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## Short-term nitrogen additions can shift a coastal wetland from a sink to a source of N<sub>2</sub>O

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#### ABSTRACT

Coastal salt marshes sequester carbon at high rates relative to other ecosystems and emit relatively little methane particularly compared to freshwater wetlands. However, fluxes of all major greenhouse gases (N<sub>2</sub>O, CH<sub>4</sub>, and CO<sub>2</sub>) need to be quantified for accurate assessment of the climatic roles of these ecosystems. Anthropogenic nitrogen inputs (via run-off, atmospheric deposition, and wastewater) impact coastal marshes. To test the hypothesis that a pulse of nitrogen loading may increase greenhouse gas emissions from salt marsh sediments, we compared N<sub>2</sub>O, CH<sub>4</sub> and respiratory CO<sub>2</sub> fluxes from nitrate-enriched plots in a Spartina patens marsh (receiving single additions of NaNO<sub>3</sub> equivalent to 1.4 g N m<sup>-2</sup>) to those from control plots (receiving only artificial seawater solutions) in three short-term experiments (July 2009, April 2010, and June 2010). In July 2009, we also compared N<sub>2</sub>O and CH<sub>4</sub> fluxes in both opaque and transparent chambers to test the influence of light on gas flux measurements. Background fluxes of N<sub>2</sub>O in July 2009 averaged  $-33 \mu mol N_2O m^{-2} day^{-1}$ . However, within 1 h of nutrient additions, N<sub>2</sub>O fluxes were significantly greater in plots receiving nitrate additions relative to controls in July 2009. Respiratory rates and CH<sub>4</sub> fluxes were not significantly affected. N<sub>2</sub>O fluxes were significantly higher in dark than in transparent chambers, averaging 108 and 42  $\mu$ mol N<sub>2</sub>O m<sup>-2</sup> day<sup>-1</sup> respectively. After 2 days, when nutrient concentrations returned to background levels, none of the greenhouse gas fluxes differed from controls. In April 2010, N<sub>2</sub>O and CH<sub>4</sub> fluxes were not significantly affected by nitrate, possibly due to higher nitrogen demands by growing S. patens plants, but in June 2010 trends of higher N<sub>2</sub>O fluxes were again found among nitrate-enriched plots, indicating that responses to nutrient pulses may be strongest during the summer. In terms of carbon equivalents, the highest average  $N_2O$  and  $CH_4$  fluxes observed, exceeded half the magnitude of typical daily net carbon sequestration rates by salt marshes. Thus, anthropogenic additions of nitrate to coasts can substantially alter N<sub>2</sub>O fluxes from marshes, although substantial temporal variation in these fluxes was observed. To better assess the climatic roles of salt marshes, greenhouse gas emissions need to be studied in the context of chronic nitrogen loads that impact many coastal ecosystems.

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#### 1. Introduction

Fossil fuel combustion and land use changes have increased global average CO<sub>2</sub> emissions to the atmosphere by 35% since preindustrial times (Forster et al., 2007). Along with CO<sub>2</sub>, methane (CH<sub>4</sub>) and nitrous oxide (N<sub>2</sub>O) have increased by 48% and 18%, respectively, above pre-industrial levels. N<sub>2</sub>O is 298 times more effective than CO<sub>2</sub> at trapping heat in the atmosphere on a molar basis over a period of 100 years (Denman et al., 2007) and together, CH<sub>4</sub> and N<sub>2</sub>O make up 25% of global mean radiative forcing. These changes in greenhouse gases are a major cause of global warming in the last 100 years (Forster et al., 2007).

Ecosystems can influence climate via microbial production or consumption of all greenhouse gases. Although ecosystem carbon sinks or sources have been extensively studied, relatively few studies have quantified the role of natural ecosystems as net sources or sinks





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of CH<sub>4</sub> and N<sub>2</sub>O (Dalal and Allen, 2008). About one third of CH<sub>4</sub> emissions and more than half of N2O emissions have been estimated to come from natural ecosystems (Denman et al., 2007; Townsend-Small and Czimczik, 2010). Nonetheless, emissions factors for N<sub>2</sub>O, particularly from aquatic ecosystems, are uncertain (Kroeze et al., 1999). Moreover, the manner and extent to which anthropogenic disturbance alters biogenic emissions of greenhouse gases needs to be better understood. Nitrogen loading, from fertilizer-enriched run-off, groundwater, and atmospheric deposition, may have a particularly strong effect on greenhouse gas emissions from ecosystems. N<sub>2</sub>O and CH<sub>4</sub> emissions were found to increase by 216% and 97% in several terrestrial ecosystems relative to un-enriched controls (Liu and Greaver, 2009). Although CO<sub>2</sub> sinks may also increase in response to nitrogen addition (by 0.35–0.58 Pg C per year), these benefits could largely be offset by increases in global CH<sub>4</sub> emissions, reductions in CH<sub>4</sub> uptake, and increases in N<sub>2</sub>O emissions from terrestrial and agricultural ecosystems (Liu and Greaver, 2009).

