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IMPACT OF CHRONIC NITROGEN LOADING ON GREENHOUSE GAS

FLUXES IN COASTAL WETLANDS

BY

KATELYN ANN SZURA

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE

REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE IN

BIOLOGICAL AND ENVIRONMENTAL SCIENCES

UNIVERSITY OF RHODE ISLAND

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MASTER OF SCIENCE IN BIOLOGICAL AND ENVIRONMENTAL SCIENCES

OF

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# ABSTRACT

Coastal wetlands are valuable ecosystems that historically have not been protected and have been lost at rapid rates. Recently, they have gained attention for their potential role in climate change mitigation given that they have the ability to sequester and store large amounts of atmospheric carbon dioxide ($CO_2$). While other ecosystems can sequester and store carbon as well, salt marshes have the unique ability to store vast amounts of carbon while emitting relatively negligible amounts of methane ($CH_4$) and nitrous oxide ($N_2O$). These are additional greenhouse gases (GHGs) that can be emitted from ecosystems, particularly $CH_4$ in large quantities from freshwater wetlands. These gases are 45 and 270 times, respectively, greater at trapping heat in the atmosphere than $CO_2$.

However, anthropogenic nitrogen (N) inputs into coastal estuaries have the potential to shift biogeochemical cycling within coastal wetlands, possibly switching salt marshes from $CO_2$ sinks to being sources of one or more of the three major GHGs. Excessive anthropogenic N inputs are a threat to overall ecosystem health on local, regional, and global scales. Salt marshes are natural and efficient filters of excess N entering into these systems, although they cannot filter out unlimited quantities. Excess N in coastal systems can lead to a suite of negative consequences including poor water quality as a result of over stimulation of primary productivity and overall habitat degradation. The threat of anthropogenic N to coastal areas is only increasing as populations grow and concentrate along desirable coastal locations. For coastal wetlands that already face threats of habitat loss from increased rates of sea level rise (SLR) and urban development, N inputs can exacerbate rates of marsh loss. As efforts

expand to protect these valuable ecosystems through development of financial incentives, such as carbon trading markets, it is important to quantify how N loading impacts GHG fluxes within wetlands and rates of N transformation. Most research to date in salt marsh systems has focused on impacts from short-term N additions on GHG fluxes.

The goal of this research was to examine the role of chronic N loading on GHG fluxes in *Spartina alterniflora*-dominated marshes and to assess quantities of N available for transformation through measurement of denitrification enzyme activity (DEA). To accomplish these goals, we first examined the role of chronic N loading on GHG fluxes using three salt marshes located along a historic N gradient (high, medium, low) within Narragansett Bay, RI. Narragansett Bay is an ideal location for this work since it has received chronic N loading, mainly from wastewater inputs, since the late 1800s. To asses impacts of N loading on GHG fluxes, $CO_2$, $CH_4$ and $N_2O$ were measured for one field season in 2016. Along with measured fluxes, plant properties, edaphic parameters, and nutrient availability were measured. Relationships of fluxes to these additional parameters were then explored. We then compared rates of DEA at the opposite ends (high, low) of the N gradient within Narragansett Bay in 2017, focusing on four marsh zones (creekbank, mudflat, low marsh, high marsh) at two sites to assess any differences in N availability and rates of N transformation. Additionally, GHG fluxes were measured at the high N site in 2017 to explore relationships with DEA rates.

As a result of this work, we found that the site receiving the highest N loading experienced the highest $CO_2$ uptake as well as the highest emissions of $CH_4$ and $N_2O$ compared to the other two sites along the N gradient. However, these emissions were

not on an order of magnitude to significantly offset $CO_2$ uptake. This was as expected, however, the other measured parameters (plant properties and edaphic variables) and DEA did not necessarily fall along expected trends of the N gradient. There were no significant differences in DEA among sites or zones, suggesting each site had similar amounts of N available for transformation and that soil in each zone had equal ability to transform N. At the marsh with the highest historic N loading, GHG fluxes fell along expected trends among zones with increased uptake of $CO_2$ within vegetated zones contrasting with $CO_2$ emission in non-vegetated zones. $CH_4$ fluxes were highest in the bare creekbank zone, but were similar among the three remaining zones. Surprisingly, no significant $N_2O$ fluxes were measured in any of the four zones, suggesting along with DEA results that most N inputs are completely reduced to $N_2$ via denitrification.

In an effort to strengthen research and policy aimed at protecting and restoring these valuable ecosystems, it is important to continue to explore the dynamics between N, DEA rates, and all three GHGs. Of particular importance is to measure GHG fluxes and DEA across longer temporal scales. Additionally, examining actual denitrification rates from these marshes and also discerning key factors that help maintain the capacity for N transformation even as marsh landscapes shift as a result of SLR are important future directions.

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## DEDICATION

*To Kathy Szura and Gladys Keenan, for being strong, independent role models who taught me to love all things wild, be a little wild, and to pursue my wildest dreams.*

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HOW DOES CHRONIC NITROGEN LOADING IMPACT GREENHOUSE GAS
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**Introduction**

Coastal wetlands (salt marshes, mangroves, and seagrass beds) have been gaining attention in recent years for their ability to play a significant role in climate change mitigation. While already well known for their beneficial abilities to buffer coastlines against storm events (Costanza et al., 2008), filter nutrients from runoff (Kennish, 2001), and provide wildlife habitat, they most recently have been gaining attention for their ability to sequester and store large amounts of carbon (Lu et al., 2017; McLeod et al., 2011). These systems sequester atmospheric carbon dioxide ($CO_2$) through photosynthesis and then store it as carbon, termed blue carbon, in leaves, roots, and sediments. The vast majority of carbon in wetlands is stored within the sediment and is able to be retained for millennia due to the anaerobic conditions in their wet soils (Duarte et al., 2005; McLeod et al., 2011). Anaerobic conditions reduce decomposition rates, enabling wetlands to store more carbon per unit area than any other ecosystem (Chmura et al., 2003; Murray et al., 2011). This ability to remove and store large amounts of $CO_2$, a greenhouse gas (GHG), from the atmosphere has led to increased interest for understanding and quantifying the role coastal wetlands play in climate change mitigation, especially in the face of global climate change.

Although coastal wetlands are extremely important ecosystems, they are currently being lost at rapid rates (McLeod et al., 2011; Pendleton et al., 2012). In the U.S. alone, 50 percent of original salt marsh habitat has been lost (Kennish, 2001). Direct and

indirect stressors from human impacts threaten coastal marshes on both regional and global scales. Predominant threats include increasing rates of sea level rise (SLR) caused by climate change, excess nutrient inputs from wastewater and agriculture (Deegan et al., 2012; Diaz and Rosenberg, 2008; Wigand et al., 2014), diminished sediment supplies from dam installations (Weston, 2014), and habitat conversion. Southern New England is a hotspot for SLR with rates roughly three to four times the global average (Sallenger et al., 2012; Watson et al., 2016a). Studies have found Rhode Island marshes are not maintaining elevation with SLR (Raposa et al., 2016), and as much as 17.3 percent marsh loss has occurred over the past four decades due to associated erosion (Raposa et al., 2015; Watson et al., 2016c). A recent analysis found of Rhode Island's 3,321 acres of salt marsh in Narragansett Bay, 13-87 percent may be lost under projections of three to five feet of future SLR (Narragansett Bay Estuary Program, 2017).

### *GHG Fluxes from Wetlands*

While $CO_2$ is often the GHG that gains the most attention for contributing to global warming due to its relative abundance, methane ($CH_4$) and nitrous oxide ($N_2O$) are additional potent GHGs that also significantly contribute to warming. Concentrations of all three GHGs have been rapidly increasing in the atmosphere as a result of human activities since the Industrial Revolution (IPCC Climate Change Report, 2014), resulting in myriad consequences that pose significant threats to natural and human-made systems. Although less abundant in the atmosphere, $CH_4$ and $N_2O$ are 45 and 270 times, respectively, more efficient at trapping heat in the atmosphere than $CO_2$

(Neubauer and Megonigal, 2015). All three of these GHGs are present within coastal wetlands and wetlands can act as both sinks and sources of GHGs. The production of all three GHGs is sporadic both temporally and spatially from salt marshes, fluctuating with seasons as temperature and plant dynamics shift (Dalal et al., 2003; Le Mer and Roger, 2001; Moseman-Valtierra et al., 2016). GHGs within wetlands are produced through biogeochemical processes involving plant and soil microbial respiration (Picek et al., 2007; Reddy and DeLaune, 2008). Processes that generate GHGs within marshes are continuously cycling, consuming or producing each gas, and whether a wetland is a sink or source at a given time depends on the overall net exchange (i.e., if more gas is being consumed or produced).

In coastal wetlands, $CO_2$ is sequestered from the atmosphere during photosynthesis and emitted through respiration. Generally, salt marshes are reported to act as net sinks of $CO_2$, with the rate of sequestration dependent upon different plant community compositions, physiologies, and photosynthetic rates, which are influenced by time of day, tidal cycles, and season (Moseman-Valtierra et al., 2016). Coastal wetlands are negligible sources of $CH_4$ (Poffenbarger et al., 2011), despite freshwater wetlands overall being a significant source. Freshwater wetlands are responsible for one third of global $CH_4$ emissions (Bridgham et al., 2013) since biogeochemical cycling in salt marshes inhibits methane production. A controlling factor on $CH_4$ production is the availability of sulfate. If more sulfate is available, methanogenic bacteria are outcompeted for energy sources by sulfate-reducing bacteria, thus limiting the production of $CH_4$ (Bodelier and Laanbroek, 2004; Poffenbarger et al., 2011). Salinity

is a proxy for the amount of sulfate available; thus, with higher salinities less $CH_4$ will be produced, and with lower salinities, more $CH_4$ will be produced.

Coastal wetlands are typically sinks of $N_2O$. $N_2O$ is consumed or produced in salt marshes through the soil microbial processes of nitrification and denitrification (Dalal et al., 2003; Liu and Greaver, 2009). Coastal wetlands have the potential to be N cycling hotspots and to act as a filtering buffer, preventing land derived N additions from reaching coastal waters (Bowen et al., 2009). Critical to the process are nitrification and denitrification that filter out excess N (ammonium and nitrate) by converting it into inert $N_2$. $N_2O$ is consumed during denitrification and may be produced as a byproduct during both nitrification and denitrification. The regulation of $N_2O$ production depends on temperature, oxygen and sulfide availability, as well as plant and microbial community composition (Alvarez-Rogel et al., 2016). Of particular importance on the regulation of $N_2O$ is nitrogen (N) availability (Liu and Greaver, 2009).

