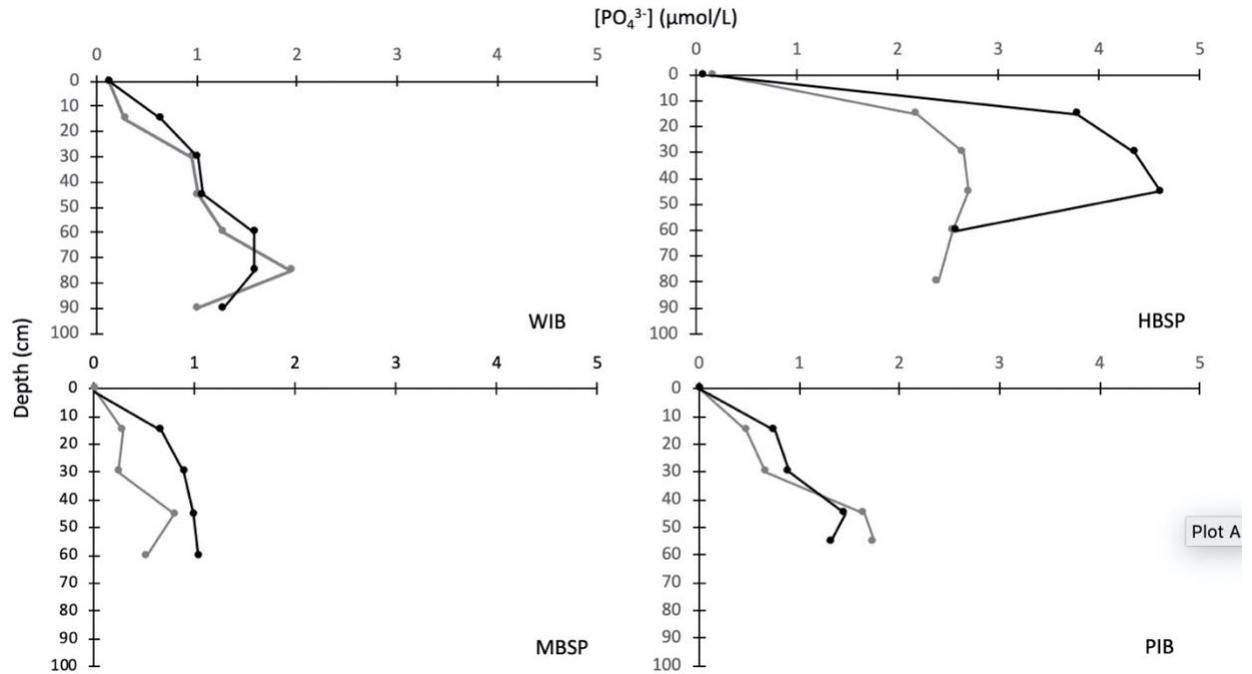
Figure 6 Duplicate phosphate concentration (μmol/L) profiles with depth (cm) in February 2019 at the four study sites along the South Carolina Grand Strand: WIB: Waities Island Beach, HBSP: Huntington Beach State Park, MBSP: Myrtle Beach State Park, and PIB: Pawley's Island Beach.

