Organic carbon transformation along a salinity gradient in Louisiana wetland soils

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Abstract

Wetlands constitutes one of the major sources of global terrestrial carbon (C) pool and play an important role in global carbon cycle. In this study, organic C transformation and its relation to C gas and N_2O emissions in wetland soils of a forest swamp (FS), freshwater marsh (FM) and saline marsh (SM) in coastal Louisiana were studied. Molecular C compositions of bulk soils and purified humic acids were determined using NMR and pyrolysis GC/MS. Carbon gas emissions and the impacts of electron acceptors were investigated through incubations. The three wetland soils exhibited distinctive molecular C characteristics with more polyphenols in FS as compared to more lignin in FM. Both NO_3^- and SO_4^{2-} inhibited CH_4 production but only NO_3^- decreased CO_2 production from FM soil under anaerobic condition. On the other hand, FM soil tended to yield greater incomplete denitrification, which could result in higher emission of N_2O. Higher contents of phenolics and aldhydes/ketonics in SOM, however, decreased denitrification in these wetland soils.

Key Words

Soil organic carbon, wetlands, greenhouse gas, humic acids.

Introduction

Louisiana coastal wetlands, located on the Mississippi delta plain, have been subsiding due to the compaction of recent alluvial sediments. As a result, these wetlands have been increasingly under the influence of seawater intrusion. Mississippi river water is currently being diverted into these wetlands with the aim to decrease salinity and provide sediments (LDNR 2005). While the seawater intrusion brings in SO_4^{2-} and other ionic species, the diverted Mississippi river water carries elevated levels of NO_3^- (Donner 2004). These nutrient environments could have different impact on soil organic carbon (SOC) transformation and C gas emissions in these wetlands, which has not been fully evaluated. Recently, organic matter accretion along with sediment addition has been considered as major controlling factors in stabilizing these wetlands (DeLaune and Pezeshki 2003). Yet, little is known about organic matter structure and its transformation especially under existing and anticipated conditions (Dodla *et al.* 2008). Therefore, this study was carried out to characterize SOC transformation in these wetland soils within a salinity gradient and evaluate the specific effects of NO_3^- and SO_4^{2-} on C gas productions (CH_4 and CO_2) from these wetlands.

Methods

Site and soil characteristics

Three sites of a bottomland forest swamp (FS), freshwater marsh (FM), and saline marsh (SM) located in the Louisiana Barataria Basin estuary were selected for this study. Mississippi River water has periodically diverted in to the northern region of the Basin as part of effort to restore these wetlands (LDNR 2005). The major vegetation types in FS, FM, and SM are *Taxodium distichum*, *Sagittaria lancifolia*, and *Spartina alterniflora* respectively. The soils at the FS, FM and SM sites were Barbary muck (Very-fine, smectitic, nonacid, hyperthermic Typic Hydraquents), Allemands muck (Clayey, smectitic, euic, hyperthermic, Terric Haplosaprists), and Timbalier muck (Euic, hyperthermic, Typic Haplosaprists), respectively. Fifteen composite soil samples from different horizons at each site were collected and thoroughly mixed. A portion of each sample was freeze-dried and the reminder was stored frozen or directly analyzed (Table 1).

Table 1. Selected physical and chemical properties.

Site	Soil	pH	EC dS/m	TOC	Total N
				(------g/kg-----)	
FS	Barbary muck	6.2	1.2	66	4.6
FM	Allemands muck	6.3	3.1	292	18.2
SM	Timbalier muck	7.3	38.9	159	8.7

NMR and Pyrolysis-GC/MS characterization

Molecular C composition of wetland SOM and humic acids purified based on the procedure of International Humic Substances Society (Swift 1996) was determined using solid-state ^{13}C nuclear magnetic resonance (NMR) and pyrolysis-gas chromatography/mass spectrometry (Py–GC/MS). ^{13}C NMR spectra were obtained using a Bruker Avance wide bore 400 MHz instrument with a double resonance 4mm CP-MAS probe. The cross polarization total sideband suppression magic angle spinning (CP-TOSS-MAS) technique was used to acquire the ^{13}C NMR spectra (Cook and Langford, 1998). Chemical shifts were expressed relative to tetramethylsilane (TMS). The peaks between 0 -230 ppm chemical shift range were assigned to various C moiety groups as aliphatic C (0-50 ppm), polysaccharides (50-108 ppm), aromatic C (108-165 ppm), carboxyl C (165-190 ppm), and aldehydes and ketonic C (190-230 ppm). Chemical shift range 108-165 ppm was further divided into aryl C (108 -140 ppm) and phenolic C (140 – 165 ppm). Py-GC/MS analysis was performed using a CDS 5000 pyrolyzer, directly connected to a Varian 3900 GC coupled to a Varian Saturn 2100T ion trap mass spectrometer. The identification of pyrolysis products was based on a comparison of their mass spectra with those of standard compounds and NIST 2005 mass spectral library, literature data and GC/MS characteristics.