*Impacts of Nitrogen on Coastal Wetlands*

N additions from human activities can alter biogeochemical cycling within coastal wetlands, resulting in both positive and negative effects. Salt marshes are naturally N limited (Mendelssohn, 1979; Valiela and Teal, 1974), but human activities have been generating an ever-increasing supply of N through agricultural, industrial, and wastewater practices, altering the amount of reactive N entering into these systems. This is resulting in a problematic overabundance of the nutrient on a global scale (Diaz and Rosenberg, 2008; Galloway et al., 2003). When nutrient additions alter

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biogeochemical cycling in coastal wetlands, rates of $CO_2$ uptake can be altered. Initially N inputs can be beneficial, increasing above and belowground biomass (Fox et al., 2012). However, excess nutrients within coastal systems can lead to eutrophication (Diaz, 2001) as well as increased rates of respiration and decomposition (Wigand et al., 2009). Deegan et al. (2012) found high levels of experimentally added N additions on an ecosystem level led to increased levels of decomposition and significant marsh slumping and loss along creekbanks over the course of nine years. When marsh is eroded, the carbon that has been stored within the soils is released, switching the system from a net sink to source of $CO_2$, and simultaneously diminishing any future carbon burial within the system (Murray et al., 2011; Pendleton et al., 2012). N inputs also can switch marshes from being sinks to sources of $CH_4$ and $N_2O$ (Chmura et al., 2016; Irvine et al., 2012; Kearns et al., 2015; Moseman-Valtierra et al., 2011).

While coastal wetlands are N cycling hotspots, these systems cannot filter out unlimited quantities of N (Valiela and Cole, 2002). Rates of denitrification can naturally differ within the marsh landscape since varying soil and plant community compositions affect biogeochemical cycling (Moseman-Valtierra et al., 2016; Wigand et al., 2004). However, if denitrification conditions are not ideal, N can fail to undergo the full conversion to inert $N_2$, leading to the termination of denitrification at $N_2O$, resulting in increased emissions (Liu and Greaver, 2009; Moseman-Valtierra et al., 2015). Since N additions can alter marsh structure and function, rates of denitrification may be altered as marsh landscapes shift in response. Wigand et al. (2004) found that rates of potential denitrification enzyme activity (DEA) increased as N loading increased along the N gradient within Narragansett Bay. N additions can shift microbial communities within

salt marshes, decreasing densities of bacteria responsible for completing denitrification (Kearns et al., 2015). The filtering out of N by denitrification is critical to water quality. If this function is lost, water quality degrades, negatively impacting coastal communities.

Despite growing research on the impacts of N loading to coastal systems, there is a lack of information on how *chronic* nitrogen loading impacts GHG fluxes within salt marshes. Few studies have been conducted to examine the impact of N on all three GHGs (Liu and Greaver, 2009). The majority of the research has focused on impacts from experimentally applied, short-term N additions to marsh systems on smaller landscape scales (Liu and Greaver, 2009; Moseman-Valtierra et al., 2011). More research is needed to examine how chronic N loading from anthropogenic sources across broad landscape scales impacts GHG fluxes as even short-term N additions have been shown to result in significant $N_2O$ emissions (Moseman-Valtierra et al., 2011).

The goal of this research was to examine the role of chronic nitrogen loading on GHG fluxes in *Spartina alterniflora*-dominated New England salt marshes, and to test relationships of those fluxes to plant properties (height, biomass) and nutrient availability. We examined fluxes of $CO_2$, $CH_4$, and $N_2O$ from three marshes along an established N gradient in Narragansett Bay, RI. This work was conducted over the course of six months (June-November) in 2016. We hypothesized that the marsh experiencing higher N loading would have altered biogeochemical cycling and increased aboveground biomass productivity, resulting in increased uptake of $CO_2$, but higher emissions of $CH_4$ and $N_2O$ compared to the marshes experiencing lower N loads due to microbial respiration. Overall between the sites we expected biomass and

nutrients (ammonium) concentrations to be negatively related to $CO_2$ uptake and positively related to $CH_4$ and $N_2O$ emissions.

To provide context for fluxes observed during the 2016 field season, we also examined potential DEA rates by conducting DEA assays in the late-spring and mid-summer of 2017. The aim of this work was to use the DEA assays as a means of indirectly measuring N loading to the sites to support observed $N_2O$ fluxes. We additionally examined DEA within four different marsh zones. Since there is heterogeneity within marsh landscapes, examining multiple zones allowed for determining any differences within and among sites for potential denitrification and $N_2O$ fluxes. We hypothesized that higher N loading would result in higher rates of potential DEA and that each zone would experience different potential DEA rates as a result of varied biogeochemical cycling between zones. While not discussed in detail here, this research will contribute to a larger collaborative project called Bringing Wetlands to Market aimed at examining the feasibility of creating a carbon market to provide an economic incentive to protect and restore wetlands (Emmer et al., 2014). Understanding the dynamics between nitrogen, blue carbon, DEA rates, and all three GHGs will help strengthen efforts aimed at protecting and restoring these valuable coastal systems.

**Materials and Methods**

*Study Locations*

Narragansett Bay is one of the most densely populated estuaries in the USA. As a result, some areas of the bay have historically received high N loads since the late

1800s, mainly from wastewater originating from point sources. The largest point source within the bay has been wastewater treatment facilities (WWTFs) (Nixon and Pilson, 1983; Oczkowski et al., 2008). Beginning in 2005, policy decisions and upgrades to WWTFs in the area have lessened the overall amount of N entering into the bay and as of 2012 it has been reduced by 50% from previous levels (Krumholz, 2012). While the reduction of N loading into the bay has significantly reduced N loads within bay water, N loading at sites directly adjacent to wastewater inputs from septic systems or agricultural inputs likely has not changed.

We chose three field sites along an established and historical N gradient within Narragansett Bay, RI (Figure 1), representative of high (Mary's Creek, 4.5 ha), medium (Mary Donovan, 24.1 ha), and low (Nag Marsh, 28.8 ha) N loads with an overall 200-fold difference (Table 1) (Watson et al., 2016c; Wigand et al., 2003). The N loads entering into Mary's Creek are dominated by wastewater inputs from surrounding residential development while the majority of N inputs at Mary Donovan are agriculturally derived from surrounding farms. Nag Marsh, which is part of the Narragansett Bay Estuarine Research Reserve, lacks significant development adjacent to the field site and is located on an island within the middle of the bay, overall receiving limited anthropogenic N inputs (Wigand et al., 2003). Each site is predominantly composed of the common marsh grass, *Spartina alterniflora,* which is the most inundation tolerant species of marsh vegetation. At each of the sites, and the majority of marshes in New England, *S. alterniflora* has largely displaced high marsh vegetation as SLR has increased the extent and duration of inundation in the area (Smith, 2009; Watson et al., 2016b).

GHG Fluxes Along Nitrogen Gradient

*Experimental Design*

To examine the influence of chronic N loading on GHG fluxes, six plots were established in May 2016 equidistant from each other within the low marsh zone at each of the three field sites. Plots were established parallel to the dominant creek at each site. At Mary Donovan and Nag Marsh plots were spaced roughly 15 m apart, and at Mary's Creek plots were spaced roughly 5 m apart due to the smaller scale of the site (Table 1) (Watson et al., 2016c). An aluminum flashing collar (10 cm tall x 28 cm diameter) was installed in each plot, inserted to a depth of 6 cm. Each collar had six evenly spaced holes (3 cm tall x 0.5 cm diameter) directly below the sediment surface for drainage after rainfall or inundation. Collars were installed at least two weeks prior to any measurements and left in place for the duration of the experiment (June-November 2016). These collars provided a base for chambers used in repeated GHG flux measures from the plots throughout the study. Mary Donovan and Nag Marsh experienced plant stress after collar installation, evidenced by plant discoloration and wilting, thus new collars were installed within one meter of the original collars in July 2016.

Soil temperature, salinity, redox, pH, soil moisture, and photosynthetic active radiation (PAR) were also measured at each plot (Table 2). Soil temperature was measured using a temperature sensor (Hobo® U23-004, Onset, Bourne, MA) inserted to a depth of 10 cm, recording measurements every 10 s. A handheld refractometer was used to measure the salinity of water, squeezed and filtered from approximately the top 2 cm of surface soil. Soil redox was measured using an ORP probe (Mettler Toledo,

Greifensee, Switzerland). Soil pH was measured from a soil slurry (5 mL plug of soil mixed with 10 mL of distilled water) using an Orion$^{TM}$ Star A326 Multiparameter Meter (ThermoScientific) from July-September and an AG SG68 meter (Mettler Toledo, Greifensee, Switzerland) from September-November, due to a probe failure of the Orion. Soil moisture was measured in two haphazardly selected locations within each flux collar using an EC-5 soil sensor (Decagon Devices, Pullman, WA), inserted to a depth of 5 cm. PAR was measured twice, at the beginning and end of each flux measurement, using an Active Eye Quantum PAR Meter (Hydrofarm). A PVC well 2 meters in length was installed at each field site, placed in the middle of the plots, but roughly 2 m away from the transect of flux collars. A pressure sensor (Hobo® Model U20L-04, Onset, Bourne, MA) was hung inside each to measure fluctuations in depth to water table, recording pressure measurements every 15 minutes (Table 2).

*GHG Flux Measurements*

Greenhouse gas fluxes were measured *in situ* using two different real-time analyzers with closed, transparent chambers. $CO_2$ and $CH_4$ were measured with a cavity ring-down spectroscopy (CRDS) analyzer (Model G2508; Picarro Inc., Santa Clara, California, USA). $N_2O$ fluxes were measured using an off-axis integrated cavity output spectroscopy (OA-ICOS) analyzer (Model $N_2O/CO$, Los Gatos Research (LGR), Mountain View, California, USA). While the CRDS analyzer is capable of measuring all three GHGs, the OA-ICOS analyzer has a lower detection limit and is better able to detect small concentrations of $N_2O$ (Brannon et al., 2016).