Dissolved inorganic nitrogen and phosphate should be present in the marine environment with a 16 to 1 ratio based on the Redfield Richards Ratio. When DIN and PO_4 were plotted against one another the trend lines were all positive but all of the correlations were less than half of the predicted 16 to 1 ratio (Figure 7). Despite the deviation from a slope of 16, data from Pawley's Island (PIB) lie along the 16:1 line.
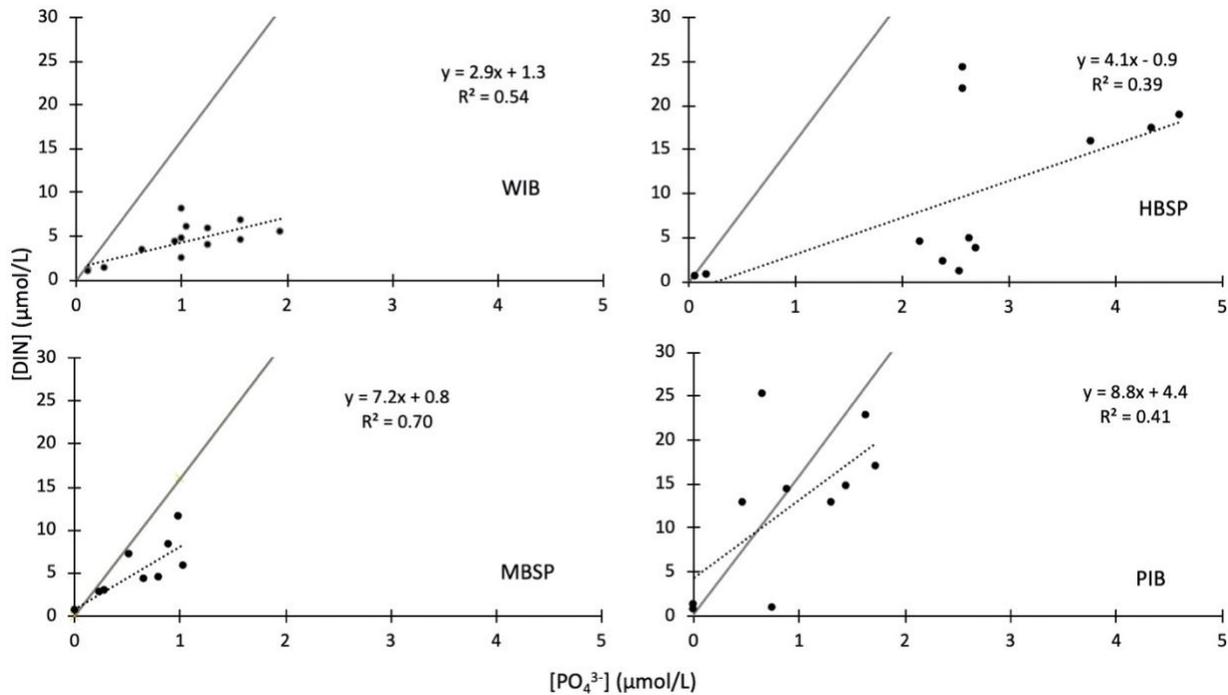

Figure 7 Dissolved Inorganic Nitrogen vs phosphate concentrations (µmol/L) in February 2019 at the four study sites along the South Carolina Grand Strand: WIB: Waities Island Beach, HBSP: Huntington Beach State Park, MBSP: Myrtle Beach State Park, and PIB: Pawley's Island Beach. The straight lines indicate the relationship y=16x. The dotted lines and associated statistics represent lines-of-best-fit generated by linear regression.

