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# UNIVERSITY OF CALIFORNIA RIVERSIDE

# Evaluating the Effects of Organic Amendment Applications on Nitrous Oxide Emissions From Salt-Affected Soils

A Dissertation submitted in partial satisfaction of the requirements for the degree of

Doctor of Philosophy

in

Soil and Water Sciences

by

Namratha Pulla Reddy Gari

December 2013

Dissertation Committee: Dr. David M. Crohn, Chairperson Dr. David E. Crowley Dr. Laosheng Wu

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Committee Chairperson

University of California, Riverside

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# **DEDICATION**

This dissertation is dedicated to my mother and brother, Uma Rani and Nagin Kumar, for their unwavering support and encouragement during my graduate studies. I am indebted to my Uncles, Babu Rao and Chandra Sekhar, for their help in providing me with an opportunity for better education. I would also like to thank my friends at UCR, Vijay Chaganti and Julie Escalera, for their continued support and encouragement during tough times. Lastly, I dedicate my work to my large family who have inspired and motivated me to take interest in science.

#### ABSTRACT OF THE DISSERTATION

## Evaluating the Effects of Organic Amendment Applications on Nitrous Oxide Emissions From Salt-Affected Soils

by

Namratha Pulla Reddy Gari

Doctor of Philosophy, Graduate Program in Soil and Water Sciences University of California, Riverside, December 2013 Dr. David M. Crohn, Chairperson

Soil salinization and greenhouse gas emissions are major global environmental concerns. The extent of salinization and associated negative effects on soils and crop yields make the reclamation of these soils an international priority. With increasing interest in the use of organic amendments for remediating salt-affected soils, it is important to investigate their interactive effects on soil biogeochemical processes including greenhouse gas emissions, particularly carbon dioxide (CO<sub>2</sub>) and nitrous oxide (N<sub>2</sub>O). The objectives of this dissertation are to: 1) evaluate the effects of soil salinity, temperature, and carbon availability from organic amendments on CO<sub>2</sub>, N<sub>2</sub>O, and N<sub>2</sub> emissions; 2) determine the effect of changes in salinity and temperature on soil mineral N concentration from salt-affected soils following organic amendment applications; and 3) determine whether CO<sub>2</sub> and N<sub>2</sub>O emissions under field conditions were comparable qualitatively to those observed in the laboratory incubation studies. Organic amendments

used in this research included: active greenwaste (AGW), cured greenwaste compost (CGW), active dairy manure (ADM), and cured dairy manure compost (CDM). The methods used in this research included monitoring  $CO_2$  and  $N_2O$  emissions, estimating  $N_2$  emissions using acetylene block technique, and analysis of soil mineral N concentrations in the laboratory and field studies.

Results from laboratory incubations showed that increases in soil salinity enhanced cumulative  $N_2O$ -N losses but decreased cumulative  $CO_2$ -C and  $N_2$  emissions and  $N_2$  to  $N_2O$ -N ratios. Increases in soil temperatures greatly enhanced cumulative  $CO_2$ -C,  $N_2O$ -N, and  $N_2$  emissions and ratios of  $N_2$  to  $N_2O$ -N from all treatments. In the field, results validated the laboratory findings that active organic materials, particularly AGW, reduced  $N_2O$  emissions compared to cured amendments. In general, dairy manure amendments produced higher  $N_2O$  emissions relative to the greenwaste treatments. In both laboratory and field studies, soils amended with greenwaste materials had lower soil nitrate concentrations compared to those treated with dairy manure amendments.

Overall, this work showed that soil salinization resulted in greater  $N_2O$  emissions following organic amendment applications. Nitrous oxide emissions are dependent on climatic conditions (*e.g.*, precipitation and temperature), soil properties (*e.g.*, electrical conductivity, microbial respiration, and nitrate concentration), organic amendment properties (*e.g.*, feedstock and processing stage), and their interactions.

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#### **1. LITERATURE REVIEW**

Soil degradation is a major widespread environmental constraint with severe negative effects on agricultural productivity. According to Global Assessment of Human-induced Soil Degradation (GLASOD), 1964 Mha of land is degraded globally with 46% under moderate and 16% under strong and extreme levels of degradation (Oldeman, 1994). Soil degradation can occur due to physical (*e.g.*, erosion, desertification, and slaking), chemical (*e.g.*, acidification, alkalinization, salinization, and nutrient depletion), and biological (*e.g.*, depletion of soil organic carbon and decline in biodiversity) processes (Lal et al., 2004).

## **Soil Salinization**

Soil salinization is considered to be the second largest cause of land degradation after soil erosion by the United Nations Environmental Program (UNEP). Saline soils are characterized by excess levels of carbonates, bicarbonates, chlorides, and sulfates of sodium and calcium in the soil solution sufficient to adversely impact plant growth and development. Salt-affected soils occur in more than 100 countries and pose a serious economic problem as they decline agricultural productivity. These soils are more common in arid and semi-arid regions of the world due to the low precipitation and high evaporative demands prevalent in these areas (Pitman and Läuchli, 2002). In addition,

anthropogenic activities such as improper land and water management practices particularly irrigation with poor quality water and lack of drainage systems also contribute to soil salinization. The total area of salt-affected soil is about 950 million hectares (Rengasamy, 2006). It is estimated that nearly 20% of the global and 25-30% of the United States irrigated land is salt-affected (Nelson and Maredia, 2001; Wichelns, 1999).

Salt-affected soils are classified into three categories based on the electrical conductivity of saturated soil paste extracts (EC<sub>e</sub>) and sodium adsorption ratio (SAR): (i) Saline soils having EC<sub>e</sub> > 4 dS m<sup>-1</sup> and SAR < 13; (ii) Sodic soils with EC<sub>e</sub> < 4 dS m<sup>-1</sup> and SAR > 13; and (iii) Saline-Sodic soils with EC<sub>e</sub> > 4 dS m<sup>-1</sup> and SAR > 13 (Richards, 1954). Excessive salts in the soil have detrimental effects on plant growth and yield by limiting plant-available water and or by inducing ion toxicity. Several soil physical, chemical, and biological properties are influenced by soil salinity and or sodicity. These include reduced water and nutrient holding capacity, depressed soil infiltration rates, poor soil aggregation, low cation exchange capacity, and inhibited microbial activity (Lauchli and Grattan, 1990; Tejada et al., 2006).

The seriousness and extent of soil salinization problems around the world necessitates urgent solutions to abate their spread, particularly in arid and semi-arid regions. For many countries, a key to reducing food insecurity will be to effectively ameliorate salt-affected soils to improve their productivity, especially in areas where irrigation infrastructures have been well established (Qadir et al., 2006). Over the past

century, many different approaches including chemical amendments, particularly gypsum, tillage operations such as deep plowing, and irrigation strategies have long been used to reclaim salt-affected soils with varying results (Amezketa et al., 2005; Oster et al., 1996). More recently, organic amendments such as manures and composts, varying in their levels of processing and characterization, have been investigated for their reclamation as a low-cost alternative to chemical amendments (Liang et al., 2005; Tejada et al., 2006). It has been demonstrated that the application of organic amendments to saline soils can improve crop yields, as well as soil properties such as fertility, structural stability, bulk density, water infiltration, microbial biomass, and enzymatic activities (Lakhdar et al., 2008; Liang et al., 2003; Liang et al., 2005; Tejada et al., 2006).

While the effects of soil salinization on soil physical, chemical, and biological properties have been well studied, their effects on greenhouse gas emissions such as carbon dioxide ( $CO_2$ ) and nitrous oxide ( $N_2O$ ), particularly when being reclaimed using organic amendments remain relatively unexplored.

## **Nitrous Oxide Emissions**

There are several natural and anthropogenic sources of atmospheric  $N_2O$ including oceans, biomass burning, industrialization, and soil. Of these, however, soils are identified as a major source of global  $N_2O$  emissions with 6.6 Tg yr<sup>-1</sup> from natural soils and 4.2 Tg yr<sup>-1</sup> from agricultural soils out of an estimated total of 17.7 Tg yr<sup>-1</sup> from all sources (IPCC, 2001). In the United States, average  $N_2O$  emissions from agricultural soils were approximately 0.79 Tg in 2011 of which cropland accounted for 0.4 Tg, a 21% increase since 1990 (EPA, 2013). In 2005, California Energy Commission (CEC) estimated that about 64% of total N<sub>2</sub>O emissions come from agricultural soils. The reliability of this estimate is uncertain, however, due to a lack of sufficient field measurements in California and to the high spatial and temporal variability of N<sub>2</sub>O fluxes from soils.

#### **Environmental Impact of Nitrous Oxide**

Nitrous oxide can directly contribute to greenhouse effect by absorption of infrared radiation thereby trapping thermal radiation emitted from the earth's surface. The global Warming Potential (GWP) concept originally developed by IPCC is an index that relates the climate impacts of a greenhouse gas emission to that of an equivalent mass of  $CO_2$  produced (IPCC, 2001). In 2013, the GWP of  $N_2O$  was estimated at 310 times that of  $CO_2$  and approximately 15 times that of  $CH_4$  over a 100-year period by the United States Environmental Protection Agency (U.S.E.P.A). Its efficiency in trapping light in the infrared region makes it important as a greenhouse gas. Nitrous oxide is a stable and potent greenhouse gas with an atmospheric lifetime of 120 years and plays an important role in stratospheric chemistry (EPA, 2013).

Ozone losses result in higher intensity of UV-B radiation reaching the earth's surface. As a precursor to  $NO_x$  gases which include nitric oxide (NO) and nitrogen dioxide (NO<sub>2</sub>), nitrous oxide (N<sub>2</sub>O) plays a vital role in regulating stratospheric ozone chemistry. Several studies have reported the depletion of stratospheric ozone with

increased N<sub>2</sub>O concentrations (Bouwman, 1990; Crutzen, 1979; Crutzen and Ehhalt, 1977; Hahn and Junge, 1977). The ozone depletion potential of a chemical (ODP), defined as the amount of ozone depletion caused by a compound relative to that caused by trichlorofluoromethane (CFC-11), was estimated for N<sub>2</sub>O to be 0.017 by Ravishankara et al. (2009). This value is comparable to an ODP of less than 0.02 documented for many Class II ozone-depleting substances including hydrochlorofluorocarbons (HCFCs) such as HCFC-123,124, 225ca and 225cb (IPCC, 2005; WMO, 2007) that are currently being included in the Montreal Protocol, an international treaty designed to reduce and or eliminate the production and consumption of ozone depleting substances responsible for the depletion of the ozone layer (UNEP, 2010).

Apart from depleting the ozone layer,  $N_2O$  emissions from soils reduce the efficiency of the applied nitrogen (N) fertilizer thereby reducing the soil N pool available for plant uptake. The origin of this gas from agricultural soils is primarily attributed to the anaerobic reduction of nitrate by denitrifying microorganisms; however, aerobic oxidation of ammonium *i.e.* nitrification also contributes to  $N_2O$  emissions (Blackmer et al., 1980; Bremner and Blackmer, 1978; Bremner and Blackmer, 1979).

## Nitrogen Cycle and N<sub>2</sub>O Emissions

Nitrogen is an essential nutrient present in all living organisms including soil microbes such as bacteria and fungi within cells where it is bound in proteins and DNA. Mineralization is a biological process by which free  $NH_4^+$  is formed from the decomposition of organic N compounds by microbes. A two-step process known as

nitrification further oxidizes  $NH_4^+$  to  $NO_2^-$  and subsequently to  $NO_3^-$ . Immobilization of N which involves the incorporation of inorganic N to organic N forms may also occur, thus altering the dynamics of soil N. As a general rule, substrate C:N exceeding a threshold value of 25:1 have been shown to immobilize N whereas those with lower C:N ratios are associated with net N mineralization (Janssen, 1996).

Nitrogen immobilization, mineralization, and nitrification processes occur under aerobic conditions in which heterotrophic microorganisms utilize the available C and N in the substrate to meet their metabolic needs. Under anaerobic conditions, however, NO<sub>3</sub><sup>-</sup> can be reduced to N<sub>2</sub> gas during the process of biological denitrification, commonly considered as the last step in soil N cycle. Denitrification is a respiratory pathway performed by a variety of facultative aerobic and heterotrophic microorganisms such as Archaea, bacteria, and fungi with most denitrifiers falling under four major genera: *Pseudomonas, Alcaligenes, Bacillus,* and *Flavobacterium* (Tiedje, 1988). The pathway for complete denitrification involves the reduction of NO<sub>3</sub><sup>-</sup> to N<sub>2</sub> gas through a series of intermediate by-products including nitrogen dioxide (NO<sub>2</sub>), nitric oxide (NO), and nitrous oxide (N<sub>2</sub>O) catalyzed by a range of reductase enzymes (Tiedje, 1988). Denitrifiers thus utilize NO<sub>3</sub><sup>-</sup> and N oxides as terminal electron acceptors instead of O<sub>2</sub> in the electron transport phosphorylation to synthesize energy. Denitrifiers mainly depend on the substrate and its availability to produce N<sub>2</sub>O or N<sub>2</sub>. Both nitrification and denitrification are known to regulate  $N_2O$  production in soils (Davidson et al., 1986). Nitrous oxide is predominantly produced during biological denitrification of  $NO_3^-$  to  $N_2$  gas as an intermediate byproduct. Despite the strong role of soil microorganisms, several abiotic factors including soil properties regulate fluxes of  $N_2O$  (Bremner and Shaw, 1958).

### Influence of Soil Properties on N<sub>2</sub>O Emissions

A wide array of soil factors can be identified as potentially significant to the formation of  $N_2O$ , including soil texture (Groffman and Tiedje, 1991; Sexstone et al., 1985; Skiba and Ball, 2002), pH (Firestone et al., 1980; Focht, 1974; Goodroad and Keeney, 1984), moisture (Maag and Vinther, 1996; Zheng et al., 2000), temperature (Goodroad and Keeney, 1984; Maag and Vinther, 1996; Smith et al., 1998), and organic matter (Aulakh et al., 1991; Chang et al., 1998; Huang et al., 2004; Meng et al., 2005).

#### Texture

Soil texture largely influences denitrification by controlling aeration and water holding capacity. In general, coarse textured soils contain more macropores and are therefore well aerated compared to fine textured soils that contain more micropores. Oxygen is a direct and dominant abiotic regulator of denitrification and clay soils can easily become anaerobic than loamy and sandy soils (Papendick and Campbell, 1981) thereby causing greater N<sub>2</sub>O production in fine textured soils. Groffman and Tiedje (1991) found higher denitrification rates in clay loam soils even under well-aerated

conditions compared to loam soils. Also, increase in clay content has been shown to increase water holding capacity of soils (Gupta and Larson, 1979). Sexstone et al. (1985) documented an increase in denitrification rates in clay loam soil than in a sandy loam soil due to the ability of clay loam soils to retain water for longer duration.

#### pН

Although denitrification can occur in both acidic and basic soil environments, the optimum pH for denitrification is considered to be 6 to 8 (Bremner and Shaw, 1958). Several studies have demonstrated that denitrification rates are highly correlated with soil pH and increase linearly with increase in pH from 4 to 8 (Struwe and Kjøller, 1994; Wijler and Delwiche, 1954). Bremner and Blackmer (1978) reported that the influence of  $NO_3^-$  on  $N_2O$  emissions is substantially enhanced by soil acidity. Firestone et al. (1980) likewise observed that acid soils produced greater  $N_2O$  emissions than those with neutral or alkaline pH. This is likely due to high sensitivity of the terminal reductase enzymes to low soil pH resulting in the accumulation of denitrification intermediates such as  $N_2O$  (Focht, 1974).

#### Moisture

Soil moisture is a direct and dominant regulator of denitrification in soils. The rate of nitrification and the activity of microbial population is often high in soils following a wetting event (Birch, 1958; Griffiths and Birch, 1961). In general, increases in soil moisture increase denitrification from soils. This can be inferred from several studies. Aulakh et al. (1991) demonstrated that WFPS is a better determinant of

denitrification than overall soil water content. Denitrification follows a hysteresis response to soil wetting and drying cycles. Groffman and Tiedje (1988) showed that denitrification rates sharply increased following a wetting cycle and decreased during the drying process. Denitrification rates substantially increased as soil wets from 20-60% WFPS and further wetting of soils to field capacity and saturation did not enhance denitrification to a greater extent. Several authors have demonstrated that incipient denitrification appears to have a threshold value of 60% WFPS and at approximately 80% WFPS, most N gas flux occurs as N<sub>2</sub> (Aulakh et al., 1991; Davidson et al., 1991; Parton et al., 1988). Weier et al. (1993) found that ratios of N<sub>2</sub> to N<sub>2</sub>O increased with increasing WFPS from 60-90% in silt loam soils and the conversion of N<sub>2</sub>O to N<sub>2</sub> was more profound in treatments receiving greater carbon additions.