Field carbon gas emission and laboratory microcosm experiments

Monthly characterizations of CO_2 and CH_4 emissions from these sites were conducted over a two year period to evaluate the difference in C gas emissions among these sites. Laboratory anaerobic incubation experiments were also carried out to determine the influence of NO_3^- and SO_4^{2-} on C gas production from the FM soil. Ten-gram field moist soil samples were weighed into glass jars followed by adding 130 mL of deionized water. Sample slurries in the jars were flushed with N_2 gas to remove any dissolved/ trapped O_2. Treatment solutions were added to bring final concentrations of NO_3^- to 3.2 and 5 mM NO_3^- and SO_4^{2-} to 2 and 5 mM, respectively. All incubations were carried out in triplicates and conducted in dark at room temperature (22±0.5 °C) for 214 days. The CO_2 and CH_4 in the headspace of each jar were periodically analyzed using a Varian 3800 GC. In addition, separate incubations were carried out to determine potential denitrification rates (PDR) of these wetland soils. In doing so, 10 g field-moist soils were mixed with 10 mL solutions of 0.14 or 0.71 mM NO_3^- -N in sample vials. The mixtures were treated with or without acetylene and incubated. The N_2O concentration in the headspace of each sample vial was determined using a Shimadzu GC. The amount of N_2O present in the headspace of sample vials with acetylene represents the potential for the amount of NO_3-that can be denitrified, whereas the amount of N_2O in the head space of sample vials without acetylene represents the potential for incomplete denitrification (Hunt *et al.* 2007). PDR was estimated from the steepest portion of the curve plotted between total amount of N_2O released (with acetylene treatment) and incubation time (Dodla *et al.* 2008).

Results

Soil organic carbon characteristics

Pyrolysis-GC/MS analysis of bulk samples of these wetland soils showed that out of all identified peaks, organic matter in FS soil was dominated by compounds derived from polyphenols whereas organic matter in FM soil was by those derived from lignin. SM soil organic matter contained the lowest percentage of N-bearing compounds (Table 2). ^{13}C NMR analysis showed that humic acids extracted from FM soil were significantly more aromatic than SM humic acids (Figure 1). The aromaticity of the humic acids, estimated by % peak area between 110 to 165 ppm to peak area between 0 to 165 ppm was 47.2 % for FM-HA as opposed to 35.4% and 39.7% respectively for humic acids from FS and SM soils. On the other hand, FS humic acids were found to be more aliphatic than those from SM and FM. Closer examination of aliphatic region indicated an increasing intensity in 31 ppm spectrum peak along with these wetlands of increasing salinity (Figure 1). This peak has been attributed to long crystalline or condensed polymethylenic $(CH_2)_n$ chains (Hu *et al.* 2000). The result could suggest that the increased salt concentration or associated saline environment enhance the crystallinity of alkyl C in humic acids in these soils.

Table 2. Relative distribution of C compounds determined by Py – GC/MS for three wetland soils.

Soil	Alkyl	Lignin	N-containing	Polyphenols	Polysaccharides	Total
	(------------	------------	------------	%------------	------------	------------)
FS	19.5	16.0	12.4	26.7	11.4	86
FM	20.0	31.3	16.1	5.4	10.1	82.9
SM	21.5	20.8	9.7	11.5	13.9	77.4

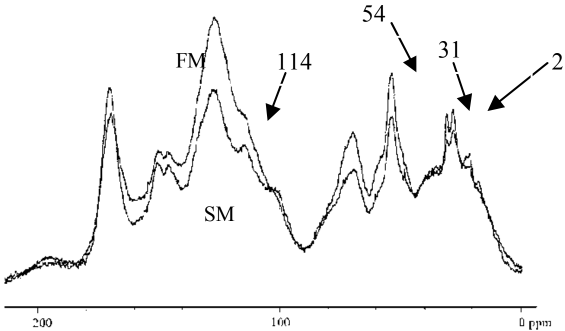

Figure 1. **^{13}C NMR spectra of FM and SM soils.**

Carbon gas emissions

Field monitoring showed that FS soil had generally higher CH_4 emissions than FM and SM soils (Figure 2). FS soil also had higher CO_2 emissions than FM and SM soils. The emission difference between FM and SM soils was small.