Measurements were taken biweekly, or monthly, alternating between the two analyzers and sampling followed previously outlined methods (Martin and Moseman-Valtierra, 2015; Moseman-Valtierra et al., 2011). GHG fluxes were collected by sealing a transparent chamber (41 cm tall x 27 cm diameter) at the marsh surface with the vegetation left intact inside of the chamber. For collection, a polyethene foam ring was slid onto the previously installed collars, which the transparent chamber was then placed. The chamber was coupled to an analyzer via a vacuum pump (for the Picarro G2508) or an interior pump (for the LGR $N_2O$/CO) with nylon tubing (0.46 cm inner diameter and approximately 61 m in total length), creating a closed loop system. Two small battery operated fans within the chamber aided in homogenizing the air being sampled. Equilibrium with outside atmospheric pressure was maintained with a coiled stainless steel tube (inner diameter of 0.8 mm). Measurements were conducted for 8-10 minutes each. A temperature logger (Hobo® UA-002-08, Onset, Bourne, MA) was suspended within the chamber, recording air temperature measurements every 10 s. Over the course of the study, Nag Marsh was sampled less frequently due to logistical constraints. As a result of the previously described plant stress some flux measurements were omitted. Additionally, two flux measurement dates from Mary's Creek were omitted in two months where it was sampled twice with the Picarro G2508 to allow for more equal comparisons of one flux measurement day per month for all three sites. This was done as those two dates fell at different times of the month than the dates for the other two sites. Due to poor weather hampering flux measurements, Mary's Creek measured on August 3rd, 2016 was counted as a July measurement day.

*Plant and Environmental Properties*

Plant heights (10 random stems) and stem density were measured within each collar monthly. Above and belowground plant biomass samples were collected at the beginning of September 2016. To determine aboveground biomass at each site, a 25 cm x 25 cm quadrat was placed within one meter of each replicate flux measurement plot. All aboveground biomass within the plot was clipped at the shoot base, stored in a plastic bag on ice, and refrigerated until processing (within five days). The biomass was rinsed in a two mm sieve, dried at 70 °C for 48 hours, and then weighed. To determine belowground biomass, soil cores were taken from within the clipped quadrat plot with a peat corer (50 cm tall x 5 cm diameter). These cores were cut in half. One half was used for belowground biomass and the other for bulk density analysis. As we were only interested in the active root zone (Valiela et al., 1976) for belowground biomass due to its potential impact on gas transport (Picek et al., 2007), this half for biomass was sectioned to a 20 cm depth. The half for bulk density was sectioned to 4 cm, as this is the depth most likely influencing fluxes since microbial activity and diffusion of gases decrease with depth (Ball et al., 1997; Smith et al., 2003). The portion for belowground biomass was rinsed over a 2 mm sieve, separating out macro organic matter from soil. Macro organic matter was then separated out into roots and rhizomes with rhizomes distinguished as greater than 2 mm in diameter. Any macro organic biomass was saved, placed in paper bags, dried for 48 hours at 60 °C, and weighed. To calculate bulk density the soil samples were dried at 60 °C for 48 hours, weighed, and then the weight was divided by the known soil volume.

Porewater samples for nutrient analysis were taken outside of each gas flux measurement plot, within 25 cm, and to a depth of 10 cm during flux sampling events in June and September. Rhizon samplers (Soil Moisture Co., Goleta, CA) connected to 60 mL nylon syringes were used to collect 10 mL of porewater. Each sample was filtered, placed into a plastic vial, and frozen at -20 °C until analysis. Each sample was run for ammonium ($NH_4^+$) on an Orion™ Aquamate 7000 spectrometer following Solorzano (1969).

DEA Across Marsh Zones

*Experimental Design*

The difference in potential DEA for Mary's Creek and Nag Marsh was examined in 2017. Small soil cores (5.1 cm diameter x 10 cm depth) for DEA analysis were collected at each site to capture the opposite ends of the N gradient. In each marsh, cores were collected from the following four zones: bare creekbank, die-back area converted to mudflat, low marsh (*S. alterniflora*-dominant), and high marsh (*Spartina patens*-dominant). Each zone had four replicate plots, spaced one meter apart. Samples from the four zones at the two sites were collected at low tide in late spring and mid-summer.

To compare GHG fluxes across the marsh landscape, measurements were taken approximately monthly (June-September) 2017 at Mary's Creek in each of the four zones where DEA rates were studied. Four collars were installed at least two weeks prior to GHG flux measurements, spaced one meter apart within homogenous sections of these zones and oriented parallel to the shoreline. These measurements were taken with the Picarro G2508 as described above. Flux sampling was conducted in the low

marsh and creekbank zones monthly, while the mudflat and high marsh zones were sampled twice over the course of the study. The total number of fluxes taken per zone were as follows; creekbank: 13, mudflat: 8, low marsh: 15, high marsh: 8. Due to logistical constraints with the analyzer exceeding maximum operating temperature in September, only one flux from the creekbank zone was able to be measured. Additionally, only three fluxes were able to be collected from the low marsh zone in August due to retreating daylight.

*Denitrification Enzyme Activity (DEA)*

All cores were processed within three days of collection and refrigerated until processing. DEA was measured using short-term anaerobic assays following previously described methods (Gardner, 2008; Groffman and Tiedje, 1989; Smith and Tiedje, 1979). The top 3 cm of each core was used for DEA analysis, split into two sections from which a homogenized 6 g soil sample was taken from each half, generating two replicates per core. Each soil sample was placed into a clear, glass 125 mL flask. Ideal conditions for DEA were then created for each soil sample following the procedure detailed in Wigand et al. (2004), adding 1.4 mg $KNO_3$, 1 mg glucose, and 0.25 mg chloramphenicol per g of sediment wet weight. These were then combined with ultrapure water, generating a solution in which 12 mL was added to each 6 g of sediment. Flasks were then flushed with ultrapure helium (Airgas, Radnor, Pennsylvania) for two minutes to begin the nonlimiting conditions for DEA. The soil slurries were then allowed to incubate under anaerobic conditions with gas samples

collected at 0 and 90 minutes. Gas samples were analyzed for $N_2O$ by electron gas chromatography, using a Shimadzu 2014 Greenhouse Gas Analyzer.

*GHG Flux Comparisons Across Zones*

To complement the DEA assays, GHG flux measurements were taken approximately monthly using the Picarro G2508 for four months in the summer of 2017. All fluxes were taken at Mary's Creek as this is the site where we expected the highest DEA rates. Sampling was conducted in the low marsh and creekbank zones monthly, while the mudflat and high marsh zones were sampled twice over the course of the study.

*Statistical Analysis*

GHG fluxes were calculated for each measurement period based on the chamber volume and linear changes in gas concentration over time using the Ideal Gas Law (PV=nRT). All fluxes were calculated using R (R Core Team, 2016). Only fluxes that were above detection limits (Brannon et al., 2016) and statistically significant were used. Minimum detectable fluxes were calculated for each gas using minimum detectable slopes from Brannon et al. (2016) and average chamber temperatures recorded during flux measurements. The minimum detectable flux for $N_2O$ measured with the LGR was $0.02 \, \mu mol \, m^{-2} \, h^{-1}$. For the Picarro, the following minimum detectable fluxes applied: $CO_2$: $0.85 \, \mu mol \, m^{-2} \, s^{-1}$, $CH_4$: $0.53 \, \mu mol \, m^{-2} \, h^{-1}$, and $N_2O$: $2.7 \, \mu mol \, m^{-2}$ $h^{-1}$. A flux was determined to be statistically significant for $CO_2$ and $CH_4$ if the $R^2$ was greater or equal to 0.9 and the p-value less than or equal to 0.05. $N_2O$ fluxes were

determined to be statistically significant if the $R^2$ was greater than or equal to 0.7 (due to wide variability in $N_2O$) and the p-value less than or equal to 0.05.

Linear mixed effects analyses were used to test for differences in GHGs as well as plant properties (height, density) and edaphic parameters (redox, salinity) among the sites in 2016. This analysis was also used to examine the relationship of zones with $CO_2$ and $CH_4$ fluxes for the 2017 field season. To determine significant relationships between sites and response variables such as GHG fluxes, plant properties, and edaphic parameters, models were generated with and without a fixed effect of interest. Sites or zones were fixed effects within the model, while months were a random effect. Likelihood ratio tests were then performed on the full model with both effects present and a model with the fixed effects removed, generating a p-value to test for significant interactions. Tukey's Honestly Significant Difference (HSD) post-hoc tests were run to examine differences among sites for 2016 and zones for 2017 (Martin and Moseman-Valtierra, 2017).

One-factor ANOVAs were used to compare above and belowground plant biomass, as well as soil bulk density among sites. A two-factor ANOVA was used to examine the relationship of site and month on porewater ammonium concentrations. A Pearson's Correlation Analysis was used to test for a relationship between $CO_2$ and plant height, and Spearman's Correlation Analyses were performed to examine the relationship between GHGs to plant properties and site parameters. DEA sample replicates were averaged per core and then examined using a three-factor ANOVA and a Tukey's HSD post-hoc test to explore differences among sites, seasons, and zones. Significance was assigned at $\alpha=0.05$ for all statistical tests. Linear mixed effects

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analyses were performed in R, using the *lme*4 package (R Core Team, 2016). All other statistical analyses were run in JMP 13.0 (JMP 13.0).

**Results**

GHG Fluxes Along Nitrogen Gradient

*GHG Flux Measurements*

$CO_2$ uptake was significantly greater at Mary's Creek than Nag Marsh, but not Mary Donovan ($X^2_2$=6.83, p=0.03; Table 3). Mean $CO_2$ fluxes ranged from -1.44 to -7.33 µmol $m^{-2}$ $s^{-1}$ with a mean of -4.63 µmol $m^{-2}$ $s^{-1}$ (Table 4; Figure 2a). The largest and lowest $CO_2$ fluxes (-9.53 µmol $m^{-2}$ $s^{-1}$ and -1.00 µmol $m^{-2}$ $s^{-1}$, respectively) were observed at Mary Donovan. In November, three $CO_2$ measurements at Mary's Creek and all of the $CO_2$ measurements at Mary Donovan were below the detection limit of the Picarro G2508 (0.85 µmol $m^{-2}$ $s^{-1}$).