#### *Temperature*

Temperature both plays an important role in regulating the nitrification process and has a profound effect on N<sub>2</sub>O emissions from the denitrification process. Goodroad and Keeney (1984) showed increased rates of nitrification and N<sub>2</sub>O production with increasing temperatures from 10 to 30° C. They concluded that under isothermal constant moisture conditions, N<sub>2</sub>O production was proportional to nitrate production and that 0.1-0.2% of the nitrified N was evolved as N<sub>2</sub>O in dry, well-structured soils. Keeney et al. (1979) reported increased denitrification rates with temperature above 15°C with an optimum of 60°C. They reported that at 40°C, N<sub>2</sub>O comprised up to 88% of the total  $(N_2O+N_2)$  gas evolved. However, in laboratory studies using a silt loam soil, Lensi and Chalamet (1982) observed that an optimum temperature for denitrification was between 37-45°C, which is a temperature range more typical of soil environments in arid and semi-arid climates, particularly Southern California, where salt-affected soils are commonly found; however, at these temperatures conditions are such that moisture is limiting. Furthermore, the simultaneous effect of soil salinity and temperature on  $N_2O$ emissions is still unknown.

#### Soil Salinity

Typically, microbial biomass and activity are concentrated in the top few centimeters of soil profile (Lavahun et al., 1996; Murphy et al., 1998). Hence, salinization near the soil surface is likely to affect a series of microbiologically mediated processes. Many researchers have reported on the interaction between salt accumulation and soil microbial activity. Some investigations on the effect of soil salinity on soil microbial properties have been shown to suppress soil microbial communities and their biochemical activities (Rietz and Haynes, 2003; Yuan et al., 2007). Nitrification rates have also been shown to decrease with increasing soil salinity due to reduced N mineralization (McClung and Frankenberger, 1985; Pathak and Rao, 1998).

Soil salinity negatively affects nitrification thereby reducing the accumulation of  $NO_3^-$ , so it may also influence denitrification by inhibiting microbial activity and associated enzyme activity. Ruiz-Romero et al. (2009) reported that under anaerobic conditions, N<sub>2</sub> production was larger compared to N<sub>2</sub>O in a loamy sand soil with EC 12.5 dS m<sup>-1</sup> than in a sandy clay loam soil with EC 56 dS m<sup>-1</sup>. This suggests that under moderately saline conditions, more N<sub>2</sub>O was reduced to N<sub>2</sub> due to active synthesis of N<sub>2</sub>O reductase enzyme by denitrifying bacteria, thereby reducing the N<sub>2</sub>O emissions. In case of the highly saline soils (EC 56 dS m<sup>-1</sup>), production of N<sub>2</sub>O was enhanced indicating a decreased N<sub>2</sub>O reductase enzyme activity (Ruiz-Romero et al., 2009).

While decreased ammonification and nitrification rates are considered to be the primary effects of soil salinity on N dynamics, information on the effects of saline soils amended with organic materials on nitrification, denitrification rates, and associated  $N_2O$  emissions is scant. Because denitrifiers are hetereotrophic microorganisms that obtain energy from available C (Tiedje, 1988), addition of organic C is likely to promote the denitrification process.

#### Influence of Organic Amendments on N<sub>2</sub>O Emissions

Organic amendments directly contribute to the release of  $N_2O$  from C and N compounds present in them. They may also produce  $N_2O$  indirectly through their effects on various physical, chemical, and biological properties of soils. Organic carbon compounds in the added amendments serve as a source of electron donors for energy and synthesis of cellular constituents for many soil microorganisms including nitrifiers and denitrifers. As most denitrifiers are heterotrophic bacteria, the process of denitrification is strongly correlated to the availability of soil carbon.

Nitrous oxide is produced in soils by nitrification and denitrification. Because these processes require  $NO_3$ -N and organic C, applying organic materials to soil may result in increased  $N_2O$  production due to enhanced mineralization. Several studies have reported increased rates of denitrification with the application of organic matter to soils in the form of plant residues, green manures, and farm yard manures compared to unamended or mineral N treated soils (Anderson and Levine, 1986; Ding, 2007; Meng et al., 2005). This is because application of easily decomposable organic matter results in increased demand for nitrate as electron acceptor due to depletion of soil  $O_2$ concentration during decomposition (Anderson and Levine, 1986). Therefore, in soils abundant in mineral N, increased amount of easily decomposable C is more conducive to denitrification.

The production of N<sub>2</sub>O from soils treated with organic materials depends on their mineralization potential. Overall, the most important factor to consider while selecting an organic amendment is the C:N ratio because it influences rates of net mineralization, immobilization, and denitrification (Aulakh et al., 1991). Vigil and Kissel (1991) reported that applying residues with a low C:N ratio encouraged mineralization, but applying residues with a higher C:N ratio enhanced N immobilization. Several researchers documented reduced N<sub>2</sub>O emissions following incorporation of organic materials with high C:N ratios due to N immobilization (Baggs et al., 2000; Hao et al., 2001; Velthof et al., 2002). McKenney et al. (1993) demonstrated that denitrification rates depend on the C:N ratio of the crop residue. They investigated the denitrification rates from hairy vetch (Vicia villosa Roth), red clover (Trifolium pretense L.), annual ryegrass (Lolium temulentum), and corn which varied in C:N ratio from 11 to 66. In a 5day aerobic incubation study preceding the denitrifying conditions, they documented 5-17 fold increases in gaseous N losses from soils treated with residues at rates of 5-10 mg kg<sup>-1</sup> compared to the unamended control with greatest N losses from hairy vetch and lowest from corn amended soils. Furthermore, application of organic materials with high C:N ratios in N limited soils resulted in decreased denitrification losses due to N immobilization (Huang et al., 2004; Yo and Hatano, 2007). Abundant research on the effects of organic matter additions on N<sub>2</sub>O emissions have been conducted in non-saline soils. However, the interactive effects of salinity and organic amendments on  $N_2O$ emissions are still unknown.

Soil salinity is one of the many factors affecting C and N mineralization rates by directly influencing microbial activity. However, the effect of increased salinity on N mineralization has been a subject of controversy. Reitz and Haynes (2003) documented decreased N mineralization rates at higher soil salinity levels whereas Laura (1974) concluded that soil salinity even up to 5.1% salt addition did not inhibit ammonification. However, Pathak and Rao (1998) demonstrated that addition of *Sesbania Cannabina* to saline soils stimulated N mineralization up to salinity levels of 70 dS m<sup>-1</sup> and thereafter N mineralization was negatively correlated with salinity. They also demonstrated that soil enzymes such as protease, amidases, and deaminases involved in N mineralization were still active at high salt concentrations. Furthermore, Khoi et al. (2006) found that soil salinity adversely affected N mineralization rates for a short duration and increased at a later stage likely due to the recovery and adaptation of soil microbes to osmotic stress. Since N<sub>2</sub>O production is positively correlated to soil NO<sub>3</sub><sup>-</sup>-N content (Mosier et al., 1983), we may assume that soil salinity and N<sub>2</sub>O emissions are also related.

While several studies have investigated the effects of incorporation of organic amendments on greenhouse gases and documented enhanced  $N_2O$  emissions from nonsaline soils, it is unknown however, if denitrification rates increase in salt-affected soils following application of organic amendments. Additionally, the effect of soluble salts on microbial activity is influenced by soil moisture content and temperature. At low soil moisture levels, dissolved ions are concentrated; at high soil moisture levels, dissolved ions are diluted in the soil solution. This affects the availability of water and substrate to the microbial cells. Microorganisms such as bacteria and fungi adapt to increases in soil

salinity either by accumulating solutes (*e.g.*, ammonium and potassium) necessary for their metabolism in their cytoplasm or by selectively excluding salt ions (*e.g.*, sodium and chloride) from their cells to maintain osmotic balance with their surrounding soil solution (Killham, 1994). Furthermore, addition of organic amendments influence soil properties such as water holding capacity, aeration, pH, and substrate availability that are key regulators of denitrification. Therefore, it is also important to understand and relate the impact of applying degradable organic matter such as manures and composts to saltaffected soils on properties that influence N<sub>2</sub>O production.

As the United States seeks to develop more low-cost alternative methods to remediate salt-affected soils, vast acreages of these soils are expected to be reclaimed with organic amendments in lieu of inorganic amendments. In order to minimize the ecological impact of reclaiming these arid lands, it is critical to evaluate the contribution of various organic and inorganic amendments to the greenhouse gas emissions such as nitrous oxide and carbon dioxide.

This work examines the effect of incorporating organic amendments varying in their characterization on carbon dioxide, nitrous oxide, and dinitrogen gas emissions from salt-affected soils in Southern California. Chapter 2 quantifies the effects of soil salinity in governing greenhouse gas emissions by regulating the C and N dynamics of the added organic amendments. Specific objectives of chapter 2 are: 1) to evaluate the effects of soil salinity on N<sub>2</sub>O and CO<sub>2</sub> emissions and N<sub>2</sub> to N<sub>2</sub>O ratios following the addition of organic amendments; and 2) to investigate the impact of labile carbon availability from

active and cured organic amendments on the conversion of  $N_2O$  to  $N_2$  gas. Chapter 3 examines the impacts of varying temperatures on greenhouse gases, specifically addressing the objectives of: 1) examining the effect of extreme salinity and sodicity on  $CO_2$ ,  $N_2O$ , and  $N_2$  emissions; 2) investigating organic amendment effects on the N dynamics of a saline-sodic soil; and 3) determining how a varying soil temperature altered these processes. Chapters 2 and 3 are laboratory experiments. Lastly, chapter 4 focuses on evaluating  $N_2O$  and  $CO_2$  emission rates from an extreme saline-sodic soil under field conditions and the role of active and cured materials in regulating these greenhouse gases.

The different approaches used to study the role of organic amendment amelioration of salt-affected soils allow us to evaluate the impact of active and cured forms of organic amendments on greenhouse gas emissions. These approaches at varying scales from laboratory experiments under controlled conditions to field-scale patterns help advance our understanding of the impact that these organic amendments have on mitigating N<sub>2</sub>O emissions. This is essential to make informed decisions prior to further encouraging large scale use of organic amendments to remediate salt-affected soils.

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## 2. EFFECTS OF SOIL SALINITY AND CARBON AVAILABILITY FROM ORGANIC AMENDMENTS ON NITROUS OXIDE EMISSIONS

## Abstract

Soil salinity negatively affects the mineralization and nitrification processes of the N cycle and may also affect the production of nitrous oxide (N<sub>2</sub>O) and N<sub>2</sub> to N<sub>2</sub>O-N ratios. Application of organic amendments such as manures and composts improve soil physical, chemical, and biological properties of salt-affected soils. However, because these materials both mineralize N and serve as substrates for denitrifiers, they may also increase N<sub>2</sub>O emissions. We studied the effect of organic amendments applied to saline soils on N<sub>2</sub>O emissions and on N<sub>2</sub> to N<sub>2</sub>O-N ratios. Saline soils with EC<sub>e</sub> measures of 2.8, 15.2, and 30.6 dS m<sup>-1</sup> were collected from Coachella Valley, California. Treatments included four organic amendments: active greenwaste compost (AGW), cured greenwaste compost (CGW), active dairy manure compost (ADM), and cured dairy manure compost (CDM). Treatments were incorporated at 50 Mg ha<sup>-1</sup> and incubated at 65% water-filled pore space (WFPS) for 60 days at 25°C. Evolving CO<sub>2</sub>-C and N<sub>2</sub>O-N were monitored along with soil ammonium (NH<sub>4</sub><sup>+</sup>-N) and nitrate (NO<sub>3</sub><sup>--</sup>N) concentrations.

The results showed that increasing soil salinity increased cumulative N<sub>2</sub>O-N losses but decreased CO<sub>2</sub>-C and N<sub>2</sub> emissions and N<sub>2</sub> to N<sub>2</sub>O-N ratios. Of all the amendments, the highest cumulative N<sub>2</sub>O-N and N<sub>2</sub> emissions were produced from the ADM treatment at all three salinity levels. In general, incorporation of active compared to cured amendments increased N<sub>2</sub> to N<sub>2</sub>O-N ratios at all three salinity levels suggesting that applying active organic materials could be useful in mitigation of N<sub>2</sub>O emissions from salt-affected soils under remediation.

## Introduction

Global warming and soil salinization are major international concerns. With an ever growing population, there is an increasing need to bring more agricultural land under production to feed people. Unfortunately development, erosion, and other pressures are reducing the earth's arable land. The problem is particularly acute in drylands where overgrazing and deforestation have led to salinization, associated problems of soil fertility, crusting, compaction, and widespread desertification (Dregne, 1983; Singh, 2009). It is estimated that more than 800 Mha of land is salt-affected globally (Martinez-Beltran and Manzur, 2005). Re-desertification of reclaimed lands can also occur if poor quality irrigation water is applied (Banin and Fish, 1996). Reclamation involves leaching after amending soils with organic materials such as manures and composts, or inorganic materials such as gypsum and sulfur. This removes salts and improves soil physical, chemical, and biological properties (Tejada et al., 2006). The extent of salinization and the rate of increase in salt-affected lands make reclamation and maintenance of these soils an international priority.

Soil amendment use also affects the emission of nitrous oxide ( $N_2O$ ), a potent gas that contributes to both global warming and ozone depletion. Nitrous oxide has been singled out as the most significant anthropogenic ozone depleting compound (Ravishankara et al., 2009). With an estimated 120-year global warming potential 310 times higher than CO<sub>2</sub>, N<sub>2</sub>O accounts for approximately four percent of United States greenhouse gas emissions (EPA, 2013). This high potency makes even relatively small changes in N<sub>2</sub>O emissions potentially significant.

The production of  $N_2O$  from agricultural soils is mostly due to the anaerobic reduction of nitrate by denitrifying bacteria. Denitrification, which contributes both  $N_2$ and  $N_2O$ , is promoted by anaerobic conditions and the presence of organic substrates for the denitrifiers. Significant  $N_2O$  emissions are most likely to occur under reduced oxygen conditions where soil nitrate concentrations are greater than 5 mg  $NO_3$ <sup>-</sup>-N kg<sup>-1</sup> dry soil, and soil temperatures exceed 5°C (Bremner and Blackmer, 1979; Bremner and Shaw, 1958). The rate of  $N_2O$  emission from soils is normally a function of soil moisture, temperature, substrate supply, and structure; but under saline conditions the influence of salts on processes such as nitrification and denitrification should also be considered (Bremner and Shaw, 1958). It is also important to understand and relate the impact of applying N enriched degradable organic matter, such as manures and composts, on soil properties that influence  $N_2O$  production including the availability of C sources as substrates for denitrifying microorganisms (Patten et al., 1980).

Many researchers have reported on the interaction between salt accumulation and soil microbial activity. Investigations have shown that saline conditions broadly suppress soil microbial communities and their biochemical activities (Rietz and Haynes, 2003; Yuan et al., 2007). Decreases in mineralization of organic C and N with increasing salt concentrations are well documented (Laura, 1974; McClung and Frankenberger, 1985; Pathak and Rao, 1998) but specific information on the effects of saline soils amended

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with organic materials on nitrification, denitrification, and associated  $N_2O$  emissions is lacking. Typically, organic matter and microbial activity are concentrated in the top few centimeters of soil profile (Lavahun et al., 1996; Murphy et al., 1998). Hence, salinization near the soil surface is likely to affect many microbiologically mediated processes including the microbial production of  $N_2O$  in soils.

Given the interest in the use of organic amendments for remediating salt-affected soils, their effects on greenhouse gas emissions particularly  $N_2O$ , merits study. The objectives of this study were therefore:

- to evaluate the effects of soil salinity on N<sub>2</sub>O and CO<sub>2</sub> emissions and N<sub>2</sub> to N<sub>2</sub>O-N ratios following the addition of organic amendments; and
- to investigate the impact of labile carbon availability from active and cured organic amendments on the conversion of N<sub>2</sub>O to N<sub>2</sub> gas.

## **Materials and Methods**

#### **Site Description and Experimental Treatments**

Soils samples from three different salt-affected areas were collected from an abandoned field site in California's Coachella Valley  $(33^{\circ} 35' 30.5'' \text{ N}, 116^{\circ} 06' 20.7'' \text{ W})$ . The soils were characterized as fine-silty, mixed, superactive, calcareous, hyperthermic Aquic Torriorthents. The site had been fallowed for at least 5 years due to salinity issues. Samples from three areas with different EC<sub>e</sub> properties (2.8, 15.2, and 30.6 dS m<sup>-1</sup>) were

collected from 0-15 cm depth, air-dried in the greenhouse, and passed through a 2 mm sieve. Particle size analysis using hydrometer method (Gee and Bauder, 1986) for the three soils indicated that the soils were clay loam in texture. Physical and chemical characteristics of the three soils used in this study are given in Table 2.1.