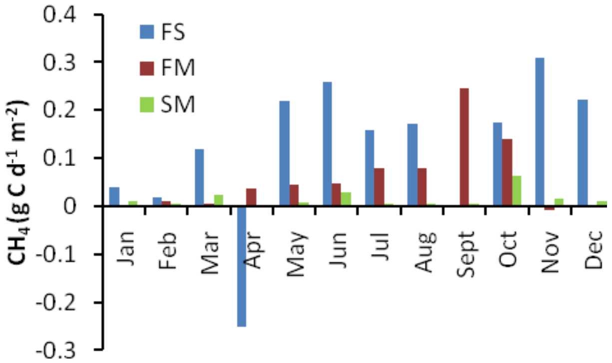

Figure 2. Two-year average seasonal emission of methane from three wetland soils.

Further laboratory incubation study of FM soil, where it is likely to be influenced by integrated effect of seawater intrusion and Mississippi river diversion, showed that the presence of NO_3^- and SO_4^{2-} affected C gas productions differently (Figure 3). Under anaerobic condition as these wetlands often are, both NO_3^- and SO_4^{2-} presence decreased CH_4 production. The NO_3^-, however, almost completely inhibited CH_4 production (> 99 %) as compared to 78-90% reduction by SO_4^{2-}. On the other hand, the presence of NO_3^- (at 3.2 mM) significantly decreased CO_2 productions from FM soil whereas SO_4^{2-} did not (Figure 3).

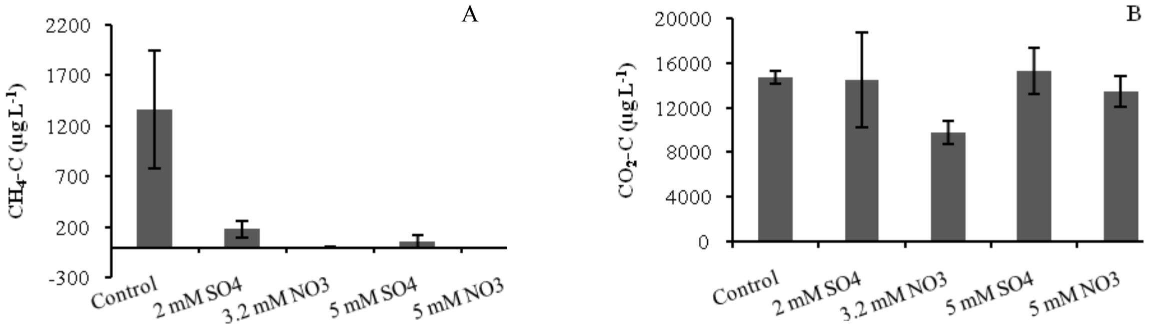

Figure 3. Total production of (A) CH_4-C and (B) CO_2-C from FM soil as influenced by different concentrations of NO_3^- and SO_4^{2-} under anaerobic incubation for 214 days.

Carbon quality and denitrification

Besides the release of C gases, transformation of SOC also affects the emission of other trace gas such as N_2O from denitrification process. Analysis of PDR and molecular C composition of SOM showed that PDR was positively related to polysaccharide-C (R^2=0.75) but negatively related to phenolic C (R^2=0.49) and aldhydes/ketonic C (R^2=0.65) in these wetland soils. On both unit weight and unit volume basis, FM soil profile exhibited the highest PDR as compared to FS and SM. In addition, FM soil tended to yield higher percentage of N_2O release as compared to the FS and SM soils (Table 3), suggesting a greater incomplete denitrification and potential for emission of N_2O into atmosphere.

Table 3. Percentage of added NO_3^- -N released as N_2O-N at two levels of treatments.

Soil	Depth (cm)	NO_3^- Treatment 0.14 mM	NO_3^- Treatment 0.71 mM
FS	0-25	15.4	2.7
	25-50	15.2	8.2
	50-75	3.3	0.9
	75-100	1.5	0.1
FM	0-25	38.3	18.8
	25-50	3.3	0.6
	50-100	23.1	0.9
	100-150	0.5	0.5
SM	0-50	-	0.03
	50-75	-	0.06
	75-100	0.9	1.02
	100-150	-	0.02

Conclusion

Wetland soils along a salinity gradient in Louisiana Gulf coast likely have different SOC transformations as evidenced by the differences in molecular C composition of humic acids as well as organic matter in bulk soils. These differences in SOC transformations could affect differently the emissions of C gases and N_2O from these soil systems.

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