Mary's Creek consistently had the highest $CH_4$ emissions across the three sites ($X^2_2$=22.12, p<0.0001; Tables 3, 4) with the highest emission (79.8 µmol $m^{-2}$ $h^{-1}$) occurring in July. Throughout the course of the study $CH_4$ had a wide range (0.61 to 79.8 µmol $m^{-2}$ $h^{-1}$), averaging 11.42 µmol $m^{-2}$ $h^{-1}$ (Figure 2b). There was a significant negative correlation between $CH_4$ and redox (Spearman's r= -0.34, p= 0.02), but no significant correlation was found between $CH_4$ emissions and salinity.

$N_2O$ fluxes differed among sites, with those from Mary's Creek higher than the other two sites by an order of magnitude ($X^2_2$=7.61, p=0.02; Tables 3, 4; Figure 2c). Overall average $N_2O$ fluxes from the three sites were minimal (-0.07 to 0.62 µmol $m^{-2}$ $h^{-1}$) (Figure 2c). The largest individual $N_2O$ flux (1.23 µmol $m^{-2}$ $h^{-1}$) observed was

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measured from Mary's Creek in July and the lowest individual $N_2O$ flux (-0.10 µmol $m^{-2} h^{-1}$; Mary Donovan in August) exhibited $N_2O$ uptake. Of the 60 fluxes taken for $N_2O$ over the course of the study, 46.7% were found to be significant. The remaining fluxes were either below the detection limit (0.02 µmol $m^{-2} h^{-1}$) of the LGR $N_2O$/CO analyzer (21.7%) or were above the detection limit, but were not significant and thus labeled a zero flux (31.7%). There was no significant correlation between redox and $N_2O$ (Spearman's r= -0.31, p=0.10).

*Plant and Environmental Properties*

Bulk density and salinity did not significantly differ among the sites (Tables 1, 2, 3). Redox significantly differed among the sites, with Mary Donovan having significantly higher average redox ($X^2_2$=78.71, p<0.0001; Table 3).

*S. alterniflora* stem height was significantly lower at Nag Marsh compared to the other two sites ($X^2_2$=7.81, p=0.02; Figure 3a). Stem density also significantly differed between the sites ($X^2_2$=39.26, p<0.0001), with Mary Donovan having significantly lower average density than the other two sites (Figure 3b). All correlation analyses between stem height and stem density for each of the three GHGs were not significant (p>0.05 for all). The only exception was a significant negative correlation between stem density and $CO_2$ (Spearman's $R^2$= -0.44, p<0.01). This correlation was found to be negative since all $CO_2$ fluxes were negative. Aboveground biomass was significantly higher at Mary's Creek than at Mary Donovan ($F_{2,15}$=4.64, p=0.03; Figure 4).

Belowground biomass did not significantly differ among sites, although there was a trend of lowest average biomass at Mary Donovan ($F_{2,15}$=3.59, p=0.05). Roots

and rhizomes also did not significantly differ among sites (Table 5), but there was a trend towards Mary Donovan having the lowest average root density, differing from Nag Marsh with the highest average root density ($F_{2,15}$=3.45, p=0.06).

Nag Marsh had significantly higher average ammonium concentrations than the other marshes ($F_{2,30}$=10.57, p<0.01) (Figure 5). Ammonium porewater concentrations were higher in September than June ($F_{1,30}$=5.19, p=0.03).

<u>DEA Across Marsh Zones</u>

*Denitrification Enzyme Activity (DEA)*

Rates of potential DEA were not found to be significantly different among sites, zones, or dates, but there were significant interactions among these factors. There were significant interactions among site x month x zone ($F_{3,48}$=5.98, p<0.01) as well as month x zone ($F_{3,48}$=4.02, p=0.01) and site x zone ($F_{3,48}$=5.46, p<0.01). The highest average rate of potential DEA (584.1 ng N $g^{-1}$ $h^{-1}$) was measured for the low marsh zone in June at Mary's Creek (Table 6), followed closely by the mudflat zone at Nag Marsh (423.1 ng N $g^{-1}$ $h^{-1}$; Table 6, Figure 6).

*GHG Flux Comparisons Across Zones*

At Mary's Creek, $CO_2$ was significantly different among zones ($X^2_2$=32.02, p<0.0001), with the low marsh and mudflat zones exhibiting $CO_2$ uptake while the creekbank zone exhibited on average emissions (Tables 3, 7). Only three of the zones (mudflat, creekbank, low marsh) had significant fluxes throughout the study and thus

were the only zones included in the analysis (high marsh excluded). While the mudflat zone was included, it only had significant fluxes on one of the two dates measured.

The creekbank had significantly higher $CH_4$ emissions than the low marsh zone, but not the high marsh and mudflat zones ($X^2_2=9.05$, p=0.03; Table 7). $CH_4$ emissions were similar among the remaining three zones. There were no significant $N_2O$ fluxes (out of 48 total fluxes measured) to report for the 2017 field season from any of the four zones.

**Discussion**

Our findings support the hypothesis that high N loading would result in increased uptake of $CO_2$ as well as increased emissions of $CH_4$ and $N_2O$. This pattern was observed for the marsh receiving the highest historical N load, Mary's Creek, relative to the other two sites with lower historical rates of N loading. However, several key parameters (plant biomass, porewater $NH_4^+$) did not fall along the expected trends of the N gradient, suggesting that N loading is likely not the only influencing factor driving GHG and DEA differences among these three sites.

*$CO_2$ Fluxes Among Marshes*

Overall the magnitude of the $CO_2$ uptake across sites was relatively large with Mary's Creek having the highest uptake among the three sites (Figure 2a). This site also had the greatest aboveground plant biomass among the sites (Table 5, Figure 4). In comparison to low marsh fluxes in a reference *S. alterniflora* marsh in New England studied with the same methods by Moseman-Valtierra et al. (2016) our $CO_2$ uptake was slightly lower at an average of -4.63 µmol m$^{-2}$ s$^{-1}$ compared to their average of -5.5 µmol

m$^{-2}$ s$^{-1}$. Above and belowground plant biomass production are critical influences on GHG fluxes and subsequent carbon sequestration in coastal wetlands (Duarte et al., 2005; Pendleton et al., 2012; Moseman-Valtierra et al., 2016). Moseman-Valtierra et al. (2016) found via factor analysis and multivariate modeling that belowground biomass had the strongest correlation to $CO_2$ fluxes in a similar temperate reference marsh (with little N loading or human impact) in New England (Sage Lot Pond) in Massachusetts. In our study, stronger relationships of $CO_2$ uptake to aboveground biomass may be due to similarities in belowground biomass among sites at the depths that we sampled (Table 5). Further, a relationship between $CO_2$ uptake and belowground biomass may have been obscured since the site with the lowest belowground biomass (Mary Donovan) often had pooling on the marsh surface even at direct low tide. The largest $CO_2$ uptake over the course of the study occurred at this site when there was an inch of water on the marsh (Katelyn Szura, personal observation), which likely capped off any soil respiration, allowing for direct measurement of $CO_2$ uptake through photosynthesis (because plants extended above the water in the chamber). The low marsh zone in the reference marsh for Moseman-Valtierra et al. (2016) had a greater average aboveground biomass of 635 g m$^{-2}$ (compare with Table 5), despite having significantly lower N inputs to the site than Narragansett Bay (McClelland and Valiela, 1998). Overall, these rates of low marsh $CO_2$ uptake are larger than fluxes reported for other native marsh zones (Martin and Moseman-Valtierra, 2015; Moseman-Valtierra et al., 2016).

Rates of $CO_2$ uptake can be altered by N additions since N can alter biomass production, generating both positive and negative impacts (Morris et al., 2013). Some studies have found N increased plant height and overall biomass (Fox et al., 2012).

However, excessive N can also lead to lowered stem density (Valiela, 2015) and increased decomposition rates, resulting in reduced belowground biomass (Langley et al., 2009; Wigand et al., 2014). Deegan et al. (2012) found marked differences in biomass production with N additions, resulting in increased stem height, but decreased belowground biomass. In that study excess fertilization with nitrate added for a decade resulted in visible marsh deterioration with creekbank slumping, leading to marsh loss. In our study, several of the plant parameters (above and belowground biomass, stem density) at Mary's Creek and Nag Marsh were surprisingly similar despite being at opposite ends of the historic N gradient, while those at Mary Donovan were significantly lower (Tables 3, 5, Figures 3, 4). It is especially interesting we did not find greater differences among our sites when visually the sites overall look vastly different in areas, with Mary's Creek having visible slumping and erosion of the back portion of the marsh. The marsh has been documented as losing roughly 20% of its areal extent in the past 40 years (Watson et al., 2016c). In comparison, Mary Donovan and Nag Marsh have been documented as losing 15% and 2% areal extent (Watson et al., 2016c), respectively, but do not exhibit the same large areas of unstable platform. Although these losses have been attributed to increased rates of SLR, the obvious erosion at Mary's Creek may be a combination of increased N and inundation. Measuring fluxes or biomass even a short distance from where the platform is stable at Mary's Creek likely would have resulted in substantial differences with increased respiration and decreased biomass.

Flux measurements in 2017 were aimed at examining differences in $CO_2$ fluxes among zones at Mary's Creek. Among the three remaining zones with significant fluxes (creekbank, mudflat, low marsh), there were obvious and expected differences with the

relatively bare creekbanks consistently exhibiting emissions while the vegetated low marsh zone exhibited $CO_2$ uptake. Overall, creekbank emissions were two to three times greater than similarly bare ponded area emissions measured in Moseman-Valtierra et al. (2016).

*$CH_4$ Fluxes Among Marshes*

As expected for our study, $CH_4$ emissions were highest at Mary's Creek. However, given that salinities did not significantly differ among sites and a linear regression showed only a trend between $CH_4$ and salinity, it is likely the higher N load was driving the higher emissions at Mary's Creek. N additions can increase $CH_4$ emissions (Bodelier and Laanbroek, 2004; Irvine et al., 2012) through the production of organic matter (Liu and Greaver, 2009), which is a necessary component of methanogenesis (Le Mer and Roger, 2001). Together, organic matter, sulfate availability, and anaerobic conditions are the greatest controlling factors of $CH_4$ production in wetlands (Poffenbarger et al., 2011). Here, a negative correlation was found with redox and $CH_4$, with lower redox values corresponding to higher $CH_4$ fluxes. This finding is not surprising given that methanogenesis requires anaerobic conditions (Le Mer and Roger, 2001; Poffenbarger et al., 2011). However, since Mary's Creek and Nag Marsh had similar redox values (Table 2) it is likely the higher N influenced the higher emissions at Mary's Creek. In comparison to Moseman-Valtierra et al. (2016) our $CH_4$ fluxes were an order of magnitude greater than the values they measured for the low marsh zone.