Four organic amendments were considered as treatments in this study: active greenwaste (AGW), cured greenwaste compost (CGW), active dairy manure (ADM), and cured dairy manure compost (CDM). The greenwaste amendments were collected from a commercial greenwaste composting facility located in California. The AGW was comprised of plant material from local roadside cuttings and was collected from an actively managed two-week old turned windrow. The CGW was collected from a screened cured compost storage pile that had also undergone 10 weeks of active windrow composting. Treatments ADM and CDM were collected from actively managed two-week old on-farm compost storage piles, respectively, at a dairy farm in California. Samples of all treatments were air-dried in a greenhouse at 20° C until moisture contents stabilized. The air-dried samples were then milled using a Wiley mill to pass through a 4 mm sieve. Chemical characteristics of treatments are presented in Table 2.2.

#### **Incubation Experiment**

The three soils used in this study were pre-incubated at 40% WFPS in the dark at 24±1°C for two weeks prior to adding the organic amendments. The mass of water required to achieve the desired WFPS was calculated using the following equation (Carter, 1993):

$$\theta_g \text{ at } \% \text{ WFPS } = \frac{WFPS \times \left(1 - \frac{\rho}{2.65}\right)}{\rho}$$
 Equation 1

where, WFPS is the fraction of total pore space filled with water (%),  $\theta_g$  at % WFPS is the gravimetric soil water content at respective WFPS (g water g<sup>-1</sup> soil),  $\rho$  is the bulk density of the soil (g cm<sup>-3</sup>), and 2.65 is the soil particle density (g cm<sup>-3</sup>). During the course of incubation, containers were weighed periodically and water was added on a gravimetric basis to maintain the desired WFPS.

Separate experiments were setup to: 1) determine soil mineral N; and 2) monitor  $CO_2$  and  $N_2O$  emissions from saline soils treated with organic amendments. Nitrogen mineralization was studied in 1 L glass jars containing 250 g of air-dried soil while  $CO_2$  and  $N_2O$  emissions were studied within 100 mL glass serum bottles containing 25 g of air-dried soil. All organic amendments (AGW, CGW, ADM, and CDM) were incorporated into the soil at an application rate of 50 Mg ha<sup>-1</sup> while control treatments received no organic amendment. The soil and amendments were mixed thoroughly and packed to achieve a bulk density of 1.25 g cm<sup>-3</sup>, a value similar to observed field conditions (Table 2.1). The soil water was maintained at 65% WFPS as this has been

shown to facilitate N mineralization and also result in denitrification losses (Maag and Vinther, 1996). The 1 L jars were closed using lids with a 1 cm diameter hole in the center to facilitate aerobic conditions while limiting excessive soil moisture loss. Three replicates of each of the five treatments and three soil types were prepared for the 1 L jars while six replicates of the same were prepared for 100 mL serum bottles. Incubations were sustained for 60 days in the dark at  $24\pm1^{\circ}$ C to best represent mean daily temperatures in the arid and semi-arid regions such as California.

#### **Soil and Gas Sampling Procedures**

Soil and gas samplings were conducted on Days 0, 4, 7, 11, 15, 20, 25, 32, 37, 45, 53, and 60 days from the commencement of the incubations. Inorganic N ( $NH_4^+$ -N and  $NO_3^-$ -N) was determined by colorimetry on extractions obtained with 2M KCl (ratio 1:5).

For the determination of  $CO_2$  and  $N_2O$  emissions, 100 mL incubation serum bottles were aerated for 30 s to remove any traces of  $CO_2$  and  $N_2O$  built-up previously and also to facilitate proper oxygenation of the environment. The bottles were then sealed with rubber septa and aluminum crimp seals for a period of 4 hrs. Of the six replicates prepared for each treatment, three replicates were injected with 10% v/v acetylene ( $C_2H_2$ ) while the other three replicates did not receive  $C_2H_2$ . After 4 hrs, the headspace air was mixed twice using a 30 mL gas syringe to remove any internal air stratification. A 30 mL gas sample was collected and injected into pre-evacuated 20 mL headspace vials and then analyzed within 72 hrs of sampling for  $CO_2$  and  $N_2O$ . Carbon dioxide was measured using an infrared gas analyzer (Model EGM-4, PP-Systems, Amesbury, Massachusetts) while N<sub>2</sub>O was measured using a HP 5790 A Gas Chromatograph (Hewlett- Packard Co., Fullerton, California) fitted with an electron capture detector with oven and injection temperatures set at 50 °C and a detector temperature of 300 °C. Standards were injected after every 10 samples to assure instrument precision.

#### **Statistical Analysis**

Cumulative emissions for CO<sub>2</sub>-C, N<sub>2</sub>O-N, and N<sub>2</sub> were calculated by linear interpolation of daily measurements across consecutive sampling days. Emission rates for each time interval were assumed equal to the average of the emissions measured at the beginning and end of that interval. Two-way analysis of variance (ANOVA) was conducted to determine significant differences (p < 0.05) for cumulative CO<sub>2</sub>-C, N<sub>2</sub>O-N, and N<sub>2</sub> emissions, soil NO<sub>3</sub><sup>-</sup>-N, and NH<sub>4</sub><sup>+</sup>-N concentrations between different soils and treatments. The effect of soil salinity and organic amendments on cumulative emissions for CO<sub>2</sub>-C, N<sub>2</sub>O-N, and N<sub>2</sub>, N<sub>2</sub> to N<sub>2</sub>O-N ratios, and soil mineral N over time was tested by performing repeated measures ANOVA. Tukey's multiple comparison tests were used to statistically separate the significant differences between various soil salinity levels and organic amendment treatments. Linear and multiple regression analyses were used to examine the relationships between cumulative CO<sub>2</sub>-C, N<sub>2</sub>O-N, and N<sub>2</sub> emissions and N<sub>2</sub> to N<sub>2</sub>O-N ratios. All statistical analyses were conducted using SPSS 20.0 software.

## Results

ANOVA results for the effects of soil salinity and organic amendment application on cumulative CO<sub>2</sub>-C, N<sub>2</sub>O-N, and N<sub>2</sub>, N<sub>2</sub> to N<sub>2</sub>O-N ratios, and soil NO<sub>3</sub><sup>-</sup>-N concentrations are reported in Table 2.3.

## **Emission of CO<sub>2</sub>**

## Effect of Salinity

Across the incubation period, soil respiration decreased significantly (P < 0.05) with increase in soil salinity in all treatments (Fig. 2.1). Elevated daily emissions of CO<sub>2</sub> occurred between weeks 3-8 for all treatments and gradually decreased over the incubation period. Controls had the lowest daily and cumulative CO<sub>2</sub> emissions over the 60 day period which ranged from 3.4-19.0 mg C kg<sup>-1</sup>. Cumulative CO<sub>2</sub> emissions ranged from 19.0-101.1 mg C kg<sup>-1</sup> for S3, 10.3-70.7 mg C kg<sup>-1</sup> for S15, and 3.4-51.0 mg C kg<sup>-1</sup> for S30 soils (Fig. 2.1). For all organic amendments, increased soil salinity resulted in decreased CO<sub>2</sub> emissions by 28-38% from S3 to S30.

#### Effect of Organic Amendments

Addition of organic amendments significantly (P < 0.01) increased the daily  $CO_2$ emissions regardless of whether the soil was from a high or low salinity level. Over the incubation period, AGW and ADM resulted in consistently higher  $CO_2$  emissions compared to CGW and CDM. Cumulative  $CO_2$  emissions across the three soil salinity levels from AGW were 1.3-1.6 times higher than from CGW while ADM losses were approximately twice that of CDM. Compared to the composted amendments (CGW and CDM), uncomposted amendments (AGW and ADM) significantly (P < 0.05) increased CO<sub>2</sub> production (Fig. 2.1). Applying AGW resulted in 25, 30, and 39% increase in CO<sub>2</sub> emissions relative to CGW amendment in S3, S15, and S30 salinity levels, respectively. Similarly, increase in CO<sub>2</sub> production of 49, 53, and 54% was recorded with the application of ADM compared to CDM amendment in S3, S15, and S30 salinity levels, respectively (Fig. 2.1).

## Emission of N<sub>2</sub>O and N<sub>2</sub>

#### Effect of Salinity

Increases in soil salinity significantly (P < 0.05) increased cumulative N<sub>2</sub>O-N but decreased N<sub>2</sub> emissions (P < 0.01) from all treatments over the incubation period. The highest peak daily loss of N<sub>2</sub>O was observed in S3 soils followed by S15 and S30 during weeks 3-5 of the incubation period. For the controls across the three salinity levels, cumulative N<sub>2</sub>O emissions ranged from 2.6-4.5  $\mu$ g N kg<sup>-1</sup>. Regardless of the treatment, compared to S3 soils, an increase in cumulative N<sub>2</sub>O-N production by 18-25 % for S15 soils and 34-87% for S30 soils was observed after the 60 day incubation period (Fig. 2.2).

Increases in soil salinity decreased cumulative  $N_2$  production from all treatments. Peak daily  $N_2$  emissions were observed in weeks 3-5 of the incubation period. Cumulative  $N_2$  emissions for the controls ranged from 4.9-14.3 µg N kg<sup>-1</sup>. Compared to S3 soils, percent reduction in cumulative N<sub>2</sub> production ranged from 14-54% for S15 soils and 44-62% for S30 soils (Fig. 2.3). Regardless of the treatment, the ratios of N<sub>2</sub> to N<sub>2</sub>O-N were significantly (P < 0.01) decreased in S15 and S30 relative to S3 soils. The ratios of N<sub>2</sub> to N<sub>2</sub>O-N ranged from 2.2-9.5 for S3, 0.8-5.2 for S15, and 0.6-3.9 for S30 soils (Fig. 2.4).

#### Effect of Organic Amendments

Regardless of the EC<sub>e</sub> of the soil, application of organic amendments significantly (P < 0.05) increased N<sub>2</sub>O emissions. In all three soils, higher N<sub>2</sub>O production was observed from the dairy manure compared to the greenwaste amendments. In case of greenwaste as organic amendment, incorporation of cured material (CGW) ultimately produced higher N<sub>2</sub>O emissions compared to the active amendment (AGW). In contrast, for dairy manure as organic amendment, active material (ADM) resulted in higher N<sub>2</sub>O emissions relative to the cured material (CDM). Cumulative N<sub>2</sub>O-N emissions using CGW compared to AGW amended soils increased by 25, 22, and 46% for S3, S15, and S30 soils, respectively. Soils amended with ADM, however, increased cumulative N<sub>2</sub>O emissions relative to CDM by 12, 15, and 21% for S3, S15, and S30 soils, respectively (Fig. 2.2).

At all three soil salinity levels, incorporation of organic amendments resulted in a significant (P < 0.01) increase in N<sub>2</sub> production. Incorporation of active materials, AGW and ADM resulted in significantly (P < 0.01) greater N<sub>2</sub> production compared to the cured materials, CGW and CDM. Dinitrogen (N<sub>2</sub>) gas emissions from active organic

amendments ranged from 207.4-552.7  $\mu$ g N kg<sup>-1</sup> while those from cured organic amendments ranged from 77.0-222.9  $\mu$ g N kg<sup>-1</sup> across the three salinity levels. Application of CGW compared to AGW reduced N<sub>2</sub> emissions by approximately 51% while incorporation of CDM relative to ADM decreased N<sub>2</sub> production by 70, 84, and 62% for S3, S15, and S30 soils, respectively (Fig. 2.3).

Application of organic amendments significantly (P < 0.05) decreased the ratios of N<sub>2</sub> to N<sub>2</sub>O-N with increasing salinity. Though ratios for CGW exceeded AGW initially in S3 soils, ultimately the active materials, AGW and ADM increased the N<sub>2</sub> to N<sub>2</sub>O-N ratios as high as 2.9 and 5.4 times compared to their respective cured materials, CGW and CDM. Ratios of N<sub>2</sub> to N<sub>2</sub>O-N for active materials ranged from 1.3-9.5 while those for cured materials ranged from 0.6-3.7 (Fig. 2.4).

#### **Inorganic** N

#### Effect of Salinity

At the commencement of the incubation (Day 0), all three soils had similar amounts of NO<sub>3</sub><sup>-</sup>-N and NH<sub>4</sub><sup>+</sup>-N. After 60 days of incubation, the amount of soil NO<sub>3</sub><sup>-</sup>-N (Fig 2.5) and mineral N significantly decreased (P < 0.01) with increases in soil salinity. No trend was observed for NH<sub>4</sub><sup>+</sup>-N alone (data not shown). Across the incubation period, for the controls, the NO<sub>3</sub><sup>-</sup> concentrations gradually decreased in S15 and S30 but increased in S3 soils. The mineral N content at the end of the incubation did not significantly differ among the three control soils varying in EC<sub>e</sub>.

#### Effect of Organic Amendments

In all three soils, NO<sub>3</sub><sup>-</sup>-N, NH<sub>4</sub><sup>+</sup>-N, and mineral N concentrations after the 60 day incubation period differed significantly (P < 0.01) between the organic amendment treatments. Regardless of soil EC<sub>e</sub>, AGW and CGW showed marked decrease in NO<sub>3</sub><sup>-</sup>-N and mineral N concentrations during the first 28 days while the decrease with ADM and CDM was recorded only during the first 10 days (Fig. 2.5). For all three soils, addition of AGW and CGW significantly decreased the soil NO<sub>3</sub><sup>-</sup>-N (Fig 2.5) and mineral N (data not shown) content compared with ADM and CDM. Greater NO<sub>3</sub><sup>-</sup>-N concentrations were observed for the ADM and CDM treatments compared to the AGW and CGW amendments. At Day 60, compared to S3 soils, NO<sub>3</sub><sup>-</sup>-N and mineral N concentrations for S15 and S30 soils amended with greenwaste decreased by 16-33% and reduction with dairy manure by 4-17% were recorded (Fig. 2.5).

## Relationship between CO<sub>2</sub>, N<sub>2</sub>O, N<sub>2</sub>, and Soil Inorganic N Concentrations

Soil salinity significantly (P < 0.05) and negatively correlated ( $r^2 > 0.56$ ) with soil NO<sub>3</sub><sup>-</sup>-N concentrations. Cumulative N<sub>2</sub>O-N and N<sub>2</sub> emissions and total denitrification losses (N<sub>2</sub>O+N<sub>2</sub>) were significantly and positively correlated (0.45 <  $r^2 \le 0.88$ ; P < 0.05) with cumulative CO<sub>2</sub>-C emissions and soil NO<sub>3</sub><sup>-</sup>-N concentrations (0.55 <  $r^2 \le 0.81$ ; P < 0.01) at S3, S15, and S30 salinity levels. However, weaker and negative correlations between N<sub>2</sub> to N<sub>2</sub>O-N ratios and cumulative CO<sub>2</sub>-C production (0.28<  $r^2 \le 0.46$ ) and soil NO<sub>3</sub><sup>-</sup>-N concentrations (0.40 <  $r^2 \le 0.68$ ) were observed at S3, S15, and S30 salinity levels (Table 2.4).

## Discussion

## **Production of CO<sub>2</sub>**

Soil salinity significantly and negatively affected cumulative  $CO_2$ -C emissions suggesting an increased osmotic stress on the soil microbial communities causing a reduction in their activity (Fig. 2.1). Several authors have reported reduced soil respiration rates with increasing soil EC<sub>e</sub> (Laura, 1974; McCormick and Wolf, 1980; Pathak and Rao, 1998).

Curves representing cumulative CO<sub>2</sub>-C emissions with time at all three salinity levels indicate that soil amendments AGW and ADM had higher cumulative CO<sub>2</sub>-C evolution than CGW and CDM (Fig. 2.1). The C substrates in AGW and ADM amendments were decomposed more rapidly than in CGW and CDM which had stabilized during curing. This trend for increased CO<sub>2</sub>-C emissions from uncured materials was similar to that reported by Tejada et al. (2006). Cook and Allan (1992) also reported that the labile organic matter fraction is the most degradable and therefore, highly susceptible to mineralization. This may also indicate the presence of greater labile C fraction in AGW and ADM than in CGW and CDM.

Also, our results at each salinity level using regression analysis showed that cumulative CO<sub>2</sub>-C emissions significantly and positively correlated with soil NO<sub>3</sub><sup>-</sup>-N concentrations, cumulative N<sub>2</sub>O-N, and N<sub>2</sub> emissions. Stepwise regression used to identify the factors affecting CO<sub>2</sub>-C emissions in our study indicated that soil NO<sub>3</sub><sup>-</sup>-N, cumulative  $N_2O$ , and  $N_2$  emissions together accounted for nearly 75% of variability. Microorganisms active in denitrification and the N mineralization rely on organic substrates for energy and generate  $CO_2$  as waste product. The remaining variability is contributed by the degree to which heterotrophs release N at different rates depending on their own needs and substrate characteristics and possibly to the chemotrophic nature of the nitrification process (Robertson and Groffman, 2007).