Although nitrogen is a major limiting nutrient in pristine coastal ecosystems (Vitousek et al., 1997) anthropogenic N inputs have led to eutrophication at least 60% of coastal rivers and bays in the U.S. (Howarth et al., 2002) by more than doubling the availability of reactive nitrogen on land (Galloway et al., 2008). Nitrate is the dominant form of anthropogenic nitrogen inputs from rivers and groundwater to many coastal ecosystems (Fenn et al., 1998; Drake et al., 2009). With eutrophication, low oxygen availability promotes anaerobic microbial processes, including those that lead to emissions of N<sub>2</sub>O and CH<sub>4</sub>. Mean soil respiration rates in coastal marshes have been found to increase significantly along gradients of watershed nitrogen loading (Wigand et al., 2009). Denitrification, the microbial conversion of nitrate to predominantly N<sub>2</sub>, can instead terminate in release of N<sub>2</sub>O, particularly in the nitratereplete, low oxygen, and organic-rich conditions that characterize eutrophic coastal ecosystems (Herbert, 1999). A better estimate of the magnitude of N<sub>2</sub>O and CH<sub>4</sub> fluxes from coastal ecosystems, particularly in response to excessive nutrient loading, could inform strategies for reducing anthropogenic impacts on climate.

Among all coastal ecosystems, salt marshes may be particularly key sites for constraining the magnitude of greenhouse gas fluxes. The high primary productivity in salt marshes is known to translate into exceptionally high rates of carbon sequestration (Chmura et al., 2003). However, few measurements of CH<sub>4</sub> and N<sub>2</sub>O have been made in these dynamic ecosystems. Further, the abundance of sulfide in coastal salt marshes may increase N<sub>2</sub>O:N<sub>2</sub> ratios produced via denitrification (Jensen and Cox, 1992).

In this study, our primary objectives were (1) to experimentally test the effects of a nitrate pulse on N<sub>2</sub>O and CH<sub>4</sub> fluxes and respiration rates in a temperate salt marsh (2) to measure temporal variability in the response to such nutrient pulses (in July 2009, April 2010, June 2010) and (3) to test the influence of light on measurements of N<sub>2</sub>O and CH<sub>4</sub> fluxes with dark and transparent chambers. Our experiments focus on nitrate because this is the main form in which anthropogenic inputs reach coastal wetlands (Cole et al., 2006; Drake et al., 2009). In July 2009, background fluxes of greenhouse gases (N<sub>2</sub>O, CH<sub>4</sub>) and respiration rates (CO<sub>2</sub>) were measured. We focused our studies in a Spartina patens salt marsh. The short-term nitrate additions we applied to the marsh surface mimicked inundation with a pulse of nitrate-enriched estuarine surface water. We hypothesized that short-term nitrate additions would increase fluxes of N<sub>2</sub>O from the marsh, particularly during summer months when temperatures and microbial activities are high. We also quantified CH<sub>4</sub> fluxes and respiration rates in order to more completely assess the effects of nitrogen inputs on greenhouse gas fluxes. Further, we hypothesized that fluxes measured in the presence of light (with transparent chambers) would be lower than those in the dark (measured with opaque chambers).

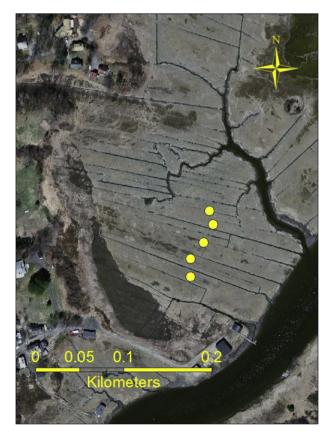
### 2. Materials and methods

#### 2.1. Site description

This study was conducted in an intertidal *S. patens*-dominated salt marsh at Rowley, Massachusetts in the Plum Island LTER reserve (latitude +42.759, longitude -70.891). In this reserve, nitrogen inputs are low despite some development and human modification of the watershed (Deegan et al., 2007). Creek banks are dominated by a narrow zone of tall-form Spartina alterniflora, but the marsh platform, which is flooded about 12% of the time, is dominated by S. patens, which covers roughly 40% of the marsh (Deegan et al., 2007). In the S. patens zone, five sites with similar plant composition and density were established for greenhouse gas measurements (Fig. 1). These sites in the S. patens platform are flooded diurnally and our studies were conducted at low tide within one week of spring tides. Sites were separated on average by 20 m and aligned parallel to the shoreline of the main river. Paired metal collars (approximately 28 cm diameter, 6 cm deep) were installed for measurement of N<sub>2</sub>O and CH<sub>4</sub> fluxes at each of these 5 sites. In addition, a smaller PVC collar (11 cm diameter), was concentrically positioned inside each of those collars respiration measurements. All collars were set in place 1 month prior to flux measurements. Paired collars were placed 3 m apart to prevent possible interference between treatments.

#### 2.2. Greenhouse gas flux measurements and respiration rates

To determine  $N_2O$  and  $CH_4$  fluxes, transparent polycarbonate chambers (28 cm diameter, 18 cm height) were placed on top of the previously-installed steel collars. As plants can be conduits for



**Fig. 1.** Map of field site at the Rowley River in the Plum Island Long Term Ecological Research Reserve in Rowley, MA. Each circle marks the position of paired chamber locations.

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