For GHG flux measures in 2017, the creekbank had the highest $CH_4$ emissions of all four zones, while the lowest emissions were from the high marsh zone. This is likely due to more aerobic conditions in the high marsh zone, which can allow for the oxidation of methane and lower $CH_4$ emissions than more anaerobic zones (Le Mer and Roger, 2001; Poffenbarger et al., 2011).

*$N_2O$ Fluxes Among Marshes*

We found a trend that Mary's Creek had the highest mean $N_2O$ emissions, by an order of magnitude over the other two sites (Tables 3, 4). This finding agrees with other studies that have found N additions can switch salt marsh systems and other ecosystems from being sinks to sources of $N_2O$ (Chmura et al., 2016; Liu and Greaver, 2009; Moseman-Valtierra et al., 2011). However, our lowest N site, Nag Marsh, did not exhibit the lowest $N_2O$ emissions, and overall the magnitude of our $N_2O$ emissions were low in comparison to other studies (Murray et al., 2015). It is surprising that we observed relatively low $N_2O$ emissions from our sites within Narragansett Bay considering the estuary has received chronic N loading since the late 1800s (Nixon et al., 2008). Most studies documenting increased $N_2O$ emissions from experimentally fertilized plots have typically only added fertilizer for less than a decade. Moseman-Valtierra et al. (2011) found mean levels of $N_2O$ emissions from short-term, nitrate-fertilized plots to be 1.8 $\mu$mol m$^{-2}$ h$^{-1}$, even reporting a flux as large as 6.8 $\mu$mol m$^{-2}$ h$^{-1}$. In contrast, our mean $N_2O$ flux across the 2016 season was an order of magnitude lower at 0.18 $\mu$mol m$^{-2}$ h$^{-1}$, and the largest individual flux was 1.23 $\mu$mol m$^{-2}$ h$^{-1}$. Six year experimental additions of organic N by Chmura et al. (2016) yielded mean $N_2O$ fluxes of 0.30 $\mu$mol m$^{-2}$ h$^{-1}$ and

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0.08 µmol m$^{-2}$ h$^{-1}$ at macrotidal and microtidal marshes, respectively. The largest N$_2$O flux (1.23 µmol m$^{-2}$ h$^{-1}$) measured was during July, which corresponds to the highest mean soil temperature (Table 2). It was the only day of measurements where all six fluxes measured were significant, averaging 0.62 µmol m$^{-2}$ h$^{-1}$. It is likely that these higher fluxes were due to increased microbial activity, which is positively correlated with temperature (Reddy and DeLaune, 2008).

Zonation is an important factor to consider when examining N$_2$O fluxes. In our study, our measurements were concentrated in the *S. alterniflora*-dominated low marsh zone. For the 2017 field season we then expanded to other marsh zones and tested for differences in N$_2$O fluxes among them. However, there were no significant fluxes measured within any of the zones (creekbank, mudflat, low marsh, high marsh) as they were all below the detection limit (2.7 µmol m$^{-2}$ h$^{-1}$) of the Picarro G2508 (Table 7). Both studies mentioned above (Chmura et al., 2016; Moseman-Valtierra et al., 2011) were conducted in *Spartina patens*-dominated marshes. Low marsh zones are flushed more regularly with daily tides and are more anaerobic than high marsh zones, thus perhaps more likely to retain less N than upland marsh portions (Childers et al., 2000; Wigand et al., 2004) as it either exports out after inundation or is transformed into inert N$_2$ gas through complete denitrification (Hamersley and Howes, 2003). The relatively small N$_2$O fluxes in 2016 and lack of significant N$_2$O fluxes during the 2017 season, may be due to both export and complete denitrification. This is further supported by findings of similar rates of DEA among zones in 2017 discussed below.

*Ammonium (NH$_4^+$) concentrations*

We found surprisingly overall high $NH_4^+$ concentrations, particularly within Nag Marsh with a collective mean that surpassed Mary's Creek by an order of magnitude (139.7 µM and 85.2 µM, respectively; Figure 5). Although higher levels of $NH_4^+$ can be linked to fertilization (Valiela et al., 1978), these high levels may be indicative of other stressors. RI marshes have been documented as not keeping pace with SLR in the region (Raposa et al., 2016) and as a result they are experiencing vegetation shifts from *S. patens* to the more inundation tolerant *S. alterniflora* as well as increased erosion (Raposa et al., 2015; Watson et al., 2016a,b). It is possible these $NH_4^+$ levels reflect increased decomposition of organic matter as a result of decomposing peat due to increased inundation. While Nag Marsh has the highest median elevation of the three sites (Table 1), and thus may experience less inundation in comparison, these $NH_4^+$ values may still be linked to decomposition since rates of SLR in the area are three to four times the global average (Sallenger et al., 2012) and Nag Marsh as well as Mary's Creek have been documented as experiencing significant erosion within the past 40 years (Watson et al., 2016c). Although $NH_4^+$ was found to be similar between these two sites, nitrate may not follow the same pattern and could further help constrain overall N loading.

*Denitrification enzyme activity (DEA)*

Wigand et al. (2004) found rates of DEA increased with watershed N loading in Narragansett Bay salt marsh soils; this continues to be true, even after the decrease in N loading into the bay from WWTFs upgrades (Fulweiler and Heiss, 2014). However, rates of DEA may shift as time goes on, as evidenced by Fulweiler and Heiss's (2014)

examintation of subsurface sediments in Narragansett Bay. Within our study, we did not observe significant differences in DEA between Mary's Creek and Nag Marsh (Table 6, Figure 6), which may suggest that they now both have equal amounts of N available for transformation if the N gradient is no longer as strong as it was historically. Considering that the N loads were calculated for the bay from surrounding land use in Wigand et al. (2003) it is possible N loading to the sites has shifted since then. A recent study has shown the recent upgrades to the WWTFs have decreased nutrient standing stocks by 60% within the bay (Oviatt et al., 2017). However, sites such as Mary's Creek which are directly adjacent to septic systems or those with direct agricultural run-off are not as likely to be impacted by the bay-wide reduction in N loading. N loading to soils can have a legacy effect, remaining in the system decades even after reductions have been made (Grimvall et al., 2000). Future work is needed to constrain the current N loading in salt marshes within the bay.

Similarity in DEA rates between the bare creekbank and mudflat zones as well as the vegetated zones of the marshes was surprising since denitrification has been linked to organic matter availability as a controlling factor and plants are a major source (Eyre et al., 2013). But given the organic rich soils in New England marshes, there may be ample substrates among even unvegetated zones to support heterotrophic denitrifies. It is also surprising to not have found differences in DEA rates between the high and low marsh zones, as previous studies have found significant, but variable, differences in DEA between these zones (Koop-Jakobsen and Giblin, 2009; Wigand et al., 2004). Koop-Jakobsen and Giblin (2009) found higher rates of DEA within the high marsh zone, while Wigand et al. (2004) found the opposite trend. While similarly high rates of

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DEA among the zones highlights the large potential ability for N transformation across the marsh landscape, areas that do not have vegetation, such as creekbanks and mudflats, are more susceptible to erosion. With less marsh area, there is less available habitat to fully transform N and this could potentially lead to increased emissions of $N_2O$ and decreased water quality as land-derived nutrients export out into coastal waters.

*Comparison of GHGs*

In order to equally assess and compare all three GHGs measured over both field seasons, we converted mean values of both and $CH_4$ and $N_2O$ emissions into $CO_2$ equivalents using their respective global warming potentials, 45 and 270, respectively (Neubauer and Megonigal, 2015). Comparing these values to the mean $CO_2$ uptake over the course of both growing seasons we found that only two percent of it was offset by $CH_4$ and $N_2O$ emissions and that this small offset was driven in larger part by $CH_4$ emissions.

*Conclusion*

Our study highlights the robust functional role of salt marshes in mitigating harmful GHGs and excess nutrients from anthropogenic sources. While we did observe increased $N_2O$ and $CH_4$ emissions at our high N site, they were not on an order of magnitude to significantly offset $CO_2$ uptake. Comparing all three GHGs by converting them into $CO_2$ equivalents revealed the amount of $CO_2$ uptake over the course of the study was only offset by two percent by $N_2O$ and $CH_4$ emissions. This work highlights the large capacity of *S. alterniflora*-dominated marshes to filter out excess N while

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releasing relatively small amounts of more potent GHGs. Additionally, similar rates of DEA among zones and across marshes at the opposite ends of the N gradient highlight the large capacity for these ecosystems to filter out excess N, despite differences in plant communities or chronic N loading and deterioration.

Since the problems of excess N entering into coastal ecosystems and increasing GHGs overall in the atmosphere will only increase in the upcoming years, it is important to quantify the beneficial services coastal marshes provide in order to foster incentives for protecting these valuable systems. This will be particularly important for Narragansett Bay since 13-87 percent of Rhode Island's 3,321 acres of salt marsh may be lost under projections of three to five feet of future SLR (Narragansett Bay Estuary Program, 2017). Of particular importance to expand upon this work would be to measure GHGs and DEA rates across longer temporal scales. Particularly for DEA, it would be helpful to examine actual denitrification rates among sites and to discern what key factors enable marshes to maintain their ability to transform N, even when faced with changing landscapes due to SLR. Understanding how N impacts GHGs is important for gaining a holistic view of climatic forcing from wetland ecosystems, which can be used to inform research and policy geared towards protecting and restoring these valuable systems. It is important to protect and restore coastal wetlands in order to retain the many beneficial services they provide.