#### **Inorganic N**

Excessive amounts of salts are known to affect microbiological processes such as C and N mineralization which are crucial for the decomposition of organic matter. It has been well established that processes such as N mineralization and nitrification decrease with increasing soil salinity (Laura, 1977; McClung and Frankenberger, 1985). In addition, studies have shown that when soils are amended with high C:N organic materials, soil microbes assimilate the available N into their biomass and utilize it to decompose the added materials (Parton et al., 2007; Taylor et al., 1989). For amendments such as AGW and CGW which are relatively low in N, N was immobilized immediately after the amendments were applied thereby reducing the concentration of NO<sub>3</sub><sup>-</sup>-N, a substrate for N<sub>2</sub>O production during denitrification. In the high N treatments (ADM and CDM) however, more NO<sub>3</sub><sup>-</sup>-N was available after Day 10 and therefore soils amended with these organic materials resulted in greater N<sub>2</sub>O emissions (Fig. 2.5). A strong correlation was observed between mineral N and N<sub>2</sub>O and N<sub>2</sub> emissions at 65%

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WFPS which was also consistent with a study by Bremner and Blackmer (1981) who found positive correlation between mineral N and N<sub>2</sub>O emissions.

## Production of N<sub>2</sub>O and N<sub>2</sub>

Nitrous oxide is produced during N transformations in the soil through two important biological processes: nitrification in the presence of aerobic conditions and denitrification under anaerobic conditions. In this study, aerobic conditions were maintained in the headspace and soil moisture content was adjusted to 65% WFPS to drive the N transformation towards nitrification process (Maag and Vinther, 1996). Although aerobic conditions were maintained throughout our study, denitrification losses can still occur due to the presence of anaerobic microsites in soil aggregates (Müller et al., 2004).

There was also a decrease in N<sub>2</sub> to N<sub>2</sub>O-N ratios with increasing soil EC<sub>e</sub>. The NO<sub>3</sub><sup>-</sup>-N in soil is the electron-acceptor for denitrifiers responsible for N<sub>2</sub>O and N<sub>2</sub> emissions and elevated N<sub>2</sub>O and N<sub>2</sub> emissions are generally associated with greater soil NO<sub>3</sub><sup>-</sup>-N concentrations. In this incubation study however, we observed higher cumulative N<sub>2</sub>O-N emissions from S30 soils which had lower soil NO<sub>3</sub><sup>-</sup>-N concentrations compared to S3 and S15 soils. In contrast, greater cumulative N<sub>2</sub> emissions were noticed in S3 soils followed by S15 and S30 soils suggesting that the reduction of N<sub>2</sub>O to N<sub>2</sub> was decreased with increasing in soil salinity (Fig 2.3). Nearly all N<sub>2</sub>O produced was reduced to N<sub>2</sub> in S3 soils. It is likely that osmotic stress at the higher salinity levels may have slowed the denitrifiers responsible for reducing N<sub>2</sub>O to N<sub>2</sub> or alternatively salts may have

interfered with N<sub>2</sub>O reductase activity or its de novo synthesis. A trend of increased cumulative N<sub>2</sub>O-N and decreased N<sub>2</sub> emissions with increasing soil salinity was similar to that observed by Ruiz-Romero et al. (2009) who found elevated N<sub>2</sub>O emissions in soils with EC<sub>e</sub> 56 dS m<sup>-1</sup> compared to 12 ds m<sup>-1</sup>.

Substrate availability also affects N cycling. The ratios of N<sub>2</sub> to N<sub>2</sub>O-N were higher for AGW and ADM compared to CGW and CDM amendments (Fig. 2.4). Positive correlations for cumulative CO<sub>2</sub>-C emissions and N<sub>2</sub> to N<sub>2</sub>O-N ratios at all three salinity levels suggest that substrate availability limited the reduction of N<sub>2</sub>O to N<sub>2</sub>, particularly in the cured materials. The higher N<sub>2</sub> to N<sub>2</sub>O-N ratios for active amendments is most likely due to increased support of the microbial biomass due to the bioavailability C from these treatments compared to the cured amendments resulting in enhanced reduction of N<sub>2</sub>O to N<sub>2</sub> via denitrification (Firestone and Davidson, 1989; Huang et al., 2004).

Denitrification is an anaerobic process, but Müller et al. (2004) found that even under aerobic conditions  $NO_3^-$  reduction is responsible for  $N_2O$  production in a grassland soil. Their study demonstrated that with 15-21%  $O_2$  concentration in the entire soil profile, denitrification was still responsible for  $N_2O$  emissions. Observations from our incubation study are also consistent with those reported by McKenney et al. (1993) who showed that addition of organic residues resulted in higher denitrification rates in aerobic than in anaerobic conditions. Production of  $CO_2$  may be a factor in the development of anaerobic microsites thereby encouraging denitrification (Huang et al., 2004). Active organic amendments such as AGW and ADM resulted in greater cumulative  $CO_2$ -C

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emissions and total denitrification losses compared to their respective cured amendments, CGW and CDM. Measurements using acetylene inhibition technique which blocks the further reduction of  $N_2O$  to  $N_2$  via denitrification also confirms the contribution of denitrification as the primary process responsible for  $N_2O$  and  $N_2$  emissions in our study. Although conditions in our incubation study were controlled to favor nitrification, anaerobic microsites likely were present due to enhanced oxygen consumption following the addition of organic amendments and or saturated soil aggregates (Cannavo et al., 2004; Leffelaar, 1986) and should be further investigated.

Organic amendments used for remediating salt-affected soils are often applied repeatedly to the same field. Continual applications could eventually result in more N being mineralized and released into soils than with single application. We did not consider the effect of multiple applications of organic amendments in this study. In addition, N release rates and C decomposition from active and composted organic materials widely vary over time. Therefore, long-term experiments with multiple organic amendment applications would help to evaluate N<sub>2</sub>O and N<sub>2</sub> emissions from active and composted greenwaste and dairy manure materials.

## Conclusions

Incorporation of organic amendments derived from greenwaste and dairy manure to salt-affected soils significantly affected soil CO<sub>2</sub>, N<sub>2</sub>O, and N<sub>2</sub> emissions. Cumulative CO<sub>2</sub>-C and N<sub>2</sub> emissions decreased with increasing soil salinity. In contrast, enhanced cumulative N<sub>2</sub>O-N emissions were recorded as the EC<sub>e</sub> of soil increased. The production of N<sub>2</sub> was larger than N<sub>2</sub>O-N from active amendments (AGW and ADM) compared to cured amendments (CGW and CDM) resulting in high N<sub>2</sub> to N<sub>2</sub>O-N ratios even in soil with EC<sub>e</sub> of 30.6 dS m<sup>-1</sup>. The main factor related to enhanced N<sub>2</sub> emissions was greater cumulative CO<sub>2</sub>-C emissions from active organic amendments which promoted the completion of the denitrification process. Therefore, use of active organic amendments to remediate salt-affected soils can prove to be beneficial in mitigating  $N_2O$  emissions. However, further field research must be conducted to evaluate management practices such as application rates to determine long-term effects of these added amendments on trace gas emissions. Although uncured amendments were shown to reduce  $N_2O$ emissions by promoting the production of N<sub>2</sub>, once in the soil these materials will eventually stabilize and their performance may converge to follow the N cycling patterns observed for the cured materials.

Doromtor	Non-Saline	Saline	Highly Saline	
r aranner	(\$3)	(S15)	(S30)	
Sand (%)	25.8	29.4	26.3	
Silt (%)	40.0	32.5	37.2	
Clay (%)	34.2	38.1	36.5	
Bulk Density (g cm <sup>-3</sup> )	1.22	1.25	1.24	
$EC_e (dS m^{-1})$	2.8	15.2	30.6	
pH	7.86	7.32	7.91	
Total C (%)	1.18	1.38	0.90	
Inorganic C (%)	0.72	0.83	0.48	
Organic C (%)	0.46	0.55	0.42	
Total N (%)	0.12	0.13	0.08	
C:N	10.19	10.49	15.48	
$NO_{3}^{-}-N (mg kg^{-1})$	180.18	175.15	177.39	
$NH_4^+-N (mg kg^{-1})$	2.80	2.47	2.18	
Inorganic N (mg kg <sup>-1</sup> )	182.98	177.62	179.57	

Table 2.1: Soil	physical an	d chemical	properties of to	p 0-15 cm soil layer.

Amendment	Total C (% <del>)</del>	Total N (%)	C:N	$NO_3$ -N (mg kg <sup>-1</sup> )	$NH_4^+-N$ (mg kg <sup>-1</sup> )
Active Greenwaste (AGW)	33.6	0.76	44.2	3.49	19.1
Cured Greenwaste Compost (CGW)	25.7	0.84	30.6	4.42	53.06
Active Dairy Manure (ADM)	30.9	2.37	13.0	8.46	173.06
Cured Dairy Manure Compost (CDM)	13.1	1.15	11.4	31.93	82.72

Table 2.2: Organic amendment properties.

Source	Cumulative CO <sub>2</sub> -C	Cumulative N <sub>2</sub> O-N	Cumulative N <sub>2</sub>	N <sub>2</sub> :N <sub>2</sub> O-N	NO <sub>3</sub> <sup>-</sup> -N	$\mathbf{NH_4}^+$ -N
Soil Salinity (S)	*	*	**	**	**	ns
Organic Amendment (A)	**	*	*	*	**	**
Interaction (S×A)	ns	ns	ns	ns	ns	ns

Table 2.3: Analysis of variance for different parameters as affected by soil salinity and organic amendments.

ns, \*, and \*\* represent no significance, significance at P < 0.05 and P < 0.01, respectively.

Treatment	Pagragion Equation	Combined r <sup>2</sup>	
Treatment	Regression Equation	(adj)	
Cumulative CO <sub>2</sub>	$1.262 - 0.307 \text{ EC}_{e} + 0.043 \text{ NO}_{3}^{-} + 0.099 \text{ N}_{2} + 0.050 \text{ N}_{2}\text{O}$	0.613	
Cumulative N <sub>2</sub> O	$-71.773 + 2.058 \text{ EC}_{e} + 0.349 \text{ NO}_{3}^{-} + 0.093 \text{ N}_{2} + 0.159 \text{ CO}_{2}$	0.653	
Cumulative N <sub>2</sub>	106.364 - 2.341 $EC_e$ - 0.356 $NO_3^-$ + 3.920 $CO_2$ + 1.155 $N_2O$	0.606	
Ratio of N <sub>2</sub> to N <sub>2</sub> O-N	18.018 - 0.220 $\text{EC}_{e}$ - 0.056 $\text{NO}_{3}^{-}$ + 0.015 $\text{N}_{2}$ - 0.040 $\text{CO}_{2}$	0.418	

Table 2.4: Stepwise regression analysis of cumulative CO<sub>2</sub>, N<sub>2</sub>O, and N<sub>2</sub> emissions with soil properties.

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Note: Units for selected variables are reported as: soil electrical conductivity (dS m<sup>-1</sup>); NO<sub>3</sub><sup>-</sup> concentrations (mg N kg<sup>-1</sup>), CO<sub>2</sub> emissions (mg C kg<sup>-1</sup>), and N<sub>2</sub>O and N<sub>2</sub> emissions ( $\mu$ g N kg<sup>-1</sup>).



Fig. 2.1. Cumulative CO<sub>2</sub>-C emissions for different treatments (mean  $\pm$  std. error) from (a) S3 soils, (b) S15 soils, and (c) S30 soils.



Fig. 2.2. Cumulative N<sub>2</sub>O-N emissions for different treatments (mean  $\pm$  std. error) from (a) S3 soils, (b) S15 soils, and (c) S30 soils.



Fig. 2.3. Cumulative  $N_2$  emissions for different treatments (mean  $\pm$  std. error) from (a) S3 soils, (b) S15 soils, and (c) S30 soils.



Fig. 2.4. Ratios of  $N_2$  to  $N_2O-N$  for different treatments (mean  $\pm$  std. error) from (a) S3 soils, (b) S15 soils, and (c) S30 soils.



Fig. 2.5. Soil  $NO_3^-N$  concentration for different treatments (mean  $\pm$  std. error) from (a) S3 soils, (b) S15 soils, and (c) S30 soils.

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# 3. INFLUENCE OF TEMPERATURE AND ORGANIC AMENDMENT APPLICATIONS ON CARBON DIOXIDE, NITROUS OXIDE, AND DINITROGEN EMISSIONS FROM A SALINE-SODIC SOIL

## Abstract

Incorporation of organic amendments such as manures and composts to remediate saline-sodic soils help improve physical, chemical, and biological properties of these soils. However, little is known how organic matter applications to such soils would affect CO<sub>2</sub>, N<sub>2</sub>O, and N<sub>2</sub> emissions and soil N dynamics. The effects of soil temperature and organic matter applications to a saline-sodic soil on CO<sub>2</sub>, N<sub>2</sub>O, and N<sub>2</sub> emissions were investigated. An extreme saline-sodic soil with electrical conductivity (EC<sub>e</sub>) 100 dS m<sup>-1</sup> and pH 7.8 was used in this study. Four organic amendment treatments were selected: active greenwaste (AGW), cured greenwaste compost (CGW), active dairy manure (ADM), and cured dairy manure compost (CDM). All treatments were incorporated at 100 Mg ha<sup>-1</sup> and incubated at 70% water-filled pore space (WFPS) for 60 days at 15, 25, and 35°C. Increases in soil temperature significantly enhanced cumulative CO<sub>2</sub>, N<sub>2</sub>O, and N<sub>2</sub> emissions from all treatments. The emissions of CO<sub>2</sub> increased in the AGW and ADM by 1.5 to 2.2 fold compared to CGW and CDM amended soils at all three temperatures. Higher cumulative N<sub>2</sub>O-N emissions were released from ADM

compared to AGW and CDM compared to CGW treatments at 25 and 35°C, respectively. At 25 and 35°C, AGW and CDM increased N<sub>2</sub> emissions relative to ADM and CGW, respectively. It was found that while soil temperature had a significant effect on CO<sub>2</sub>, N<sub>2</sub>O, and N<sub>2</sub> emissions; CO<sub>2</sub> production alone influenced N<sub>2</sub> emissions indicating that active organic materials could be carefully applied to remediate saline-sodic soils while mitigating N<sub>2</sub>O emissions.
# Introduction

Soil degradation due to salinization is one of the major causes for reduced crop productivity throughout the world (Rengasamy, 2006). In arid and semi-arid regions such as California, low rainfall coupled with intense evaporation enhances salt accumulation in the upper soil profile. Negative effects of excessive salt accumulation on soil physical and chemical properties and microbiological processes have been well documented (Rietz and Haynes, 2003; Wong, et al., 2009). Adverse effects of excessive exchangeable sodium have been shown to decrease structural stability, soil permeability, and infiltration rate (Lauchli and Epstein, 1996). The effects of soil salinity on soil microbial properties include suppression of soil microbial communities and their biochemical activities (Rietz and Haynes, 2003; Yuan, et al., 2007).

In the United States, saline-sodic soils are soils with  $EC_e > 4 \text{ dS m}^{-1}$  and high amounts of soluble Na<sup>+</sup> with SAR >15 (Richards, 1954). Soil used in this study is considered "extreme saline-sodic" as  $EC_e = 100 \text{ dS m}^{-1}$  and SAR >125. Such soils are commonly degraded with poor drainage and structural stability. With nearly 20% of world's arable land and 50% of permanent cropland affected by soil salinization (Flowers and Yeo, 1995), reclamation of these soils to bring them back to productivity has become an international priority. Organic amendments such as manures and composts have been used to remediate salt-affected soils (Liang, et al., 2005; Tejada, et al., 2006; Wahid, et al., 1998). Resulting beneficial effects have been attributed to the introduction of organic matter and associated microbial processes (Pathak and Rao, 1998; Wong, et al., 2009). Soil organic matter is known to influence various physical, chemical, and biological properties of soils. Organic carbon compounds found in manures and composts serve as a source of electron donors for energy and synthesis of cellular constituents for many soil microorganisms including nitrifiers and denitrifers which are sensitive to salt toxicity. Several studies have reported decreased soil microbial processes such as organic matter decomposition and nitrification with increase in salt toxicity (Pathak and Rao, 1998; Tejada, et al., 2006). As most denitrifiers are heterotrophic bacteria, the process of denitrification is strongly correlated to the availability of soil carbon. Therefore, soil salinization may also affect nitrous oxide (N<sub>2</sub>O) production from denitrification processes.

