The greenhouse gas flux and potential global warming feedbacks of a northern macrotidal and microtidal salt marsh

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Abstract
Conversion of wetlands by drainage for agriculture or other anthropogenic activities could have a negative or positive feedback to global warming (GWF). We suggest that a major predictor of the GWF is salinity of the wetland soil (a proxy for available sulfate), a factor often ignored in other studies. We assess the radiative balance of two northern salt marshes with average soil salinities > 20 ppt, but with high (macro-) and low (micro-) tidal amplitudes. The flux of greenhouse gases from soils at the end of the growing season averaged 485 ± 253 mg m⁻² h⁻¹, 13 ± 30 µg m⁻² h⁻¹, and 19 ± 58 µg m⁻² h⁻¹ in the microtidal marsh and 398 ± 201 mg m⁻² h⁻¹, 2 ± 26 µg m⁻² h⁻¹, and 35 ± 77 µg m⁻² h⁻¹ in the macrotidal marsh for CO₂, N₂O, and CH₄, respectively. High rates of C sequestration mean that loss of these marshes would have a radiative balance of −981 CO₂eq. m⁻² yr⁻¹ in the microtidal and −567 CO₂eq. m⁻² yr⁻¹ in the macrotidal marsh.

Keywords: tidal marsh, nitrous oxide, methane, carbon dioxide, radiative forcing

1. Introduction
On an aerial basis, average rates of carbon sequestration in soils of mineral wetlands (Bridgham et al 2006, Chmura et al 2003) are equivalent to those of terrestrial grasslands (Vleeshouwers and Verhagen 2002) and faster than rates suggested for improved agricultural management or afforestation (e.g., Watson et al 2000, Lal 1999). This is due to high rates of primary production and frequently saturated soils that inhibit decomposition and hence mineralization of organic carbon to carbon dioxide (CO₂). However, the anaerobic conditions characteristic of wetland soils, while inhibiting CO₂ production, may result in an increase in the microbially mediated production of methane (CH₄) and nitrous oxide (N₂O). N₂O is formed through both nitrification and denitrification. Nitrification can occur in oxidized rhizospheres of wetland plants, or throughout the surface soil during seasonal drying of freshwater wetlands and daily drainage associated with ebb and flood of tides in tidal wetlands (Megenigal et al 2004). Because the radiative forcing of CH₄ and N₂O is considerably higher than CO₂ (Forster et al 2007), emissions of these other greenhouse gases can reduce or negate the value of wetlands as a carbon sink (e.g., Frolking et al 2006). In fact, Huang et al (2010) calculated that, in Northeast China, conversion of wetlands to croplands resulted in a decrease in radiative forcing through reduced emissions of CH₄ and N₂O, despite loss of soil organic carbon through oxidation.

In assessing the potential feedback to global warming (i.e., radiative forcing) of wetland conversion, restoration, or creation, a key factor to consider is the sulfate available in the wetland soil as sulfate-reducing bacteria may be out-competing methanogenic bacteria (Capone and Kiene 1988). Sea water provides tidal wetlands with sulfate at levels that generally increase with salinity of the sea water (Poffenbarger et al 2011). Unfortunately, the analysis of Huang et al (2010)
applied characteristics of only freshwater wetlands which have substantial evidence of significant CH₄ emissions (Bridgham et al. 2006) and those characteristics should not be applied to global estimates of greenhouse gas emissions of all wetlands. Methane emissions are negligible from tidal salt marshes with soil salinities >18 ppt (Bartlett et al. 1987, Poffenbarger et al. 2011). Magenheimer et al. (1996) examined the in situ methane flux from different plant communities at a Bay of Fundy marsh, and found that salinity and water table position were significant predictors of flux. This confirmed the results of Bartlett et al. (1987) who conducted in situ measurements to compare marshes along a salinity gradient in the Chesapeake Bay. Since those two early studies the majority of measurements of methane flux have been lab-based experiments that reduce the complexities of actual field situations such as variability within soils due to complex rhizospheres, weather and daily tides.

Measurements of N₂O emissions from freshwater wetlands are rarer, and reveal lower fluxes, but the higher global warming potential of N₂O (289 times that of CO₂ in a 100 yr time frame) may easily make these significant in terms of climate feedbacks. In comparison to freshwater wetlands, there are even fewer studies of N₂O flux in tidal salt marshes. An in situ marsh study by DeLaune et al. (1990) showed that N₂O emissions decreased with increasing salinity and Moseman-Valtierra et al. (2011) showed that N₂O changed from negative to positive fluxes with amendments of nitrate. Some studies have reported N₂O flux for tropical mangrove swamps (which grow under conditions similar to tidal salt marshes) and these also show increased emissions with nitrogen loading from experimental treatments (Corredor et al. 1999) or anthropogenic activities (Purvaja and Ramesh 2001). However, observations from these studies suggest that drainage of tidal salt marshes and mangrove swamps in unpolluted areas may result in an increase in radiative forcing.