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**Table 1. Background site information. Nitrogen loading values are estimated from Wigand et al., 2003. Marsh area and median elevation were calculated in Watson et al., 2016a. Bulk density (± SE) of top 4 cm was determined for the 2016 field experiment.**

| Site | Nitrogen Load | Marsh Area | Median Elevation | Bulk Density |
|------|---------------|------------|------------------|--------------|
| | $(g\ N\ m^{-2}\ yr^{-1})$ | (ha) | (m NAVD88) | $(g\ mL^{-1})$ |
| Mary's Creek | 200 | 4.5 | 0.54 | 0.15 ± 0.02 |
| Mary Donovan | 40 | 24.1 | 0.33 | 0.21 ± 0.02 |
| Nag Marsh | <1 | 28.8 | 0.64 | 0.17 ± 0.01 |

Table 2. Mean values (± SE) per season for physical and edaphic parameters measured concurrently with each flux measurement.

| Season* | Site | Soil Temperature (°C) | Salinity (ppt) | Redox (mV) | pH | Soil Moisture (%VWC) | Photosynthetic Active Radiation ($\mu$mol m$^{-2}$ s$^{-1}$) | Depth to Water Table (cm)† |
|---|---|---|---|---|---|---|---|---|
| Mid-Summer | Mary's Creek | 26.0 ± 0.8 | 34 ± 2 | -191 ± 10 | 6.82 ± 0.08 | 63.5 ± 0.9 | 1125 ± 78 | 3.2 ‡ |
| | Mary Donovan | 24.7 ± 0.5 | 34 ± 1 | -69 ± 11 | 6.76 ± 0.09 | 69.4 ± 0.7 | 1524 ± 162 | 8.5 |
| | Nag Marsh | 25.0 ± 0.5 | 36 ± 1 | -151 ± 10 | 7.25 ± 0.13 | 60.0 ± 1.5 | 1046 ± 75 | 4.9 |
| Late-Summer | Mary's Creek | 22.5 ± 0.7 | 36 ± 1 | -164 ± 7 | 6.02 ± 0.18 | 62.6 ± 0.6 | 834 ± 61 | 5.9 |
| | Mary Donovan | 22.5 ± 1.1 | 39 ± 1 | -26 ± 9 | 6.24 ± 0.18 | 64.3 ± 0.5 | 1023 ± 32 | 7.8 |
| | Nag Marsh | 18.5 ± 1.3 | 38 ± 1 | -180 ± 5 | 6.77 ± 0.06 | 63.6 ± 0.6 | 1168 ± 27 | 5.9 |
| Fall** | Mary's Creek | 10.6 ± 0.5 | 32 ± 1 | -130 ± 15 | 5.67 ± 0.14 | 64.8 ± 0.4 | 909 ± 32 | 9.2 |
| | Mary Donovan | 11.6 ± 0.6 | 28 ± 4 | -94 ± 18 | 6.72 ± 0.05 | 67.1 ± 0.3 | 856 ± 29 | 5.3 |

*Mid-summer includes four flux measurement days in late July, late-summer includes eight flux measurement days in August and September, and fall includes four measurement days in October and November.

**Flux measurements were not taken in the fall for Nag Marsh due to logistical constraints, thus no parameters were measured.

† Depth to water table was measured every 15 minutes at each site. Values represent an average value over time period.

‡ Standard error for depth to water table is zero for each average measurement presented.

**Table 3. Results of linear mixed effects models and post-hoc comparisons between field sites.**

| Parameter | Results of Linear Mixed Effects Models | Results of Tukey's HSD post-hoc test |
|:---:|:---:|:---:|
| **Field Experiment 2016** | | |
| $CO_2$ | $X^2_2$=6.83, p=0.03* | MCa, MDab, NMb |
| $CH_4$ | $X^2_2$=22.12, p<0.0001* | MCa, MDb, NMb |
| $N_2O$ | $X^2_2$=7.61, p=0.02* | MCa, MDb, NMab |
| Plant Height | $X^2_2$=7.81, p=0.02* | MCa, MDa, NMb |
| Plant Density | $X^2_2$=39.26, p<0.0001* | MCa, MDb, NMa |
| Salinity | $X^2_2$=4.90, p=0.09 | MCa, MDa, NMa |
| Redox | $X^2_2$=67.44, p=<0.0001* | MCa, MDb, NMa |
| **Field Experiment 2017** | | |
| $CO_2$ | $X^2_2$=32.02, p<0.0001* | CBa, MFb, LMb |
| $CH_4$ | $X^2_2$=9.05, p=0.03* | CBa, MFab, LMb, HMab |

Site names are abbrevaited as follows: MC=Mary's Creek; MD=Mary Donovan, NM=Nag Marsh

Zones are abbreviated as follows: CB=creekbank, MF=mudflat, LM=low marsh, HM=high marsh

Lowercase letters denote significant differences between sites

*Significance determined at α=0.05

Table 4. Mean (±SE) of significant greenhouse gas flux measurements per month for each field site for the 2016 season.

| Site | Month | CO$_2$ μmol m$^{-2}$ s$^{-1}$ | | | CH$_4$ μmol m$^{-2}$ h$^{-1}$ | | | N$_2$O μmol m$^{-2}$ h$^{-1}$ | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Mean | SE | n | Mean | SE | n | Mean | SE | n |
| Mary's Creek | June | -3.88 | 0.52 | 5/6 | 21.07 | 2.75 | 5/6 | - | - | - |
| | July | -5.40 | 0.49 | 6/6 | 39.22 | 8.61 | 6/6 | 0.62 | 0.20 | 6/6 |
| | August | -6.13 | 0.70 | 5/6 | 14.68 | 2.14 | 6/6 | 0.14 | 0.07 | 4/6 |
| | September | - | - | - | - | - | - | 0.07 | 0.02 | 3/6 |
| | October | -5.47 | 0.41 | 6/6 | 3.64 | 0.96 | 6/6 | - | - | - |
| | November | -1.44 | 0.08 | 2/6 | 2.84 | 0.39 | 5/6 | - | - | 0/6 |
| Mary Donovan | June | -1.65 | 0.18 | 5/6 | 7.87 | 1.75 | 6/6 | - | - | - |
| | July | -7.33 | 0.95 | 6/6 | 10.22 | 2.22 | 6/6 | <0.00 | 0.04 | 4/6 |
| | August | -4.74 | 0.15 | 6/6 | 12.10 | 2.33 | 6/6 | 0.05 | 0.04 | 5/6 |
| | September | - | - | - | - | - | - | -0.07 | - | 1/6 |
| | October | -3.33 | 0.34 | 6/6 | 2.70 | 0.35 | 6/6 | - | - | - |
| | November | - | - | 0/6 | 0.65 | 0.02 | 3/6 | 0.04 | - | 1/6 |
| Nag Marsh | June | - | - | - | - | - | - | - | - | - |
| | July | -4.31 | 0.92 | 6/6 | 6.59 | 1.50 | 6/6 | 0.07 | - | 1/6 |
| | August | -4.93 | 0.46 | 2/6 | 7.94 | 1.42 | 2/6 | - | - | - |
| | September | - | - | - | - | - | - | 0.07 | 0.02 | 3/6 |
| | October | - | - | - | - | - | - | - | - | - |
| | November | - | - | - | - | - | - | - | - | - |

*n=number of significant fluxes presented out of total number of fluxes measured

**Table 5. Mean (±SE) above and belowground plant biomass for each site. Belowground biomass is reported to a 20 cm depth and further separated into roots and rhizomes.**

| Site | Aboveground Biomass | Belowground Biomass | Roots (%) |
|---|---|---|---|
| | gdw/m$^{-2}$ | | |
| Mary's Creek | 405.5 ± 19.1 | 15522.3 ± 2014.2 | 47.8 ± 2.2 |
| Mary Donovan | 323.5 ± 24.2 | 10602.9 ± 635.1 | 53.5 ± 4.8 |
| Nag Marsh | 380.8 ± 14.0 | 15558.8 ± 1528.9 | 56.5 ± 4.5 |

**Table 6. Mean potential denitrification enzyme activity rates (±SE) across four zones at two sites on opposite ends of the Narragansett Bay N gradient.**

| Site | Season | Average DEA per Marsh Zone (ng N g$^{-1}$ h$^{-1}$) | | | |
|---|---|---|---|---|---|
| | | Creekbank | Mudflat | Low Marsh | High Marsh |
| Mary's Creek | Late-spring | 56.10 ± 10.30 | 31.60 ± 11.02 | 323.75 ± 102.35 | 90.83 ± 32.60 |
| | Mid-summer | 165.16 ± 58.88 | 50.34 ± 17.17 | 50.06 ± 23.06 | 93.06 ± 38.95 |
| Nag Marsh | Late-spring | 79.43 ± 41.37 | 225.76 ± 98.52 | 11.75 ± 1.20 | 52.20 ± 25.53 |
| | Mid-summer | 132.66 ± 29.39 | 58.26 ± 13.02 | 60.67 ± 16.87 | 94.19 ± 18.20 |

**Table 7. Mean (±SE) of significant greenhouse gas flux measurements per zone and month for the 2017 field season.**

| Month | Zone | CO$_2$ µmol m$^{-2}$ s$^{-1}$ | | | CH$_4$ µmol m$^{-2}$ h$^{-1**}$ | | |
|---|---|---|---|---|---|---|---|
| | | Mean | SE | n* | Mean | SE | n |
| June | Creekbank | 3.84 | - | 1/4 | 21.99 | 2.43 | 4/4 |
| | Low Marsh | -4.65 | 0.97 | 4/4 | 7.16 | 0.78 | 4/4 |
| July | Creekbank | 0.21 | 0.82 | 3/4 | - | - | 0/4 |
| | Low Marsh | -4.40 | 0.66 | 4/4 | 6.90 | 0.59 | 4/4 |
| August | Creekbank | 3.08 | 0.76 | 4/4 | 3.61 | - | 1/4 |
| | Low Marsh | -2.09 | - | 1/3 | 9.02 | 0.97 | 2/3 |
| | High Marsh | - | - | 0/4 | 10.42 | 1.78 | 4/4 |
| | Mudflat | -0.91 | 0.07 | 2/4 | 6.35 | 2.11 | 4/4 |
| September | Creekbank† | 2.09 | - | 1/1 | 10.45 | - | 1/1 |
| | Low Marsh | -2.43 | 0.76 | 3/4 | 10.34 | 2.04 | 4/4 |
| | High Marsh | - | - | 0/4 | 7.91 | 1.18 | 4/4 |
| | Mudflat | - | - | 0/4 | 12.48 | 5.38 | 4/4 |