With a global warming potential 310 times higher than  $CO_2$  over a 100-year period, N<sub>2</sub>O is an important greenhouse gas. This high potency makes even relatively small changes in N<sub>2</sub>O emissions potentially significant and atmospheric concentrations have been increasing since 1988 at a rate of 0.8 ppb yr<sup>-1</sup>. In 2006, atmospheric N<sub>2</sub>O concentrations reached 321.8 ppb, 3.2 ppb higher than in 2004 (IPCC, 2007). Several studies have also reported the depletion of stratospheric ozone with increased N<sub>2</sub>O concentrations (Bouwman, 1990; Crutzen, 1979; Crutzen and Ehhalt, 1977; Hahn and Junge, 1977).

Soils are identified as a major source of  $N_2O$  emissions with 6.0 Tg yr<sup>-1</sup> emitted from natural soils and 4.2 Tg yr<sup>-1</sup> from agricultural soils, accounting for nearly 70% of  $N_2O$  produced from the biosphere (IPCC, 2007). Enhanced denitrification rates with the application of organic matter to soils in the form of plant residues, green manures, and farm yard manures in the laboratory and field studies are well documented (Anderson and Levine, 1986; Cabrera, et al., 1994; Coyne, et al., 1994; Ding, 2007; Meng, et al., 2005; Rolston, et al., 1978). For example, Coyne et al. (1994) observed increased  $N_2O$  fluxes accounted for up to 39% of the total N gas flux from manure amended plots compared to plots receiving grass filters. Similarly, Rolston et al. (1978) found that approximately 70% of applied fertilizer was lost via denitrification, primarily as  $N_2$ , from a manured soil.

Several soil factors can be identified as potentially significant to the formation of  $N_2O$ , including soil texture (Vinther, 1992; Weitz, et al., 2001), moisture (Maag and Vinther, 1996; Zheng, et al., 2000), and pH (Eaton and Patriquin, 1989; Focht, 1974; Goodroad and Keeney, 1984; Martikainen, 1985). In addition to the above mentioned factors, temperature has a profound effect in regulating the C and N mineralization, and denitrification processes. Goodroad and Keeney (1984) showed increased rates of nitrification and  $N_2O$  production with increasing temperatures from 10 to 30° C. They concluded that under isothermal conditions,  $N_2O$  production was proportional to nitrate production and that 0.1-0.2% of the nitrified N was evolved as  $N_2O$  in dry, well-structured soils.

High temperature conditions coupled with high concentrations of salts in soil water are likely to impact the existing microbial community thereby affecting the decomposition of added organic amendments and denitrification. Information on the effect of reclaiming extreme saline-sodic soils using organic amendments at varying temperatures on N<sub>2</sub>O and N<sub>2</sub> emissions is lacking however. Heat may affect denitrifiers differently as they decompose available carbon under saline conditions. Because global warming and food production are both critical issues, it is of utmost importance to understand the impact that these organic amendments have on the environment prior to widely using these materials to alleviate soil salinization. We have therefore investigated how the addition of organic amendments varying in their carbon availability to an extreme saline-sodic soil at different temperatures affected the emission of  $CO_2$ , N<sub>2</sub>O, and N<sub>2</sub> in a laboratory experiment. Specific objectives of this research are:

- a) to examine the effect of extreme salinity and sodicity on CO<sub>2</sub>, N<sub>2</sub>O, and N<sub>2</sub> emissions;
- b) to investigate organic amendment effects on the N dynamics of a saline-sodic soil; and
- c) to determine how a varying soil temperature altered these processes.

# **Materials and Methods**

## **Experimental Site**

Soil was collected from the upper 10 cm of a fallow field located in San Jacinto, California (33° 50' 44.2"N, 117 ° 1' 39.6"W). The field has been abandoned for more than 5 years due to high salt content to a depth of 30 cm, poor soil structure, and impaired drainage. Taxonomic classification for this soil is Grangeville coarse-loamy, mixed, superactive, thermic fluvaquentic haploxeroll. The bulk soil samples were air-dried to 30% water holding capacity and sieved through a 2 mm sieve. Soil physical and chemical properties are illustrated in Table 3.1.

#### Treatments

Treatments included Control (no-amendment added) and four organic amendments: active greenwaste (AGW), cured greenwaste (CGW), active dairy manure (ADM), and cured dairy manure (CDM). The AGW and GWC were collected from a commercial greenwaste composting facility located in California. The AGW was comprised of plant material from local roadside cuttings and was collected from an actively managed two-week old turned windrow. The CGW was collected from a screened cured compost storage pile that had also undergone 10 weeks of active windrow composting. Organic amendments ADM and CDM were collected from actively managed two-week old turned windrow and 12-week old on-farm compost storage pile, respectively, at a dairy farm in California. Samples of all treatments were air-dried in a

greenhouse at 20° C until moisture contents stabilized. The air-dried samples were then milled using a Wiley mill to pass through a 4 mm sieve. Chemical characteristics of treatments are presented in Table 3.2.

#### **Laboratory Incubations**

Before treating with amendments, soils were pre-incubated at 40% WFPS in the dark at 25°C for two weeks. The gravimetric water content required to maintain the soils at the desired WFPS was calculated using Eq. 1.

In this study, all treatments including the controls were subjected to three temperature regimes of 15, 25, and 35°C. Soil inorganic N content and CO<sub>2</sub> and N<sub>2</sub>O emissions at each temperature condition were monitored using two different experimental setups. Inorganic N was measured in 1 L jars containing 250 g dry soil while CO<sub>2</sub> and N<sub>2</sub>O production was measured in 100 mL glass serum bottles containing 25 g dry soil. All treatments were uniformly incorporated into the soil at an application rate of 100 Mg ha<sup>-1</sup> and packed to a bulk density of 1.3 g cm<sup>-3</sup>. De-ionized water was used to maintain soil moisture content at 70% WFPS as this has been shown to maximize nitrification and still result in denitrification losses (Maag and Vinther, 1996). Aerobic conditions were maintained for all treatments in each of the experimental setups throughout this study. Three replicates of each treatment were setup for the 1 L jars while six replicates were prepared for the 100 mL serum bottles. Incubations were conducted at 15, 25, and 35°C for 60 days in the dark.

#### **Analytical Methods**

Soil and gas samplings were conducted on Days 0, 1, 3, 5, 9, 14, 20, 26, 33, 40, 50, and 60 days from the commencement of the incubations. Soil inorganic N ( $NH_4^+$ -N and  $NO_3^-$ -N) concentration was determined by colorimetry on 2M KCl (ratio 1:5) extractions.

All containers used to collect gas samples were flushed with air for 30 s to remove previously accumulated trace gases and sealed with rubber septa and aluminum crimps. Acetylene ( $C_2H_2$ ) inhibition technique was used in all treatments including controls to determine the conversion of N<sub>2</sub>O to N<sub>2</sub>. Of the six replicates prepared for measuring CO<sub>2</sub> and N<sub>2</sub>O, three received 99.999% pure C<sub>2</sub>H<sub>2</sub> that was injected to replace 10% of the headspace volume. To promote uniform distribution of the added  $C_2H_2$ , headspace gas was mixed thoroughly using a large syringe. Following a 4 hr sealed incubation, 30 mL gas samples were collected from the headspace using a gas-tight syringe and immediately transferred to 20 mL pre-evacuated gas vials. Samples were analyzed for CO<sub>2</sub> using infrared gas analyzer (Model EGM-4, PP- Systems, Amesbury, Massachusetts) while N<sub>2</sub>O was measured using HP 5790 A Gas Chromatograph (Hewlett- Packard Co., Fullerton, California) fitted with 80/100 mesh Porapak Q column and <sup>63</sup>Ni electron capture detector. Oven and injection temperatures were set at 50 °C and a detector temperature of 300 °C was maintained. Standards were injected after every 10 samples to assure instrument precision.

## **Statistical Analysis**

The statistical analysis was performed using the SPSS version 20.0 software. Linear interpolation of daily measurements across consecutive sampling days was used to assess cumulative CO<sub>2</sub>-C, N<sub>2</sub>O-N, and N<sub>2</sub> emissions. Two-way factorial analysis of variance was used to assess organic amendment and soil temperature effects on cumulative CO<sub>2</sub>-C, N<sub>2</sub>O-N, and N<sub>2</sub> emissions, ratios of N<sub>2</sub> to N<sub>2</sub>O-N, and soil mineral N concentrations. The impact of treatments and soil temperature on the aforementioned parameters over time was tested using repeated measures ANOVA. Significant differences, if any, between various soil temperature levels and organic amendment treatments were separated using Tukey's multiple comparison tests. Correlation matrices and stepwise regression analyses were conducted to examine relationships between soil temperature, CO<sub>2</sub>-C, N<sub>2</sub>O-N and N<sub>2</sub> emissions, ratios of N<sub>2</sub> to N<sub>2</sub>O-N, and soil mineral N concentrations.

# Results

#### **Emission of CO<sub>2</sub>**

#### Influence of Temperature

Soil respiration from all organic amendments was significantly increased (P < 0.05) by elevating temperatures over the incubation period (Fig. 3.1). Daily and cumulative CO<sub>2</sub> emissions increased between 15 and 25°C and 25 and 35°C. Peak daily

 $CO_2$  emission rates were observed from Days 5-14 and gradually decreased thereafter. Cumulative  $CO_2$  production ranged from 4.0-44.8 mg C kg<sup>-1</sup> at 15°C, 14.5-122.2 mg C kg<sup>-1</sup> at 25°C, and 19.7-320.7 mg C kg<sup>-1</sup> at 35°C soils. For all organic amendments, apparent values of  $Q_{10}$  for cumulative  $CO_2$ -C ranged from 2.6-3.2.

### Influence of Organic Amendments

At all three temperatures, organic amendments added to the soil significantly increased (P < 0.05) CO<sub>2</sub> production. Emissions from active materials (AGW, ADM) exceeded those from cured materials (CGW, CDM) at all three temperatures. Cumulative CO<sub>2</sub> emissions across the three temperatures from ADM were 1.8-2.3 times higher than from CDM while AGW losses were approximately 1.6 times that of CGW. Compared to CGW, addition of AGW increased cumulative CO<sub>2</sub>-C emissions by 42, 38, and 35% at 15, 25, and 35°C, respectively. Similarly a 55, 49, and 45% increase in CO<sub>2</sub> production was observed in 15, 25, and 35°C soils respectively, with the application of ADM compared to CDM treatment.

## Emission of N<sub>2</sub>O and N<sub>2</sub>

#### Influence of Temperature

Cumulative N<sub>2</sub>O-N and N<sub>2</sub> emissions were significantly enhanced (P < 0.05) with increasing temperature (Fig. 3.2 and 3.3). Greater N<sub>2</sub>O and N<sub>2</sub> production occurred from all treatments at 35°C while the lowest emissions were observed from soils at 15°C temperature. Apparent Q<sub>10</sub> values for cumulative N<sub>2</sub>O-N emissions ranged from 0.9-4.0

between 15 and 25°C and 1.7-7.3 between 25 and 35°C soils. In case of cumulative  $N_2$  production,  $Q_{10}$  values ranged from 2.4-9.2 between 15 and 25°C and 1.1-3.2 between 25 and 35°C.

Cumulative N<sub>2</sub>O-N production ranged from 1.1-49.1  $\mu$ g N kg<sup>-1</sup> at 15°C, 1.0-194.7  $\mu$ g N kg<sup>-1</sup> at 25°C, and 7.5-351.7  $\mu$ g N kg<sup>-1</sup> at 35°C soil temperature (Fig. 3.2). Cumulative N<sub>2</sub> production ranged from 0.6-51.1  $\mu$ g N kg<sup>-1</sup> at 15°C, 4.0-288.9  $\mu$ g N kg<sup>-1</sup> at 25°C, and 4.7-728.1  $\mu$ g N kg<sup>-1</sup> at 35°C temperature (Fig. 3.3). Regardless of the treatment, the ratios of N<sub>2</sub> to N<sub>2</sub>O-N were significantly (P < 0.05) higher at 25°C and 35°C compared to 15°C. The ratios of N<sub>2</sub> to N<sub>2</sub>O-N ranged from 0.5-1.5 at 15°C, 1.2-4.8 at 25°C, and 0.6-4.1 at 35°C (Fig. 3.4).

## Effect of Organic Amendments

Regardless of the temperature, application of organic amendments significantly (P < 0.05) increased N<sub>2</sub>O emissions. At all three temperatures, CGW and ADM resulted in greater cumulative N<sub>2</sub>O-N emissions relative to their counterparts AGW and CDM respectively (Fig. 3.2). Compared to AGW, application of CGW increased cumulative N<sub>2</sub>O-N emissions by 35, 73, and 24% at 15, 25, and 35°C temperatures, respectively. In contrast, use of CDM as soil amendment decreased cumulative N<sub>2</sub>O-N production by 15, 25, and 30% compared to ADM amended soils at 15, 25, and 35°C, respectively (Fig. 3.2).

At all three temperature levels, incorporation of organic amendments resulted in a significant (P < 0.05) increase in N<sub>2</sub> production. Active amendments (AGW and ADM) produced significantly greater N<sub>2</sub> emissions compared to the cured materials (CGW and CDM) at 25 and 35°C while CGW and ADM produced highest N<sub>2</sub> emissions at 15°C. Across the three temperatures, cumulative N<sub>2</sub> emissions from active amendments ranged from 31.4-728.1 µg N kg<sup>-1</sup> while those from cured treatments ranged from 22.4-467.7 µg N kg<sup>-1</sup>. Of the two active amendments used in this study, AGW produced greater N<sub>2</sub> emissions compared to ADM at 25 and 35°C temperatures. However, at 15°C temperature, an opposite trend was observed with ADM producing more N<sub>2</sub> emissions than AGW. Compared to AGW, incorporation of CGW reduced N<sub>2</sub> emissions by 63, 58, and 47% in soils maintained at 15, 25, and 35°C, respectively. Similarly, application of CDM relative to ADM decreased N<sub>2</sub> production by 48, 21, and 18% at 15, 25, and 35°C, respectively (Fig. 3.3).

Application of organic amendments significantly (P < 0.05) increased the ratios of N<sub>2</sub> to N<sub>2</sub>O-N at all temperatures. Ratios of N<sub>2</sub> to N<sub>2</sub>O-N from active materials ranged from 0.9-4.8 while that for cured materials ranged from 0.5-1.8. Increases in N<sub>2</sub> to N<sub>2</sub>O-N ratios from active materials, AGW and ADM, ranged from 1.3-4.1 times while those from cured materials, CGW and CDM, ranged from 0.8-3.3 fold at 25°C and 35°C relative to 15°C (Fig. 3.4).

## **Inorganic N**

#### Effect of Temperature

Soil mineral N concentration (P < 0.05) was significantly affected by temperature. After 60 days of incubation, the amount of soil NO<sub>3</sub><sup>-</sup>-N and total inorganic N significantly (P < 0.05) increased with increasing temperature (Fig. 3.5 and 3.6). Regardless of the treatment, gradual increase in mineral N was recorded at all temperatures after 26 days into the incubation period. This increase was more pronounced at 35°C followed by 25°C compared to 15 °C (Fig. 3.6). The amount of soil mineral N present after the 60 days incubation in soils amended with organic materials increased by 19-26% between 15 and 25°C and 27-41% between 15 and 35°C.

#### Effect of Organic Amendments

Incorporation of organic amendments significantly (P < 0.05) increased soil  $NO_3^{-}$ -N and  $NH_4^{+}$ -N concentration at all temperatures. Across the incubation period, regardless of soil temperature, lower mineral N concentrations were recorded for AGW and CGW treatments compared to the ADM and CDM amendments (Fig 3.6). Immediately after organic amendment applications, soil  $NO_3^{-}$ -N concentrations were drastically decreased in all treatments. This decreasing trend in AGW and CGW amended soils lasted for 28, 28, and 10 days at 15, 25, and 35°C, respectively. Similar decrease in soil  $NO_3^{-}$ -N concentrations were recorded for ADM and CDM treated soils as well but the decrease only lasted up to 2 weeks at all three temperatures (Fig. 3.5).

# Relationship between CO<sub>2</sub>, N<sub>2</sub>O, N<sub>2</sub>, and Soil Inorganic N Concentrations

Soil temperature significantly and positively correlated with soil NO<sub>3</sub><sup>-</sup>-N concentrations ( $r^2 = 0.67$ ; P < 0.05) and with cumulative CO<sub>2</sub>-C, N<sub>2</sub>O-N and N<sub>2</sub> emissions (0.85 <  $r^2 \le 0.92$ ; P < 0.01). Soil respiration significantly and positively correlated with N<sub>2</sub>O ( $r^2 > 0.71$ ; P < 0.05) and N<sub>2</sub> ( $r^2 > 0.88$ ; P < 0.05) fluxes at each of the sampling times. However, ratios of N<sub>2</sub> to N<sub>2</sub>O-N across all treatments were significantly but weakly explained by temperature and soil respiration (0.42 <  $r^2 \le 0.55$ ; P < 0.05). A combination of soil temperature, soil NO<sub>3</sub><sup>-</sup>, and CO<sub>2</sub> production could explain up to 89% variability while soil NO<sub>3</sub><sup>-</sup>-N concentrations alone accounted for 67% of variation in N<sub>2</sub>O-N emissions (Table 3.3). For N<sub>2</sub> emissions however, a combination of soil temperature and CO<sub>2</sub> evolution accounted for nearly 95% variation of which 93% was explained by CO<sub>2</sub> alone. This suggests CO<sub>2</sub> flux was a better predictor of cumulative N<sub>2</sub> emissions from this salt-affected soil.