We currently have a limited understanding of the trace gas emissions from salt marsh systems. It is important to document trace gas emission in a manner that considers CH₄ and N₂O in addition to CO₂ sequestration in order to determine the radiative effects of trace gas fluxes from salt water marshes and to determine the variables that control these fluxes. Here we report the flux of CO₂, CH₄ and N₂O from two Canadian salt marshes, one on the Bay of Fundy and another on the Gulf of St. Lawrence. Our goal was to quantify trace gas emissions from systems with minimal anthropogenic disturbance in order to calculate their baseline radiative balance. Changes in radiative balance caused by creation, restoration or conversion of these systems cause radiative forcing, with feedbacks on global warming. By reporting N₂O emissions, we provide a more complete assessment of trace gas emissions than many previous studies in tidal wetlands, which tend to focus on methane emissions (Poffenbarger et al. 2011). We hypothesized that fluxes of CH₄ and N₂O would vary at the two sites as differences in tidal amplitude would cause variations in environmental drivers of CH₄ and N₂O emissions.

2. Study area

In eastern Canada the majority of salt marsh area occurs along the Atlantic coasts of New Brunswick and Nova Scotia where tidal amplitudes are in the microtidal range (0–2 m) or along the coast of the Bay of Fundy where tidal amplitudes are in the macrotidal range (>4 m). Variation in tidal amplitude can cause differences in frequency of tidal flooding and opportunity for soil drainage (e.g., Byers and Chmura 2007), which affect other characteristics of the soil, and potentially, greenhouse gas fluxes. Thus, we conducted our study in two different marshes, one representative of microtidal conditions and another macrotidal.

Salt marshes of the northeastern Atlantic are characterized by extensive platforms with vegetation dominated by the grass Spartina patens, and we focused our measurements in this zone. At both marshes we selected four locations for our measurements that were at similar elevations (thus hydroperiods) within the marsh and dominated by S. patens.

At both marshes soil carbon accumulation rates had been determined previously by Chmura and Hung (2004). Dipper Harbour marsh at 45.1°N, 66.4°W (core 13 reported by Chmura and Hung 2004) is on the New Brunswick coast of the Bay of Fundy which is macrotidal. At Dipper Harbour the mean tidal amplitude is 5.4 m. The marsh on Kouchibougacais Lagoon at 46.8°N, 64.9°W (core 2 reported by Chmura and Hung 2004) is on the New Brunswick coast of the Gulf of St. Lawrence which is microtidal. The mean tidal amplitude at Kouchibougacais Lagoon marsh is 1.0 m.

3. Methods

Gas samples were collected in 2006, near the end of growing season, during low tide on August 22, 23, 25 and 29 at Dipper Harbour and on August 27, 28, 30 and September 3 at Kouchibougacais Lagoon. By timing our sampling at the end of the growing season, competition between microbes for denitrification and uptake by growing plants for soil N is reduced (Hamerseley and Howes 2005). Thus, we expect our N₂O measurements to reflect soil microbial processes alone and that these will represent the highest flux of N₂O during the growing season (excluding the spring thaw).

We used the dark static chamber technique described by Magenheimer et al. (1996), setting chambers into a rim of a plastic collar inserted into the marsh soil a minimum of two days prior to collecting gas samples. At each marsh we had four collar sample sites thus obtained 16 flux measurements per marsh.

The chamber dimensions (26 cm diameter; 18 l volume) were large enough to encompass complete grass culms. We sub-sampled gases 30, 60 and 90 min and immediately after chambers were placed on the collars. Samples of ambient air also were sampled on each day of sampling.

Environmental measurements were taken outside of, but within 1 m of the chamber collar. Soil temperature over 15 cm depth was recorded while gas samples were being collected. Other environmental measurements were taken after completion of gas sampling. Methods for determination of soil water table depth, collection of soil pore water and analysis for pH, sulfides and salinity are described by Yu and Chmura (2010). We assume that salinity provides an approximation of sulfate available as sulfate levels correspond
to salinity in seawater (Poffenbarger et al 2011). At the end of the experiment, vegetation was harvested from two randomly selected 0.1 m² circular plots within 3 m of three collar sites. Vegetation was washed, sorted into standing live and dead, and dried to constant weight for determination of end of season standing crop.

Samples for gas analysis were collected in N₂ purged and evacuated 12 ml Exetainer vials (Labco, UK). Carbon dioxide was analysed on a Licor LI-7000 CO₂/H₂O infrared gas analyser in continuous flow mode. Methane was measured using gas chromatography in a Shimadzu GC14 fitted with a FID, and N₂O was analysed on a Shimadzu GC8a fitted with an ECD. Standards were run at the start of each day (Matheson Tri-Gas Standards), throughout analysis, and at the end of a daily sample run. The combined sampling errors associated with gas sample collection and transfer from vials to analyser has been estimated to be on the order of 10% (Risk et al 2002, Kellman and Kavanaugh 2008).