*n=number of significant fluxes presented out of total number of fluxes measured

**No significant N$_2$O fluxes were measured during the 2017 season

†Only one flux was able to be measured for this zone on this date due to equipment malfunction
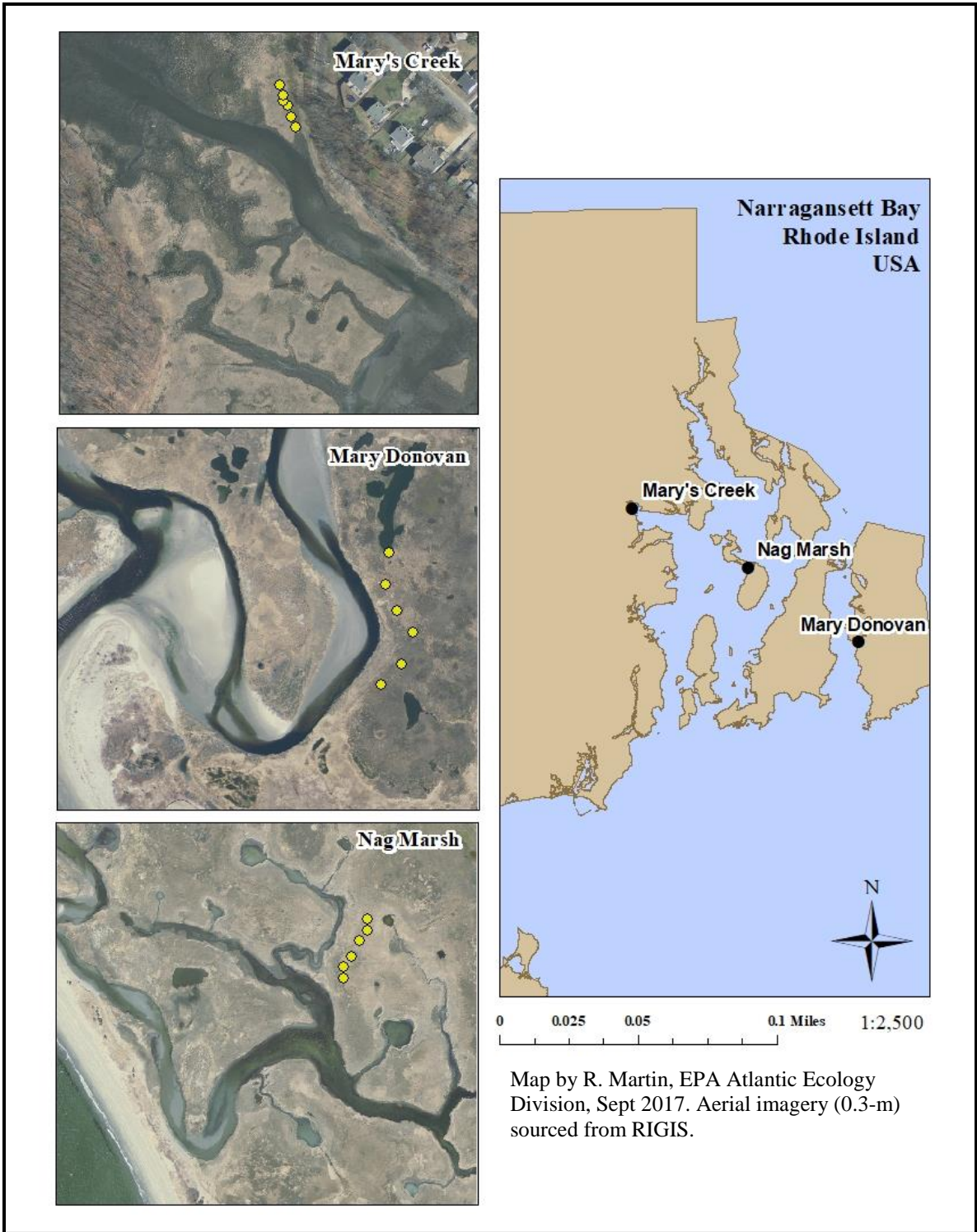
Figure 1. Map of Narragansett Bay, Rhode Island depicting the three study site locations. Marked at each site are the six replicate locations for greenhouse gas flux measurements.
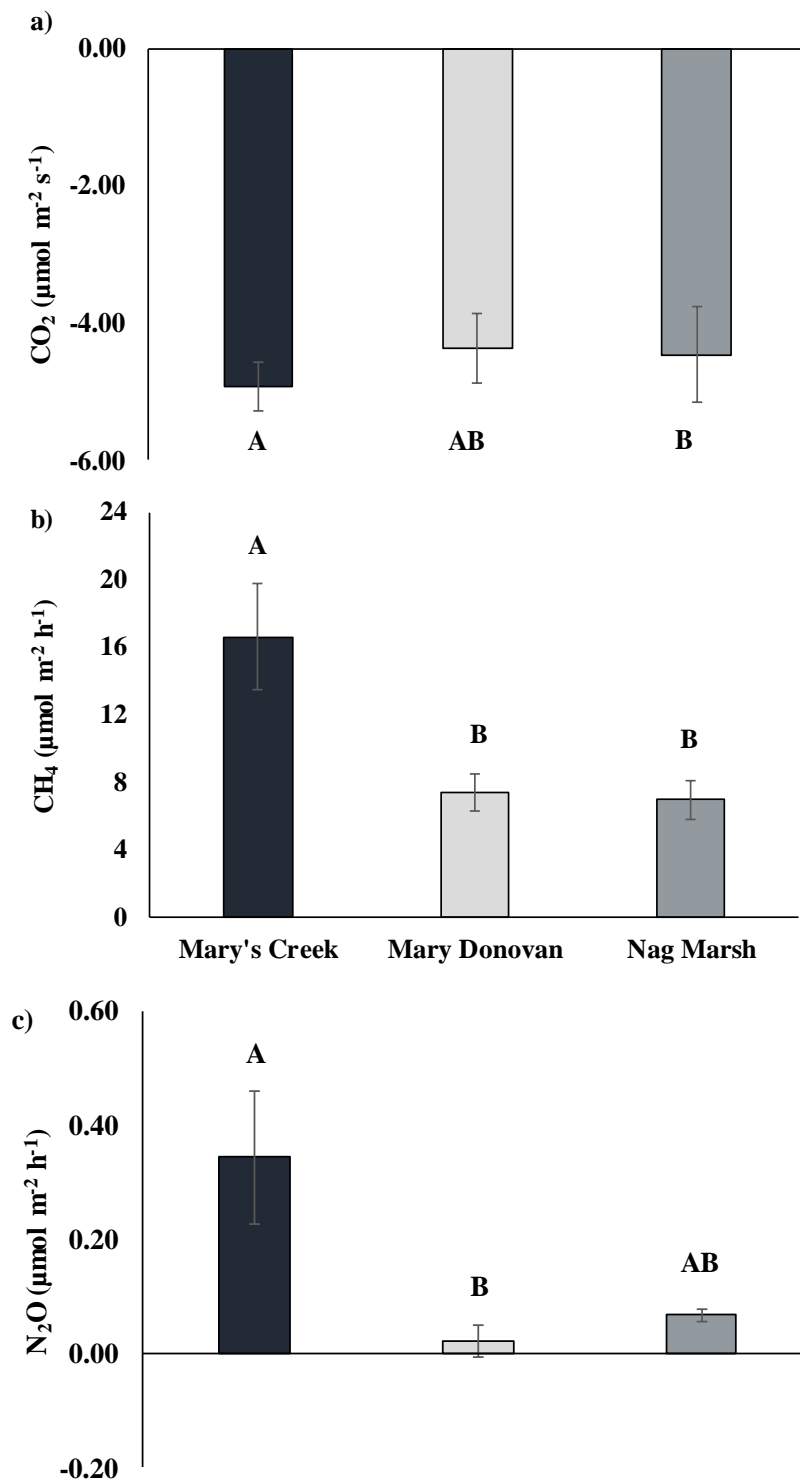
Figure 2. Significant mean (± SE) (a) $CO_2$, (b) $CH_4$, and (c) $N_2O$ greenhouse gas fluxes across the three field sites in 2016. Letters denote significant differences between sites.
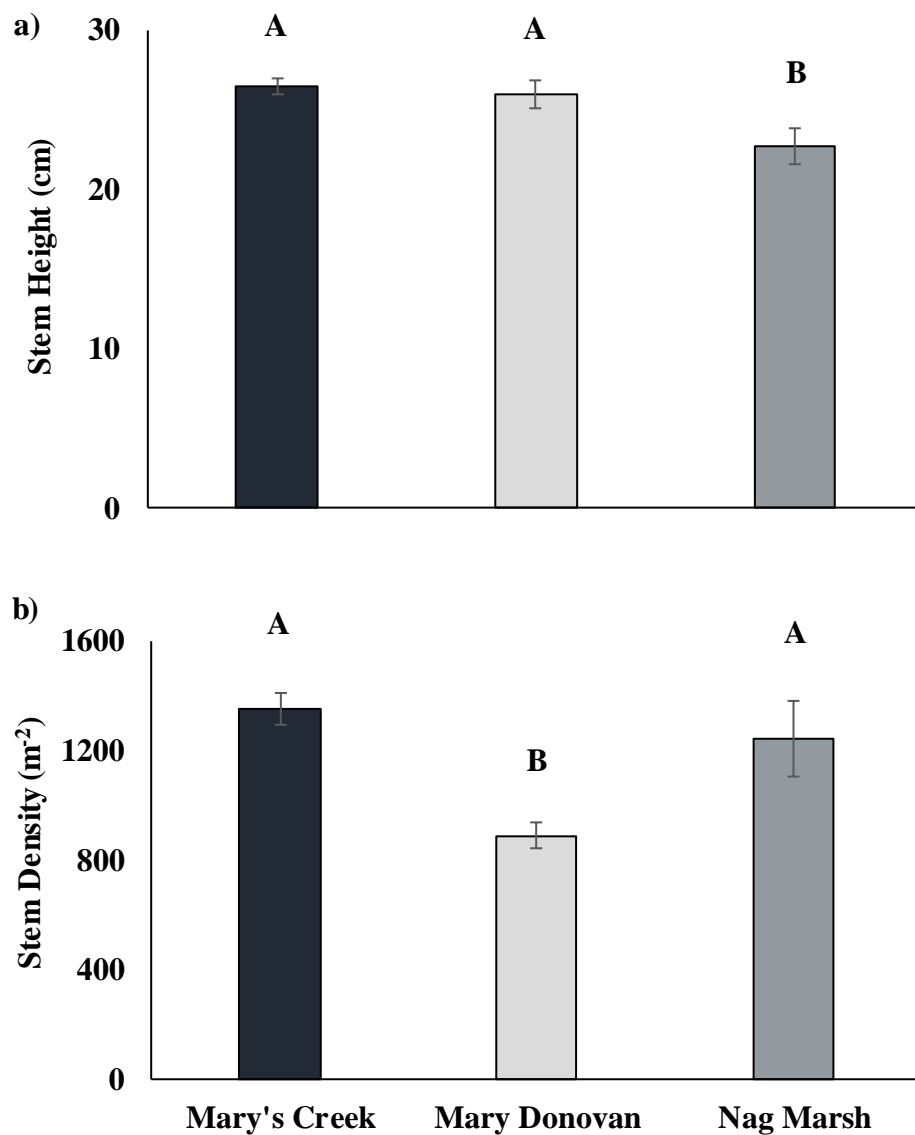