## Discussion

## **Production of CO<sub>2</sub>**

Soil respiration and microbial activity are known to be decreased in moderately saline soils ( $EC_e < 15 \text{ dS m}^{-1}$ ) due to increased osmotic stress on soil microbial community (Laura, 1974; McCormick and Wolf, 1980; Pathak and Rao, 1998). However, the production of CO<sub>2</sub> throughout the 60-day incubation period in this study suggests that the heterotrophic microbes were still active even under extremely saline conditions. Evolution of CO<sub>2</sub> was lowest at 15°C and highest at 35°C suggesting that the microbial activity was enhanced at increased temperature (Fig. 3.1). Similar findings were documented by several authors in non-saline soils (Moore and Dalva, 1993, Schaufler, et al., 2010; Schlentner and Cleve, 1985) and our results have demonstrated that this effect holds true even under extremely saline soils. Organic amendments increased soil CO<sub>2</sub> fluxes at all temperatures with significantly higher emissions from AGW and ADM compared to CGW and CDM suggesting that active treatments decomposed more rapidly than the cured counterparts. These findings are consistent with those reported by Tejada et al. (2006) who reported greater cumulative CO<sub>2</sub>-C emissions from saline soils amended with poultry manure compared to cotton gin compost. These results were likely related to the presence of large amounts of labile C in active materials than in cured amendments. The soil used in this study had a pH of 7.8 which is above the threshold carbonate dissociation value of 7.2. This eliminates the possibility of chemical dissociation of soil carbonates and subsequent evolution of CO<sub>2</sub>.

# Production of N<sub>2</sub>O and N<sub>2</sub>

Findings from this study show that organic amendment application had a major influence on  $N_2O$  and  $N_2$  emissions. These results are consistent with other studies that have shown greater  $N_2O$  emissions following organic matter applications (McKenney, et al., 1993; Meng, et al., 2005; Yao, et al., 2010). Positive correlations between  $CO_2$  and  $N_2O$  and  $CO_2$  and  $N_2$  imply that denitrification may have occurred when  $CO_2$  emissions peaked and created temporary anaerobic microsites (Cannavo, et al., 2004; Huang, et al., 2004). In addition, greater availability of C from active treatments than from cured amendments resulted in increased  $N_2$  emissions from AGW and ADM, thereby completing the denitrification process in its entirety.

The availability of N following application of organic amendments is another important factor driving the production of N<sub>2</sub>O. Losses were higher from the dairy manure than the greenwaste amendments which had more readily available N for heterotrophic denitrifiers involved in N<sub>2</sub>O production. At all temperatures considered in this study, consistently greater losses of N<sub>2</sub>O were observed from ADM followed by CDM and CGW while the lowest emissions were from AGW amendment suggesting that ADM and CDM were more prone to mineralization than AGW and CGW treatments. Presumably this difference would be reduced over time as labile compounds in the active materials decompose.

Both N<sub>2</sub>O and N<sub>2</sub> emissions were increased dramatically in all treatments by increasing soil temperature from 15 to 35°C. These results are consistent with other studies that have shown increased denitrification rates with increased soil temperatures (Goodroad and Keeney, 1984; Maag and Vinther, 1996). The apparent  $Q_{10}$  values for N<sub>2</sub>O emissions from various treatments used in this study between 15 and 35°C are in accordance with those reported in the literature which varied from 1.5-3.0 between 10 and 35°C (Jacobson and Alexander, 1980; Knowles, 1982).

Elevated N<sub>2</sub>O and N<sub>2</sub> emissions are associated with greater soil NO<sub>3</sub><sup>-</sup>N concentrations (Weier, et al., 1993). In this study, greater cumulative N<sub>2</sub>O-N emissions were obtained from ADM and CDM compared to AGW and CGW treatments at all three temperature levels. However, corresponding increases in N<sub>2</sub> emissions were not observed for the same treatments. Instead, at 25 and 35°C, greater cumulative N<sub>2</sub> production was observed from AGW and ADM followed by CDM and CGW amendments. There may be two reasonable explanations for this result. First, bioavailability of C may have been higher in active treatments compared to cured treatments as evident from cumulative CO<sub>2</sub>-C emissions (Fig. 3.1). This might have further supported the heterotrophic denitrifies responsible for reduction of N<sub>2</sub>O to N<sub>2</sub> (Huang, et al., 2004). Second, more rapid mineralization of the dairy manure treatments resulted in greater NO<sub>3</sub><sup>-</sup> availability compared to the greenwaste amendments (Fig 3.5). This created a more favorable condition for NO<sub>3</sub><sup>-</sup> reduction to N<sub>2</sub>O in ADM and CDM.

Of the various organic amendments used in this study, at all three temperatures, greater  $N_2$  to  $N_2O$ -N ratios were recorded only for the AGW treatment. This may be explained by the increased availability of C and lower availability of N from AGW than from other treatments. Although higher  $N_2$  emissions were also recorded for ADM, the ratio of  $N_2$  to  $N_2O$ -N did not increase significantly with increasing temperature. This may be attributed to the increased availability of inorganic N from ADM that enhanced  $N_2O$  emissions initially in the incubation period (Table 3.2).

## **Inorganic N**

The effect of higher concentrations of salts in the soil profile have been shown to negatively affect C and N mineralization by inhibiting microbial activity (McClung and Frankenberger, 1985; McCormick and Wolf, 1980). Studies have also shown that when soils are amended with a high C:N organic material containing <1% N, soil microbes immobilize the available N (Parton, et al., 2007; Robertson and Groffman, 2007). It was expected that AGW and CGW amendments both of which had high C:N and < 1% total N, would immobilize available N to a greater extent than ADM and CDM which had lower C:N ratios and > 1% N. The fact that there was significantly higher levels of  $NH_4^+$ -N in ADM compared to CDM and to a lesser extent in CGW than in AGW indicates that ADM and CGW were more biochemically active than CDM and AGW, respectively (data not shown). Although the percentage increase in soil mineral N differed among various organic amendments, there was a rapid increase in  $NH_4^+$ -N in order ADM > CDM > CGW > AGW. This suggests that mineralization of organic matter was greater in dairy manure compared to greenwaste amendments and this drastically increased with increasing temperature (Fig. 3.5).

In this study, all treatments were maintained at 70% WFPS and no leaching occurred throughout the incubation. Therefore, the amount of mineral N measured in organic amended soils during the incubation represents the amount of mineralized N minus the gaseous N losses as N<sub>2</sub>O and N<sub>2</sub> emissions. Both organic amendments AGW and CGW in this study had lower soil mineral N concentrations than the control by Day

28 at 15 and 25°C and Day 7 at 35°C indicating that increasing soil temperature reduced the duration of the immobilization phase in both these treatments (Fig. 3.6). This could have supplied lower amounts of  $NO_3^-$ , a substrate for denitirification, resulting in lower  $N_2O$  emission from AGW and CGW (Fig. 3.2). Similarly, greater availability of soil  $NO_3^-$  from ADM and CDM may have resulted in greater  $N_2O$  emissions as evident by significantly positive correlation between  $NO_3^-$  and  $N_2O$  production. These results are consistent with findings in the literature which indicate positive correlation between soil  $NO_3^-$  levels and denitrification (Bremner and Blackmer, 1981; Weier, et al., 1993).

Remediation of salt-affected soils using organic amendments involves repeated flooding in order to leach excess salts to deeper layers of soil profile (Hanay, et al., 2004). This is usually followed by an extended period of non-irrigated conditions and inversion of top soil by tillage. This tends to widely vary decomposition of the added amendments and dynamics of C and N over time. In this study, the effect of alternate wetting and drying conditions on N<sub>2</sub>O and N<sub>2</sub> emissions was not considered. Therefore, further studies should focus on evaluating the effects of varied moisture conditions on trace gas emissions from the added organic amendments in salt-affected soils.

# Conclusions

Organic amendments can be significant sources of CO<sub>2</sub>, N<sub>2</sub>O, and N<sub>2</sub> emissions. Cumulative CO<sub>2</sub>-C, N<sub>2</sub>O-N, and N<sub>2</sub> emissions were significantly increased at elevated temperatures. In addition, emission of N<sub>2</sub> was greater in active treatments compared to cured amendments. The main factors related to the N<sub>2</sub>O emissions were soil temperature,  $CO_2$  emissions, and soil  $NO_3$  concentrations. Manure amendments with their greater N contents, tended to increase soil NO<sub>3</sub><sup>-</sup> concentrations and associated N<sub>2</sub>O emissions compared to greenwaste treatments at all three temperatures considered in this study. Use of active organic amendments initially reduced N<sub>2</sub>O emissions compared to the application of cured materials, but presumably this benefit would be reduced as the amendments stabilize in the soil and deplete available C over time. Measured N2 to N2O-N ratios were highest at 35°C suggesting that spring applications of organic amendments may impact greenhouse gas emissions by taking advantage of elevated summer temperatures more efficiently than applications in the fall. Labile compounds would be rapidly decomposed to more stable forms resulting in more favorable N<sub>2</sub> to N<sub>2</sub>O-N ratios. Long-term effects of incorporating organic amendments in efforts to remediate saltaffected soils under varying environmental conditions prior to their adoption on a large scale also merits additional study.

Parameter	Value
Sand (%)	43.12
Silt (%)	37.43
Clay (%)	19.45
Bulk Density (g cm <sup>-3</sup> )	1.26
$EC_e (dS m^{-1})$	101.46
pH	8.24
SAR	149.75
Total C (%)	1.27
Total N (%)	0.08
C:N	15.53
$NO_3^{-}-N (mg kg^{-1})$	205.57
$NH_4^+$ -N (mg kg <sup>-1</sup> )	2.37

Table 3.1: Physical and chemical properties of top 0-15 cm soil layer.

Organic Amendment	Total C (%)	Total N (%)	C:N	$NO_3^N$ (mg kg <sup>-1</sup> )	$NH_4^+-N$ (mg kg <sup>-1</sup> )
Active Greenwaste (AGW)	33.60	0.75	44.80	3.82	19.11
Cured Greenwaste Compost (CGW)	31.86	1.08	29.50	5.69	31.39
Active Dairy Manure (ADM)	21.39	1.76	12.15	10.34	123.06
Cured Dairy Manure Compost (CDM)	14.61	1.30	11.24	30.42	82.72

Table 3.2: Characteristics of organic amendments

Treatment	Regression Equation	Combined r <sup>2</sup> (adj)	
Cumulative CO <sub>2</sub>	$152.37 - 0.621 \text{ NO}_3^- + 0.361 \text{ N}_2 + 0.359 \text{ N}_2\text{O}$	0.959	
Cumulative N <sub>2</sub> O	$-305.74 + 1.350 \text{ NO}_3^ 0.225 \text{ N}_2 + 1.007 \text{ CO}_2$	0.895	
Cumulative N <sub>2</sub>	$-308.47 + 1.247 \text{ NO}_3^- + 2.405 \text{ CO}_2 - 0.533 \text{ N}_2\text{O}$	0.949	
Ratio of N <sub>2</sub> to N <sub>2</sub> O-N	1.564 + 0.008 N <sub>2</sub> - 0.012 N <sub>2</sub> O	0.752	

Table 3.3: Stepwise regression analysis of cumulative CO<sub>2</sub>, N<sub>2</sub>O, and N<sub>2</sub> emissions with soil properties.

Note: Units for selected variables are reported as: soil  $NO_3^-$  concentrations (mg N kg<sup>-1</sup>), CO<sub>2</sub> emissions (mg C kg<sup>-1</sup>) and N<sub>2</sub>O and N<sub>2</sub> emissions (µg N kg<sup>-1</sup>).



Fig. 3.1. Cumulative CO<sub>2</sub>-C emissions for different treatments (mean  $\pm$  std. error) in soils incubated at (a) 15°C, (b) 25°C, and (c) 35°C.



Fig. 3.2. Cumulative N<sub>2</sub>O-N emissions for different treatments (mean  $\pm$  std. error) in soils incubated at (a) 15°C, (b) 25°C, and (c) 35°C.



Fig. 3.3. Cumulative N<sub>2</sub> emissions for different treatments (mean  $\pm$  std. error) in soils incubated at (a) 15°C, (b) 25°C, and (c) 35°C.



Fig. 3.4. Ratios of N<sub>2</sub> to N<sub>2</sub>O-N for different treatments (mean  $\pm$  std. error) in soils incubated at (a) 15°C, (b) 25°C, and (c) 35°C.



Fig. 3.5. Soil nitrate-N concentrations for different treatments (mean  $\pm$  std. error) in soils incubated at (a) 15°C, (b) 25°C, and (c) 35°C.



Fig. 3.6. Soil mineral-N concentrations for different treatments (mean  $\pm$  std. error) in soils incubated at (a) 15°C, (b) 25°C, and (c) 35°C.

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# 4. EVALUATING THE EFFECTS OF ORGANIC AMENDMENTS ON NITROUS OXIDE AND CARBON DIOXIDE EMISSIONS FROM A SALINE-SODIC SOIL - A FIELD STUDY

## Abstract

Incorporation of organic amendments to remediate salt-affected soils has been a common practice to improve the physical, chemical, and biological properties of soil. The high amounts of C and N added with their use may pose a threat to the environment in terms of their potential for enhanced greenhouse gas emissions. A field experiment was conducted to evaluate the influence of different organic amendments varying in composting stages on carbon dioxide (CO<sub>2</sub>) and nitrous oxide (N<sub>2</sub>O) emission rates from an extreme saline-sodic soil. Four organic waste amendments were selected: active greenwaste (AGW), cured greenwaste compost (CGW), active dairy manure (ADM), and cured dairy manure compost (CDM). All treatments were incorporated into the soil as a single application at 100 Mg ha<sup>-1</sup>. Gaseous fluxes were measured using a closed chamber method. Organic amendment applications significantly affected CO<sub>2</sub> and N<sub>2</sub>O emission rates compared to the control. Carbon dioxide fluxes were significantly increased with the application of AGW and ADM compared to CGW and CDM, respectively. Daily N<sub>2</sub>O emissions were decreased with the use of AGW compared to CGW, ADM, and CDM treatments. Average daily emission fractions of  $N_2O$  were increased by 66% and 84% in soils incorporated with cured forms compared to active forms of dairy manure

and greenwaste amendments, respectively. Compared to the cured treatments, incorporation of active organic amendments reduced average daily  $N_2O$  emission fractions by 42% most likely by reducing the availability of mineral N as evident by significant correlation matrices between  $N_2O$  fluxes and soil  $NO_3^-$  concentrations. With a global warming potential of 310 times that of  $CO_2$ , even a small reduction in  $N_2O$ emissions with the use of active organic amendments can be considered as a positive impact on the environment.

## Introduction

Soil degradation and salinization are widely recognized as mounting terrestrial sustainability concerns. According to Global Assessment of Human-induced Soil Degradation (GLASOD), nearly 1964 M ha of land is degraded globally. Of these lands, 46% have been identified as moderately impacted and 19% have been greatly degraded (FAO, 2003). The most widespread form of soil degradation is salinization which affects nearly 50% of cropland worldwide (FAO, 2003) and 25-30% of irrigated land in the United States (Wichelns, 1999). Salt-affected soils occur in more than 100 countries, mainly in the arid and semi-arid regions of the world due to the low precipitation rates and elevated evapotranspiration potentials that prevail in these areas.

Salt toxicity not only adversely effects plant growth but also negatively influences the physical, chemical, and biological processes of soil (Rietz and Haynes, 2003; Wahid et al., 1998; Walker and Bernal, 2008; Wong et al., 2009). Increasing soil electrical conductivity (EC) decreases soil enzymatic activities, structural stability, bulk density, soil permeability, and water infiltration (Tejada and Gonzalez, 2006). Because the economic, ecological, and social consequences of soil salinization can be severe, there are widespread efforts to reclaim salt-affected soils that have gone out of production (Lakhdar et al., 2009). A wide array of organic amendments such as manures and composts varying in their characteristics and processing have been evaluated for their effectiveness in remediating salt-affected soils (Lakhdar et al., 2008; Tejada et al., 2006). It is widely known that increases in soil organic C content associated with the application

of organic amendments helps to improve soil properties. Both the amount and composition of the incorporated organic amendments influence the extent to which soil physical, chemical, and biological properties are improved. In soils, organic amendments act as substrates that can stimulate microbial activity even under saline conditions (Pathak and Rao, 1998). Several studies have documented increased structural stability and infiltration rates, reduction in exchangeable sodium percentage and bulk density, and improved soil microbial biomass and enzyme activity with the incorporation of organic amendments (Calderón et al., 2004; Liang et al., 2003; Liang et al., 2005; Tejada and Gonzalez, 2006; Tejada et al., 2006). It has been demonstrated that the improvement in the biological properties of soil, particularly microbial biomass and enzyme activity, are responsible for changes in biochemical processes such as N mineralization and nitrification following organic matter additions in saline soils (Lakhdar et al., 2008; Tejada, et al., 2006).