Chlorophyll

Chlorophyll profiles varied greatly depending on the site. Overall the trend with chlorophyll was that the value at the surface would slightly increase with depth and then it decreased after a mid-depth maximum (Figure 8). Chlorophyll inventories were also correlated with both phosphate and ammonium (Figure 9, Figure 10). In both cases there was a strong negative correlation, while nitrate and nitrite did not show any correlation.
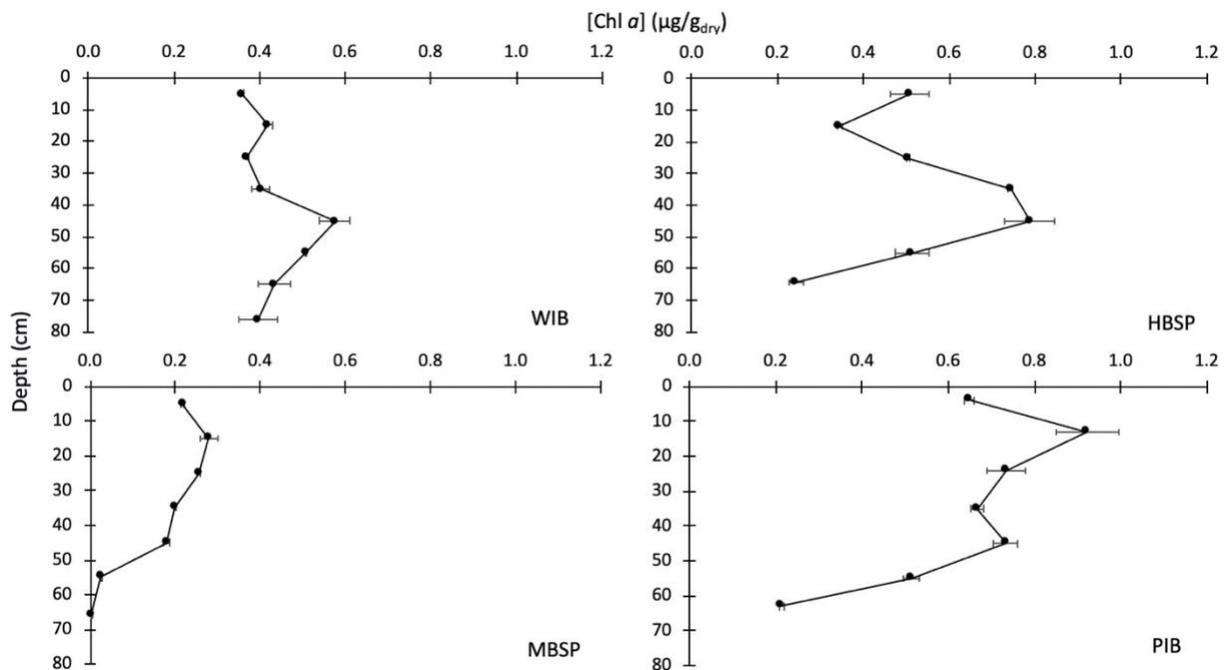