Statistical analyses (regressions, multiple linear and non-linear regressions) were performed using SPSS and STATA software packages. Analyses were performed on the suite of 16 individual measurements from each marsh (n = 32 over all marshes) as well as the flux measured at each collar averaged over the four days of measurement (n = 4 at each marsh).

4. Results

Figure 1 displays the measurement of environmental parameters associated with gas flux sampling events and collar sites. At Dipper Harbour and Kouchibouguac Lagoon the average air temperatures on sample days were 15.3 °C and 14.8 °C while soil temperatures at collar sites averaged 16.4 °C (±1.7) and 14.3 °C (±1.3), respectively. Cumulative rainfall seven days prior to sampling was 28.6 mm at Dipper Harbour and 32.5 mm at Kouchibouguac Lagoon where it also rained on the sample days 30 Aug (2.8 mm) and 3 Sept (9.6 mm) as reported by Environment Canada (2010). Sulfide concentrations, salinity and pH of soil pore water were significantly higher (p = 0.01, 0.01 and 0.02, respectively) at Dipper Harbour than Kouchibouguac Lagoon (table 1).

At both marshes the CO₂ fluxes were always positive, and higher at Kouchibouguac Lagoon (table 1). Daily CO₂ fluxes were highly variable and exploratory regressions (including linear, non-linear and multiple regression) reveal no explanatory power amongst the environmental variables we measured (figure 1).

CH₄ fluxes were negative as well as positive and were higher at Dipper Harbour (table 1). Linear regression revealed that 14.3% (adjusted R², p = 0.023) of the variability in CH₄ flux could be explained by salinity (a proxy for sulfate concentration in sea water), but no other variable had significant predictive power when considering the set of individual collar measurements. Linear multiple regression analyses of averages of all measurements at each collar (n = 8) reveals significant explanatory power of both salinity and sulfide (adjusted R² = 0.772, p = 0.011).

N₂O had negative as well as positive fluxes and were higher at Kouchibouguac Lagoon, but none of the environmental parameters explained a significant (p < 0.05) amount of variability in the N₂O flux.

5. Discussion

In situ studies of methane flux in salt marshes have been limited, but those that report salinity have demonstrated that CH₄ flux is negligible above 18 ppt salinity, as salinity generally is a good approximation for availability of sulfate which is more readily reduced than CO₂ (Bartlett et al 1987, Poffenbarger et al 2011). Although salinity tended to be higher in Dipper Harbour soils, lower water table depths in Kouchibouguac Lagoon marsh soils indicate a greater prevalence of aerobic conditions, conditions which allow oxidation of CH₄ (Megonigal and Schlesinger 2002), thus explaining the lower CH₄ flux at the Kouchibouguac marsh.

In 1993 Magenheimer et al (1996) also measured summer CO₂ and CH₄ fluxes at the Dipper Harbour marsh and reported a lower average CH₄ flux (20 µg m⁻² h⁻¹). Their lower CH₄ flux probably was due to the warmer and drier conditions reported by Magenheimer et al (1996), and more aerobic soils, thus lower CH₄ production and/or higher CH₄ oxidation. The CO₂ flux (98 µg m⁻² h⁻¹) reported by Magenheimer et al (1996) was much lower than found in this study. The previous study included earlier periods in the growing season when plant biomass, thus plant respiration would have been relatively low compared to the present study, reducing the seasonal average.

Despite the variation in tidal range, the average N₂O emission rates of our late summer measurements in

| Variable                                | Dipper Harbour Average | Dipper Harbour sd | Kouchibouguac Average | Kouchibouguac sd |
|-----------------------------------------|------------------------|-------------------|------------------------|------------------|
| Soil porewater sulfides (ppm)           | 76                     | 164               | 16                     | 23               |
| Soil porewater pH                       | 6.71                   | 0.67              | 6.41                   | 0.46             |
| Soil porewater salinity                 | 23.0                   | 7.0               | 20.0                   | 3.0              |
| Soil temperature (°C)                   | 16.4                   | 1.7               | 14.3                   | 1.3              |
| Water table (cm)                        | −12.5                  | 7.6               | −19.6                  | 9.7              |
| End of season standing crop (g m⁻²)     | 282.2                  | 47                | 340                     | 73               |
| Soil organic carbon density (g cm⁻³)    | 0.087                  |                   | 0.094                  |                  |
| Soil bulk density (g cm⁻³)              | 0.443                  |                   | 0.331                  |                  |
| Vertical soil accretion rate (cm yr⁻¹)  | 0.18                   |                   | 0.29                   |                  |
| CO₂ mg m⁻² h⁻¹                          | 398                    | 201               | 485                    | 253              |
| CH₄ µg m⁻² h⁻¹                           | 35                     | 77                | 19                     | 58               |
| N₂O µg s m⁻² h⁻¹                         | −2                     | 26                | 13                     | 30               |
| CH₄ CO₂ equivalents (m⁻² yr⁻¹)           | 8.7                    |                   | 4.7                    |                  |
| N₂O–CO₂ equivalents (m⁻² yr⁻¹)          | −2.05                  |                   | 13.9                   |                  |
| CO₂ equivalents (m⁻² yr⁻¹)               | 574.2                  |                   | 999.5                  |                  |
| GWF                                      | −567.49                |                   | −980.9                 |                  |