Agricultural soil is a significant source for two of the most important greenhouse gases: carbon dioxide (CO<sub>2</sub>) and nitrous oxide (N<sub>2</sub>O). Nitrous oxide is a potent greenhouse gas with a 120 year long atmospheric lifetime and a global warming potential (GWP) of 310 (EPA, 2013). In 2011, N<sub>2</sub>O emissions accounted for an estimated 3.7% of total greenhouse gas emissions on a mass basis in the United States; of which 69.3% was attributed to agriculture alone, a 8.5% increase compared to that in 1990 (EPA, 2013). However, the accuracy of these estimates is uncertain due to insufficient field measurements and also the high spatial and temporal variability of N<sub>2</sub>O fluxes from soils. Globally, N<sub>2</sub>O emissions are escalating at an annual rate of 0.2-0.3% and agricultural
$N_2O$  emissions are further expected to increase by 35-60% by 2030 due to increased manure and chemical fertilizer applications essential to feed the ever-growing global population (FAO, 2003).

Increased N<sub>2</sub>O emissions from agricultural soils can be largely attributed to the use of inorganic and organic fertilizers resulting in enhanced soil mineral N. Nitrification and denitrification are the two major processes responsible for N<sub>2</sub>O emissions in soils. Under anaerobic conditions, N<sub>2</sub>O is produced as an intermediate byproduct during the reduction of NO<sub>3</sub><sup>-</sup> and or NO<sub>2</sub><sup>-</sup> to N<sub>2</sub> by heterotrophic denitrifying bacteria in soils (Robertson and Tiedje, 1987). Furthermore, changes in soil properties such as soil moisture, organic C, and N may also result in production of N<sub>2</sub>O via nitrification during oxidation of NH<sub>4</sub><sup>+</sup> to NO<sub>2</sub><sup>-</sup> and further to NO<sub>3</sub><sup>-</sup> (Castaldi and Smith, 1998).

The effects of incorporating organic waste materials into non-saline soils on  $N_2O$  can vary. Studies have shown both increases and decreases in  $N_2O$  emissions following incorporation of organic waste materials such as straw, farmyard manure, greenwastes, and composts (Chang et al., 1998; Dalal et al., 2009; Ding, 2007; Huang et al., 2004). In general, organic amendments with low C:N ratios tend to produce greater  $N_2O$  emissions due to increased N mineralization than those with higher C:N ratios that cause N immobilization, thus controlling  $NO_3^-$  availability for denitrifiers (Huang et al., 2004; Velthof et al., 2003). By contrast, the simultaneous effects of soil salinity and incorporation of organic amendments for the purpose of remediation on  $N_2O$  emissions has not been studied previously.

Salt-affected soils often require leaching with large quantity of water to displace excess salts from soil surface to deeper layers. Poor soil structure and low saturated hydraulic conductivity, commonly associated with saline-sodic soils, results in ponding which in turn creates anaerobic conditions suitable for denitrification. Addition of organic amendments to remediate these soils can further promote denitrification, particularly N<sub>2</sub>O emissions by supplying organic C, a source of food for most denitrifiers which are heterotrophic.

This field study was intended to validate certain conclusions that have been drawn from laboratory incubation experiments. Laboratory incubation studies (Chapters 2 and 3) found that adding organic amendments to salt-affected soils maintained at 65-70% WFPS under controlled temperature conditions increased N<sub>2</sub>O emissions. Results from these 60-day laboratory incubations also showed that application of active materials compared to the cured amendments increased N<sub>2</sub> relative to N<sub>2</sub>O emissions due to the presence of high amounts of labile C. Also, low soil mineral N was observed for high C:N materials compared to the low C:N amendments. This trend was consistent for incubations involving both non-saline and saline soils and at varying temperatures suggesting that the availability of labile C and soil  $NO_3^{-}$ -N are important factors affecting N<sub>2</sub>O production during denitrification. However, it is important to validate these laboratory results with a field study to more fully characterize the benefits of applying active amendments relative to cured amendments. Under field conditions, soils are open to the environment and soil temperatures, wetting patterns, and other factors vary in ways that may not be fully captured using laboratory studies alone. Pulses of high N<sub>2</sub>O fluxes

observed under field conditions are often attributed to changes in soil physical and chemical properties, crop type, climate, and management practices such as irrigation, N fertilization, and incorporation of crop residues (Bouwman et al., 1993).

This study compares how wet and dry soil moisture conditions influence  $CO_2$  and  $N_2O$  fluxes from a saline-sodic soil following organic amendment applications. In the field, soil temperature and moisture conditions change with consequent effects on the C and N dynamics of the added amendments. Wet conditions can increase  $N_2O$  fluxes but the magnitude to which this occurs is controlled by many factors including the availability of C within the feedstock, a property that varies depending on the processing stage of applied organic amendments. Artificial wetting patterns were used in this study to simulate irrigation or precipitation events. However, continuous leaching was not conducted during this study as the goal was to monitor and validate the results found in the laboratory and not to remediate these soils.

The primary objective of this research was therefore to evaluate  $CO_2$  and  $N_2O$ emissions from naturally developed saline-sodic soils treated with organic amendments such as manures and composts applied for the purpose of soil remediation. Specific objectives of this study were:

- a) to assess whether active amendments decrease  $N_2O$  emissions from an extremely saline-sodic soil under varying environmental conditions; and
- b) to investigate how  $CO_2$  and  $N_2O$  fluxes respond to changes in soil moisture and temperature conditions.

Based on my previous laboratory findings, I hypothesize that incorporation of organic amendments to saline-sodic soils in the form of active manures as alternative to cured composts will reduce  $N_2O$  emissions and increase  $CO_2$  fluxes by supplying more readily available labile C. I also hypothesize that low gaseous emission rates will be detected during hot and dry periods compared to the cool and wet periods.

# Materials and methods

### **Site Description and Experimental Treatments**

The field experiment was conducted from April, 2012 to August, 2013 at a fallow site in San Jacinto, California (33° 50' 44.2"N, 117 ° 1' 39.6"W). The site is located in Southern California and this soil is characterized as a Grangeville coarse-loamy, mixed, superactive, thermic fluvaquentic haploxeroll (NRCS, 2012). The climate is semi-arid with an annual average maximum temperature of 27.2 °C, annual average minimum temperature of 9.1 °C, and average annual precipitation of 30.9 cm (WRCC, 2013). The general properties of this soil (0-25 cm) are shown in Table 4.1. The total C and N in the treatments were analyzed using a Thermo Electron Corporation NC soil analyzer, organic matter was determined by loss on ignition method, EC and pH were determined from saturation paste extracts, and mineral N was analyzed in 1:5 extracts using 2M KCl solution. All soil analyses were performed as per the guidelines of standard soil sampling and methods of analysis (Carter, 1993).

The organic amendments considered in this study were: active greenwaste (AGW), cured greenwaste compost (CGW), active dairy manure (ADM), and cured dairy manure compost (CDM). Table 4.2 reports key properties of organic materials used in this study which were analyzed using standard procedures described in the Test Methods for the Examination of Composting and Compost (TMECC) (Thompson et al., 2001). The field experiment consisted of 5 treatments: four organic amendments and an unamended control, arranged in a randomized complete block design with six replications. Plots were  $2x2 \text{ m}^2$  in size. All organic amendments were applied at 100 Mg ha<sup>-1</sup> (dry weight) except for the control which was unamended. Organic amendments were spread manually on 8 April, 2012 and immediately incorporated into the soil to a depth of 15 cm with a rotary tiller.

## **Gaseous Flux Measurements**

Carbon dioxide and N<sub>2</sub>O fluxes were monitored monthly from May 2012 through August 2013. Some measures were conducted under as-found moisture conditions while for others soils were first wetted. In 2012, gaseous fluxes were measured under unwetted conditions on: May 17, June 25, July 27, August 8, September 22, October 4, October 30, November 16, and December 12. During 2013, unwetted condition measurements for N<sub>2</sub>O and CO<sub>2</sub> fluxes were conducted on: January 24, March 27, April 18, June 25, and July 23. Prior to sampling on seven additional dates, wetted conditions for sampling air were created by filling the chambers with 0.75 L of de-ionized water simulating a 1.5 cm irrigation event one day before sampling to better understand the influence of irrigation or abrupt soil moisture changes on gaseous fluxes. Measurements under artificially wetted conditions were conducted in 2012 on: August 29, September 24, October 5, October 19, November 1, November 9, and November 20. It is a common practice to flood salt-affected soils to a depth of 1-2 cm to leach the salts in the cool season during the reclamation process (Bruce Scott, Farmer, 15 May, 2012).

Closed chambers built as per the guidelines provided by Parkin and Venterea (2010) were used to measure trace gas emissions. Briefly, chamber anchor and tops were made using polyvinyl chloride (PVC) pipes. Anchors were made by cutting a PVC pipe section measuring 240 mm i.d x 6.3 mm wall thickness x 152.4 mm deep. One anchor was inserted 10 cm deep into the soil in the center of each plot using a back-hoe 30 days after incorporating the organic amendments and remained undisturbed throughout the study. Chamber tops were made from an identical cylindrical PVC pipe (240 mm i.d., 183 mm height, 6.3 mm wall thickness) and covered with 6.5 mm thick PVC sheet. A 20 mm i.d. sampling port was installed in the center of each chamber top. During sampling, the chamber top was sealed to each anchor with a 10 cm rubber ring which formed a gas-tight seal and butyl rubber septa were used to seal the sampling port.

Before collecting air samples, all chambers were closed for 1 hr. Gas samples were taken immediately after enclosure and again after 1 hr of sealing. Samples were taken using airtight 60 mL syringes and transferred to 20 mL pre-evacuated borosilicate glass vials. After collecting the second sample, the chamber was immediately opened to establish ambient air condition within the chamber (Parkin and Venterea, 2010).

All air samples were analyzed for  $CO_2$  and  $N_2O$  within 48 hrs of collection. Samples were analyzed for  $CO_2$  using infrared gas analyzer (Model EGM-4, PP-Systems, Amesbury, Massachusetts) while  $N_2O$  was measured using HP 5790 A Gas Chromatograph (Hewlett- Packard Co., Fullerton, California) fitted with 80/100 mesh Porapak Q column and <sup>63</sup>Ni electron capture detector. Oven and injection temperatures were set at 50 °C and a detector temperature of 300 °C was maintained (Poth and Focht, 1985). Standards were injected after every 10 samples to assure instrument precision.

Two gas measurements were made in the headspace of each chamber at the start and end of 1 hr of closing and fluxes of  $CO_2$  and  $N_2O$  were estimated as the difference in gas concentration over time. Chamber heights were measured at each sampling and volume of each chamber was calculated. Average daily  $CO_2$ -C and  $N_2O$ -N emissions were calculated as the average of daily measurements across the duration of this study.

## **Average Daily Nitrous Oxide Emission Fractions**

Average daily nitrous oxide emission fractions (AEF) for treatments used in this study were calculated as the fraction of applied N that was lost as observed average daily N<sub>2</sub>O emissions from organic amendments using the following equation:

$$AEF = \frac{(E_t - E_c)}{N_a} \times 100$$
 Equation 2

where, *AEF* is the average daily N<sub>2</sub>O-N emission fraction (g kg<sup>-1</sup>),  $E_t$  is the average daily N<sub>2</sub>O-N emission (g N ha<sup>-1</sup>) from organic waste treated plot,  $E_c$  is the average daily N<sub>2</sub>O-N emission (g N ha<sup>-1</sup>) from untreated control plot, and N<sub>a</sub> is the N applied as organic amendments expressed in kg N ha<sup>-1</sup>.

# Soil Sampling and Analyses

Soil samples were collected from 0-10 cm depth from outside each chamber on the day of each gas sampling in plastic bags and stored at 4°C until further analysis. At the beginning of the irrigation events, soil samples were collected from a 25 x 25 cm<sup>2</sup> area 0.5 m north of the anchors which was also wetted to create soil conditions similar to that inside the anchors.

Soil mineral N was extracted by shaking 10 g of field-moist soils with 50 mL of 2M KCl for 1 hr. Subsequently, the extracts were obtained by filtering the soil slurry through a Whatmann no. 42 paper and analyzed for  $NO_3^-$ -N and  $NH_4^+$ -N concentrations by colorimetry (Carter, 1993).

Soil temperature (0-10 cm) was monitored in five randomly selected plots at the time of gas sampling. Gravimetric water content was determined by drying a sub-sample at 105 °C for 24 hr. Soil bulk density was determined from four undisturbed soil core samples. Soil water content represented as water-filled pore space (WFPS) was determined using Eq. 1 as described by Carter (1993) to understand the effect of varying soil moisture conditions on  $N_2O$  emissions.

## **Data Analysis**

One-way analysis of variance (ANOVA) was conducted to test significant differences in average daily  $CO_2$  and  $N_2O$  emissions, and average soil  $NH_4^+$ -N and  $NO_3^-$ -N concentrations between various treatments. Significant differences, if any, between various organic amendment treatments were separated using Tukey's multiple comparison tests. Linear and multiple regression analysis were performed to identify parameters that significantly regulated gas fluxes. Log-transformation of  $N_2O$  and  $NO_3^$ data was performed to improve the distribution of residuals. All statistical analysis was performed using SPSS 20.0 and graphs were prepared using SigmaPlot 10.0 graphing software.

# Results

Average annual air temperature, precipitation, and irrigation information at the field site from April 2012 through July 2013 are presented in Fig. 4.1. Soil temperature and soil moisture contents during the sampling events are presented in Fig. 4.2. Soil temperatures ranged from 16-27°C from May through September 2012 and June-July 2013 and gradually decreased from October 2012 through April 2013. Under unwetted conditions, soil moistures ranged from 11-35% WFPS. After wetting, soil temperatures were low (8.1-15.3 °C) and soil moisture contents were 68-77% WFPS.

### **Gaseous Emissions**

#### Measured Daily Fluxes

Daily CO<sub>2</sub> and N<sub>2</sub>O fluxes exhibited strong spatial and temporal variations (Figs. 4.3 and 4.4) throughout this study. Application of organic amendments showed significant positive effect (P < 0.05) on CO<sub>2</sub> and N<sub>2</sub>O fluxes. Across both unwetted and wetted conditions, the daily N<sub>2</sub>O fluxes of active materials ranged from 0.02-68.6 g N ha<sup>-1</sup> day<sup>-1</sup> while those from cured amendments ranged from 0.06-88.7 g N ha<sup>-1</sup> day<sup>-1</sup>. The daily CO<sub>2</sub> fluxes of active materials ranged from 0.05-24.9 kg C ha<sup>-1</sup> day<sup>-1</sup> while those from cured amendments ranged from 0.05-24.9 kg C ha<sup>-1</sup> day<sup>-1</sup>.

The highest fluxes were observed soon after artificial wetting periods in dairy manure treatments followed by the greenwaste amendments and the peak heights decreased over the course of the wetting period (Figs. 4.3 and 4.4). In general, daily N<sub>2</sub>O emission rates were lowest in AGW and highest in CDM treatments. The order of treatments for most daily N<sub>2</sub>O emission rates was: CDM > ADM > CGW > AGW while those for CO<sub>2</sub> fluxes were: AGW > ADM > CDM > CGW.

Under unwetted conditions, N<sub>2</sub>O fluxes were detected only from May-September 2012 and June-July 2013. During these periods, addition of organic amendments significantly increased (P < 0.01) N<sub>2</sub>O emissions compared to the controls. However, at each of the sampling days during this study, no significant differences in N<sub>2</sub>O fluxes between treatments were observed with the exception of AGW, the smallest contributor.

Highest  $N_2O$  fluxes were recorded on August 8 and September 22, 2012 (Fig. 4.4). Increases in  $CO_2$  and  $N_2O$  fluxes for the enclosure period (1 hr) were not detected on October 4, October 30, November 16, and December 12, 2012 or on January 24, March 27, and April 18, 2013 and were considered as outliers.