Figure 8 Average Chlorophyll* a *(μg/g$_{dry}$) with depth (cm) in February 2019 at the four study sites along the South Carolina Grand Strand: WIB: Waities Island Beach, HBSP: Huntington Beach State Park, MBSP: Myrtle Beach State Park, and PIB: Pawley's Island Beach. Error bars indicate 1 standard deviation.
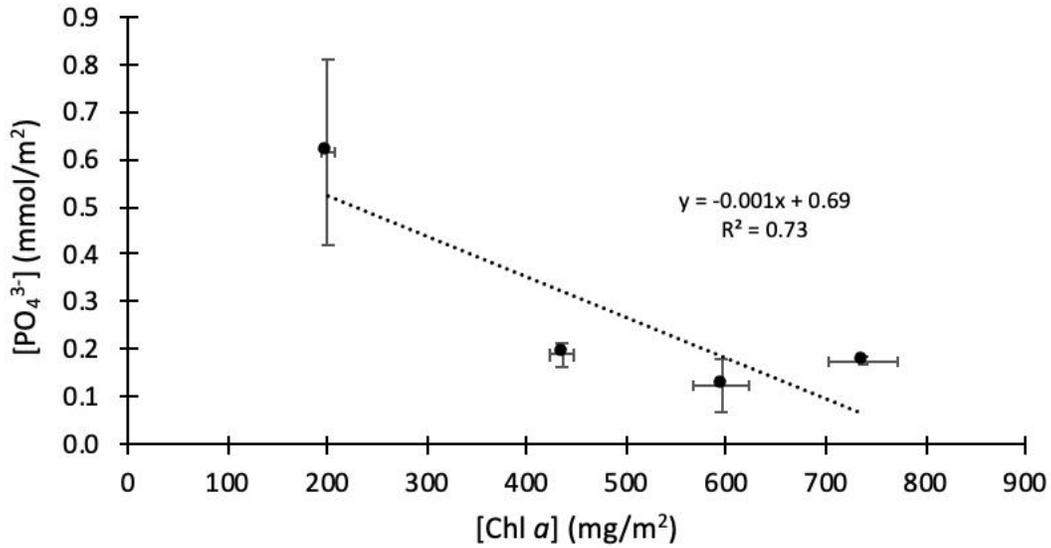
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*Figure 9 Phosphate (mmol/m₂) inventory values vs Chlorophyll **a** (mg/m₂) in February 2019 at the four study sites along the South Carolina Grand Strand. Error bars indicate 1 standard deviation. The dotted line and associated statistics represent a line-of-best-fit generated by linear regression in MS Excel.*
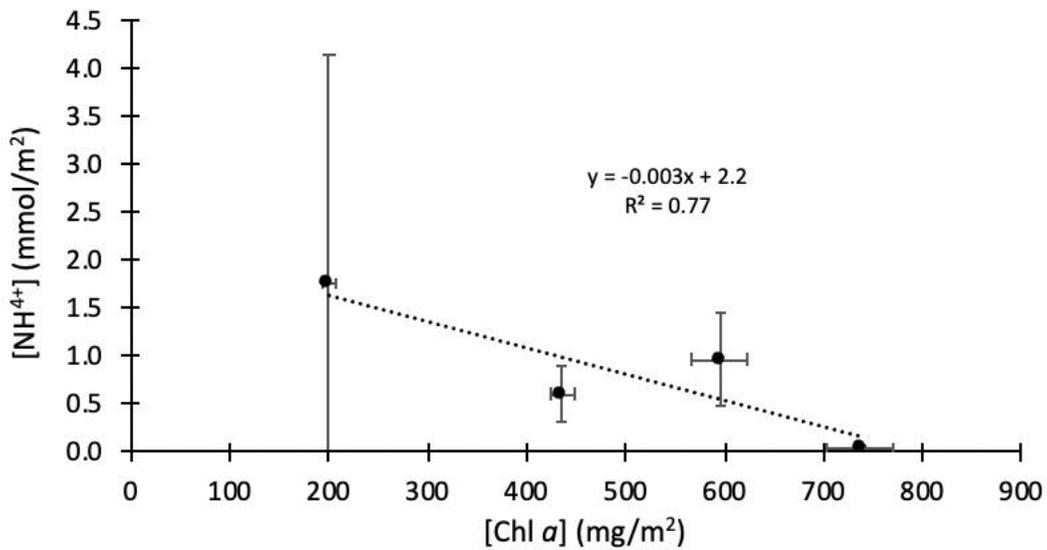

*Figure 10 Ammonium (μmol/m₂) inventory values vs Chlorophyll **a** (mg/m₂) in February 2019 at the four study sites along the South Carolina Grand Strand. Error bars indicate 1 standard deviation. The dotted line and associated statistics represent a line-of-best-fit generated by linear regression.*

Discussion

Permeability and nutrient concentrations were negatively correlated in the case of phosphate (Figure 9) and positively correlated in the case of DIN (Figure 5). The latter trend is unexpected because as permeability increases, flushing rate should increase resulting in less nutrient buildup, but it seems that this is not universally true. The squared Pearson correlation coefficient value, r_2 = 0.51, between DIN and permeability is not particularly so clearly more data generated by the Sand Biogeochemistry research group's monitoring activities will be useful in confirming this unusual outcome.

Redfield Richards Ratio comparisons (Figure 7) show that DIN is in high demand by sedimentary microbiota and depleted relative to phosphate. The most likely reason is that sedimentary respiration is proceeding by denitrification, using nitrate instead of oxygen (e.g., Hardison et al. 2015).

Chlorophyll is found at high concentrations at great depths at all sites (Figure 8). Since photosynthesis cannot happen at depth without a source of sunlight so mixing must be responsible for the high chlorophyll a values around 40 and 50 cm below the sediment surface. Chlorophyll concentrations show negative correlations with phosphate (Figure 9) and ammonium (Figure 10), as predicted by nutrient draw-down during photosynthesis (Eq. 2).

A longer study period with more data points will be necessary to confirm a correlation between nutrient buildup and sediment permeability. Sampling dates in additional months throughout the year will be analyzed later to further explore the effects of seasonality on sedimentary biogeochemistry in South Carolina Grand Strand coastal sands.

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