Figure 3. Plant properties (±SE) for the 2016 field season. (a) Mean stem height and (b) stem density within each flux collar measured each month. Letters denote significant differences between sites.
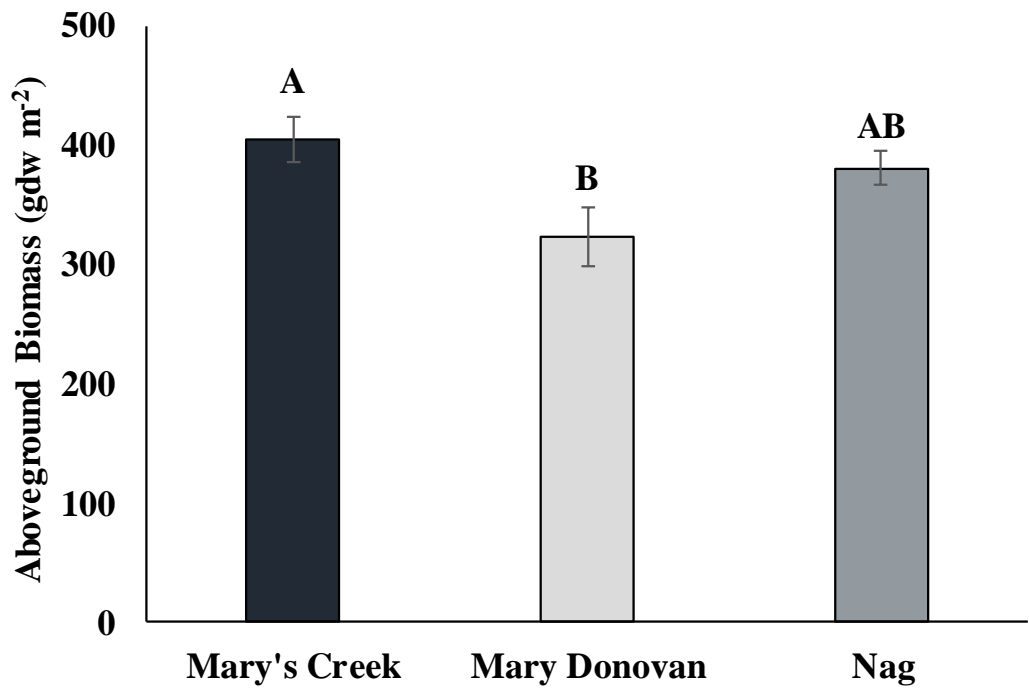
Figure 4. Comparison of mean aboveground plant biomass per site. Standard error bars are shown. Letters denote significant differences between sites.
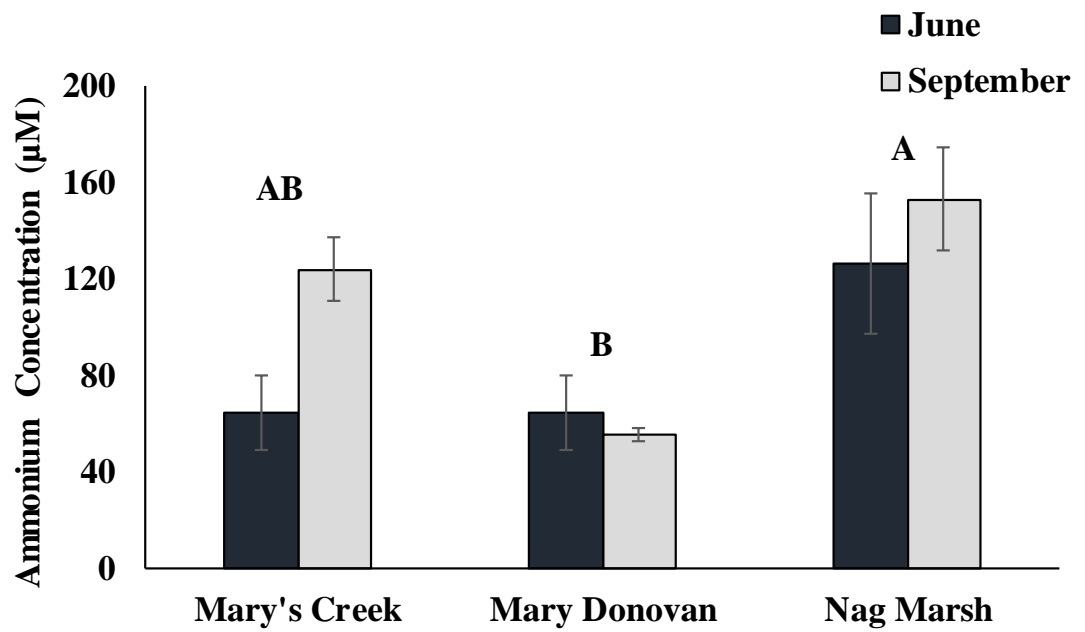
Figure 5. Mean ammonium concentrations (± SE) in soil porewater. Letters centered above bar denote significant differences between sites.
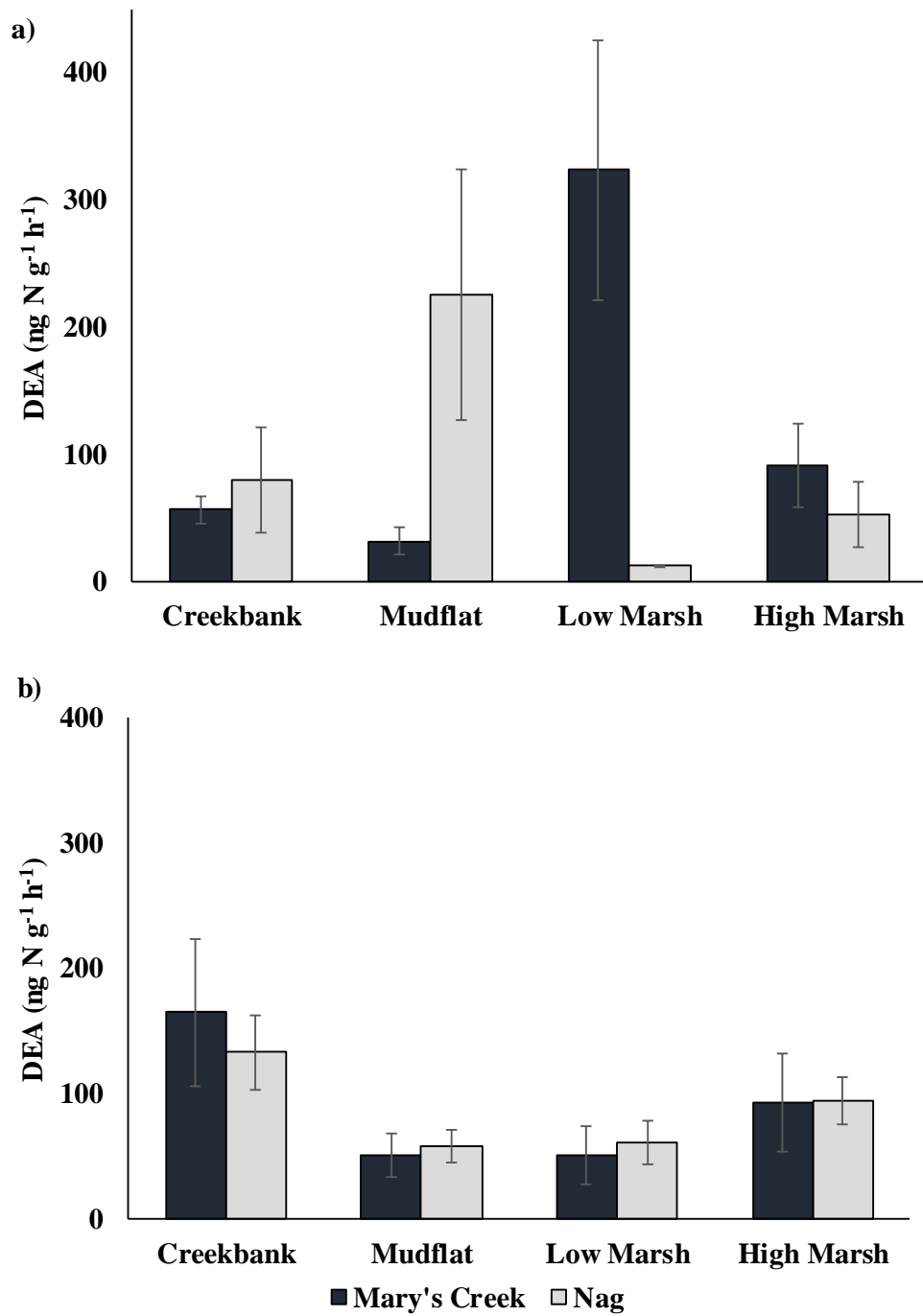
Figure 6. Mean potential denitrification enzyme activity (DEA) rates (± SE) from the high and low N sites across four zones in the 2017. Potential DEA in the months of (a) June and (b) August.

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