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| GWF                                      | −567.49                |                   | −980.9                 |                  |
Figure 1. Measurements of greenhouse gas flux and environmental parameters taken on four different days and at four collars installed in Dipper Harbour (DH, black diamonds) and Kouchibouguacis Lagoon (KB, red squares) salt marshes in New Brunswick, Canada during August. With the exception of the relationship of soil salinity and CH4, no other environmental variables were significantly related to CH4 or N2O flux over the measurement period. Soil water depth was not available for all days and sample plots.

The Canadian salt marshes (table 1) are comparable to those reported by Moseman-Valtierra et al (2011) for a Massachusetts salt marsh and fall in the low end of the range found in studies of mangroves (Kreuzwieser et al 2003, Chen et al 2010). Bauza et al (2002) assumed that the flux from mangroves they studied was due mainly to nitrification occurring in the aerobic surface 10 cm of soil. This could explain the higher N2O flux from Kouchibouguacis which...
was relatively more aerobic, but we detected no significant explanatory power of sulfide concentration or soil water depth.

Greater variation in site or seasonal environmental conditions may have revealed significant relationships between our measured factors and \( N_2O \) flux, as reported in other studies. High rates of \( N_2O \) emissions from agricultural and natural (terrestrial and freshwater) ecosystems have often been measured at spring thaw (e.g., Goodroad and Keeney 1984, Wagner-Riddle and Thurtell 1998) and a pulse of \( N_2O \) could be emitted as frozen marsh soils thaw. Although plant competition for nitrogen during the growing season may have resulted in lower atmospheric fluxes than we measured at the end of the growing season, our fluxes likely provide a reasonable order of magnitude estimate of \( N_2O \) fluxes, particularly in a natural system where \( N \) limitation coupled with high spatial variability in fluxes may not generate significant seasonal differences, an observation made at \( N \) limited forest sites (e.g., Kellman and Kavanaugh 2008).

We assume that these measurements from Canadian salt marshes sampled in this study provide a baseline for calculating the radiative balance with minimal anthropogenic influence. Studies of mangrove (e.g., Purvaja and Ramesh 2001) and salt marsh soils (DeLaune and Jugsujinda 2003, Mosteau-Valtierra et al. (2011) have shown increased \( N_2O \) flux with enrichment of nitrogen sources. Our two Canadian salt marshes have low levels of anthropogenic nutrient loading, as population density of the Province of New Brunswick is low (∼10 km\(^{-2}\)) and <6% of the Province is agricultural land (Statistics Canada 2010). In addition, rates of atmospheric deposition of nitrate are low on the coast of Eastern Canada (Galloway et al. 2008).

We calculate a preliminary radiative balance for these two salt marshes assuming gas flux over 150 days yr\(^{-1}\) and soil carbon accumulation rates determined by measuring vertical soil accumulation rates with caesium-147 dating and loss-on-ignition of the dated layers (Chmura and Hung 2004). Both marshes have a negative radiative balance (table 1). Despite positive \( N_2O \) flux, the higher rate of \( CO_2 \) sequestration in the Kouchibouguacais soils gives this marsh a lower radiative balance than Dipper Harbour. Including the combined fluxes of \( N_2O \) and \( CH_4 \) in this study to calculate radiative balance only reduced the radiative balance by 1.2 and 1.9% for the macro and microtidal marsh systems, respectively. Both marshes would continue to have a negative radiative balance even if hourly \( N_2O \) and \( CH_4 \) fluxes were positive and an order of magnitude higher than our measurements. These results provide baseline fluxes for undisturbed northern tidal salt marsh systems that demonstrate a net positive, but relatively minor influence of \( CH_4 \) and \( N_2O \) upon the total radiative balance of these systems. Anthropogenic disturbances that alter these fluxes would likely cause a positive feedback to global warming, particularly in the case of elevated \( N \) loads within the marshes. Loss of either the macrotidal or microtidal marsh would generate a positive radiative forcing as they would cease to sequester \( CO_2 \). Distinctions between saline and freshwater wetlands are essential when considering climate feedbacks of wetlands in future studies.

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