After wetting, CO<sub>2</sub> and N<sub>2</sub>O fluxes were significantly increased by organic amendments compared to the controls on all sampling days. Carbon dioxide fluxes were significantly increased in the AGW and ADM treatments compared to the CGW and CDM amendments. Fluxes of CO<sub>2</sub> ranged from 9.3- 24.9 kg C ha<sup>-1</sup> day<sup>-1</sup> for active materials and 4.0-18.9 kg C ha<sup>-1</sup> day<sup>-1</sup> for cured treatments. Significant (P < 0.05) differences between treatments on N<sub>2</sub>O emission rates occurred only on October 5, November 1, and November 20, 2012. On these sampling occasions, active treatments significantly lowered N<sub>2</sub>O emissions compared to the cured treatments.

#### Average Daily Emissions and Average Daily Emission Fractions

Average daily  $N_2O$  and  $CO_2$  emissions are presented in Table 4.3. Average daily  $CO_2$  emissions were significantly greater from the active treatments compared to the cured amendments. With the active amendments, use of AGW increased average daily  $CO_2$  emissions by 42% relative to CGW while this increase was 62% with the application of ADM compared to CDM. Feedstock types also mattered as incorporation of AGW and CGW increased the average daily  $CO_2$  emissions by 29% and 47% relative to ADM amendments, respectively.

The lowest average daily N<sub>2</sub>O emissions were detected from the AGW treatment and CDM produced the highest average daily N<sub>2</sub>O emissions during this study. Average daily N<sub>2</sub>O emissions were decreased from active treatments compared to their respective cured amendments (Table 4.3). Incorporating AGW and CGW significantly decreased average daily N<sub>2</sub>O emissions by 64% and 34% compared to ADM and CDM, respectively. Between the dairy manure amendments, ADM decreased average daily N<sub>2</sub>O emissions by 22%. Similar reduction in N<sub>2</sub>O emissions were observed with the AGW treatment, with a decrease of 58% relative to the CGW treatment.

Average daily N<sub>2</sub>O emission fractions (AEF), the proportion of applied N released as average daily N<sub>2</sub>O from treatments alone, are also listed in Table 4.3. The mean annual AEF's of N<sub>2</sub>O were on an average increased 1.7 fold from cured treatments compared to the active amendments. Dairy manure treatments contributed significantly (P = 0.03) more N<sub>2</sub>O than the greenwaste amendments. Treatments ADM and CDM increased AEF's by 42% and 27% compared to AGW and CGW amendments, respectively. Between the greenwaste amendments, CGW increased AEF's by 84% relative to AGW. Similarly, CDM enhanced AEF by 66% compared to ADM treatments, among the dairy manure amendments.

## Soil Mineral N

Mean soil  $NH_4^+$  and  $NO_3^-$  concentrations (0-10 cm) are shown in Table 4.3. Application of organic amendments significantly affected (P < 0.05) soil  $NO_3^-$ -N and  $NH_4^+$ -N concentrations compared to the control. No significant (P < 0.05) differences between treatments were observed for average soil  $NH_4^+$  levels. Soil  $NH_4^+$  concentrations for the controls were in the range of 0.07-0.82 kg N ha<sup>-1</sup> while those for active amendments ranged from 0.19-13.58 kg N ha<sup>-1</sup> and for cured treatments from 0.73-16.88 kg N ha<sup>-1</sup>. Compared to treatments AGW and ADM, average soil  $NH_4^+$  levels with the incorporation of CGW and CDM amendments increased by 15% and 53%, respectively.

Treatment effects on NO<sub>3</sub><sup>-</sup>-N concentrations were significant (P < 0.05) throughout this study. The soil NO<sub>3</sub><sup>-</sup>-N concentrations were significantly higher after the addition of amendments, with 2.3 fold and 1.8 fold increases observed in the dairy manure and greenwaste amended plots over those of the control, respectively. The NO<sub>3</sub><sup>-</sup>-N concentrations for CDM and CGW plots were on an average 16% and 12% higher than for the ADM and AGW treatments respectively, over the course of this study (Table 4.3). Lower NO<sub>3</sub><sup>-</sup>-N concentrations were recorded for greenwaste treatments than for the dairy manure amendments. Soil NO<sub>3</sub><sup>-</sup>-N concentrations for ADM and CDM treatments were on an average 33% higher than those in AGW and CGW treatments.

## Relationship between Daily N<sub>2</sub>O Emission Rates and Soil Properties

In general, daily N<sub>2</sub>O fluxes (log-transformed) were significantly and positively correlated with soil moisture, soil NO<sub>3</sub><sup>-</sup>-N concentrations, and daily CO<sub>2</sub> emissions (Table 4.4). A combination of soil moisture and NO<sub>3</sub><sup>-</sup> could explain 66% of variability in N<sub>2</sub>O fluxes. Stepwise regression analysis performed separately for active and cured treatments identified a combination of soil NO<sub>3</sub><sup>-</sup>-N and CO<sub>2</sub> emissions responsible for 48% and 32% of N<sub>2</sub>O flux variations from active and cured treatments, respectively (Table 4.5).

Some relationships applied only to wetted or unwetted conditions. No significant (P < 0.05) relationship between N<sub>2</sub>O flux and soil temperature was observed when the data for unwetted and wetted conditions were considered together but the rate of N<sub>2</sub>O emissions (log-transformed) were significantly correlated with soil temperature (P < 0.05) when unwetted conditions were considered alone. No significant relationship between soil temperature and N<sub>2</sub>O emission rates (log-transformed) existed under artificially wetted conditions. Within the observed WFPS range (15-95%), emission rates of N<sub>2</sub>O (log-transformed) increased with increasing WFPS with a significant correlation.

Under unwetted conditions, rates of N<sub>2</sub>O emission (log-transformed) were significantly (P < 0.01, n = 168) but weakly (0.37 < r < 0.42) correlated with soil moisture and NO<sub>3</sub><sup>-</sup>-N concentrations (log-transformed). In case of the wetted conditions, fluxes of N<sub>2</sub>O (log-transformed) were significantly and positively (P < 0.01, n = 168) correlated with soil moisture and NO<sub>3</sub><sup>-</sup>-N concentrations but also weakly and negatively with CO<sub>2</sub> emissions.

# Discussion

## **Effect of Organic Amendments on Gaseous Emissions**

Incorporating organic amendments increased soil CO<sub>2</sub> fluxes. Significantly higher emissions were observed from active treatments than cured amendments, an observation consistent with the material stability measures (Table 4.2). These results are consistent with those observed in the incubation experiment in Chapter 3 at 15, 25, and 35°C temperatures where in AGW and ADM significantly enhanced CO<sub>2</sub> production compared to the CGW and CDM amendments. Although these incubated and field soils had higher carbonate content, chemical release of CO<sub>2</sub> caused by the dissociation of soil carbonates can be excluded from this study. This is because the soil pH (8.1) of this soil was well above the threshold value of 7.2 for carbonate dissociation.

Daily fluxes of N<sub>2</sub>O under both unwetted and wetted conditions did not differ significantly between CGW, ADM, and CDM treatments (Fig. 4.4). Lower N<sub>2</sub>O fluxes were recorded from AGW throughout the study suggesting that soil NO<sub>3</sub><sup>-</sup> levels were too low and or that the N<sub>2</sub>O produced was converted to N<sub>2</sub> due to the availability of highly labile C. Both these possibilities cannot be excluded as I found similar results in Chapter 3 from AGW amended soils that had low soil NO<sub>3</sub><sup>-</sup> concentrations which resulted in decreased N<sub>2</sub>O production but enhanced N<sub>2</sub> emissions at 25 and 35°C. In this field study, CGW and ADM resulted in similar N<sub>2</sub>O fluxes. Contrastingly, ADM resulted in greater N<sub>2</sub>O emissions than CGW at higher temperatures of 25 and 35°C under laboratory conditions. Daily N<sub>2</sub>O emissions under different treatments in this study were in the order of CDM  $\geq$  ADM  $\geq$  CGW > AGW. In contrast, the general trend in the 60-day incubation study was of the order ADM > CDM > CGW > AGW which suggests that the availability of NO<sub>3</sub><sup>-</sup>-N for denitrification from the CDM was greater than ADM under field conditions. Losses were highest from the dairy manure treatments as N was in readily available NO<sub>3</sub><sup>-</sup> form for denitrifying bacteria as against the greenwaste amendments. Although, soil NO<sub>3</sub><sup>-</sup> concentrations did not differ significantly from October through December 2012 and January through May 2013, the gas fluxes that were considered outliers (zero flux measurements) during this study were likely due to the combined effect of very low soil moisture (11-18 % WFPS) and temperature conditions (8.1-11.6°C). Gas fluxes were increased again in June and July 2013 corresponding to 5 and 0.4 mm rainfall that occurred on June 22 and July 18, 2013, respectively (Fig. 4.1).

Average daily N<sub>2</sub>O emissions from ADM was 30.28 g N ha<sup>-1</sup>, which is significantly lower than the mean daily N<sub>2</sub>O loss of approximately 195 g N ha<sup>-1</sup> reported by Chang et al. (1998) from a non-saline soil incorporated with feedlot manure applied at 104 Mg ha<sup>-1</sup> on a dry weight basis. Average daily N<sub>2</sub>O emissions from cured organic amendments were significantly higher compared to the active treatments suggesting that the availability of NO<sub>3</sub><sup>-</sup>-N, a substrate for denitrification, to soil microorganisms was a driving factor. Compared to CDM, ADM decreased average daily N<sub>2</sub>O emissions by only 22% as opposed to a 58% reduction by AGW relative to CGW (Table 4.3). This suggests that the dairy manure treatments were more prone to mineralization than the greenwaste amendments which likely have high lignin content.

Nitrous oxide in soils is primarily produced by microbial mediated soil processes of nitrification and denitrification which may be altered by organic amendment applications (Ma et al., 2012). Khalil et al. (2002) reported negative correlation between C:N ratios of organic amendments and N<sub>2</sub>O emissions. Application of organic amendments with higher C:N ratios promote N immobilization thereby resulting in lower N<sub>2</sub>O emissions (Baggs et al., 2000; Huang et al., 2004). Soil NO<sub>3</sub><sup>-</sup>-N concentrations in the AGW and ADM (higher C:N) treatments were comparatively lower than the cured CGW and CDM (lower C:N) amendments (Table 4.3). As expected, ADM and CDM with much lower C:N ratios compared to the AGW treatment promoted N<sub>2</sub>O emissions (Table 4.2). Also, at 43, the AGW C:N ratio was slightly above the threshold value of 40 for stimulating N mineralization (Vigil and Kissel, 1991). Despite this, AGW generated NO<sub>3</sub><sup>-</sup> and produced N<sub>2</sub>O emissions. This is likely due to the decay of labile C fraction with a higher C:N ratio which would release NO<sub>3</sub><sup>-</sup> and supply the denitrifiers with energy (Flessa and Beese, 1995).

Results from Chapter 2 using soils varying in salinity suggest that increasing soil salinity increased  $N_2O$  emissions and decreased  $N_2$  production from the added organic amendments. The soil considered in Chapter 3 and this field study represents an extreme saline-sodic condition with an average  $EC_e$  104 dSm<sup>-1</sup> and SAR 148. When remediated with organic amendments, EC and SAR values are expected to decrease over time (Tejada et al. 2006; Tejada and Gonzales, 2006). Therefore, N<sub>2</sub>O emissions from these soils are likely to decrease promoting gaseous N losses in the form of N<sub>2</sub> from active organic amendments containing high amounts of labile C. However, N<sub>2</sub>O emissions from

salt-affected soils undergoing remediation with organic amendments merits further study as the comprehensive effect of temporal variations in soil properties on greenhouse gas emissions must be evaluated.

## **Average Daily Emission Fractions of Nitrous Oxide**

The applied N sources increased N<sub>2</sub>O emissions. The average daily N<sub>2</sub>O emission fractions for all organic amendments applied at 100 Mg ha<sup>-1</sup> in this study fall in the range of 0.01-0.03 g kg<sup>-1</sup>. These values were also lower than those calculated using Eq.2 from the results reported by Chang et al. (1998), which indicate an estimated AEF of  $N_2O$  up to 1.8 g kg<sup>-1</sup> in non-saline soils from feedlot manure applied at 104 Mg ha<sup>-1</sup>. The AEF values of AGW and CGW treatments observed in this study were also significantly lower than 0.08-0.11 g kg<sup>-1</sup> straw-induced range calculated using Eq.2 using the results reported by Li et al. (2013). Although 28% more N was applied with ADM compared to CDM, the AEF of N<sub>2</sub>O from ADM was 40% lower than CDM. In contrast, similar reduction in the AEF of N<sub>2</sub>O from AGW was observed even though N applied from CGW was 41% higher (Table 4.3). Two considerations arise when evaluating daily N<sub>2</sub>O emission rates from organic amendments. First, the added N is not readily available and is immobilized by soil microbes, thus reducing N<sub>2</sub>O emissions. Second, the labile C present in organic materials can induce ideal conditions for denitrification and produce greater N<sub>2</sub> emissions. Both these possibilities were demonstrated in Chapter 3 using the same saline-sodic soil and organic amendments applications exposed to temperatures similar to those observed in this study. Despite the use of average daily  $N_2O$  emissions from

observations instead of annual  $N_2O$  emissions to calculate emission fractions, these values can be used as indicators to predict the potential of the tested organic amendments on  $N_2O$  emissions. However, the quantitative effects of the added amendments on longterm  $N_2O$  emissions and associated emission factors needs further evaluation.

# Effect of Soil Properties on Carbon Dioxide and Nitrous Oxide Emissions

Daily N<sub>2</sub>O fluxes increased with increasing soil temperatures from 16-28 °C. The low correlation coefficient between N<sub>2</sub>O fluxes and soil temperature (Table 4.4) under unwetted conditions is likely due to the association of heat with dry conditions (Table 4.4). This finding is in contrast to that observed under laboratory conditions with the same soil maintained at 70% WFPS wherein soil temperature strongly and positively correlated ( $r^2 = 0.76$ ; P < 0.01) with N<sub>2</sub>O fluxes suggesting that other environmental factors besides temperature may have influenced N<sub>2</sub>O emission rates in the field.

 $N_2O$  production occurs via nitrification and denitrification processes in soil. That there was no significant relationship between the amount of  $NH_4^+$ -N in the soil and the rate of  $N_2O$  emissions, suggests that the role of nitrification in  $N_2O$  production can be deemphasized under both wetted and unwetted conditions. Soil  $NO_3^-$ -N, a substrate for denitrification, had a significant positive correlation with  $N_2O$  emissions, suggesting that denitrification is the dominant process for  $N_2O$  production in these saline-sodic soils (Table 4.4). Denitrification is an anaerobic process but it can still occur under aerobic soil conditions when there are anaerobic microsites (Renault and Stengel, 1994). This soil had relatively little structure through which to transmit  $O_2$  and anaerobic microsites would likely develop in the vicinity of decaying amendment particles. Dairy manure amendments with high initial N contents and low C:N ratios released greater soil NO<sub>3</sub><sup>-</sup> concentrations compared to greenwaste amendments, particularly AGW which tended to immobilize N. ADM and CDM consistently released N but AGW and CGW immobilized N from May through November, 2012 of this study.

Besides N availability, the artificial wetting of collars enhanced  $CO_2$  and  $N_2O$  emissions from all organic amendment treated plots (Fig. 4.3 and 4.4). Nitrous oxide fluxes strongly correlated with WFPS for active and cured amendments and weakly correlated with moisture under wetted and unwetted conditions. This is because the range of WFPS measures was much narrower under unwetted (11-37%) and wetted (55-92%) conditions compared to active (11-82%) and cured (11-92%) amendments.

Correlations observed between  $N_2O$  fluxes and  $CO_2$  emissions were weaker than between  $N_2O$  emission rates with soil moisture. Carbon dioxide fluxes positively correlated with  $N_2O$  emission rates for active and cured amendments. However,  $CO_2$ emissions correlated weakly and negatively with  $N_2O$  fluxes under unwetted and wetted conditions. Because respiration is required for both the creation of  $N_2O$  and its further reduction to  $N_2$ , respiration rates alone would be expected to correlate less strongly with overall  $N_2O$  losses (Table 4.4). Although weaker, these positive correlations are consistent with findings from other authors who reported positive correlations between  $CO_2$  and  $N_2O$  emissions both under field and laboratory studies (Ding, 2007; Groffman

and Tiedje, 1991; Huang et al., 2004). Positive correlation between  $N_2O$  fluxes with both  $CO_2$  emission rates and soil moisture likely reflects correlation between  $CO_2$  and WFPS.

Soil moisture significantly correlated with  $CO_2$  fluxes for all treatments under both wetted and unwetted conditions. Significant (P < 0.01) correlations between WFPS and  $CO_2$  emissions for active ( $r^2 = 0.64$ ) and cured ( $r^2 = 0.37$ ) organic amendments (data not shown) suggests that increases in soil moisture content likely enhanced greater C decomposition from AGW and ADM compared to CGW and CDM treatments, respectively. Decomposition of organic materials can further promote denitrification "hot spots" by depleting oxygen (Velthof et al., 2003). Furthermore, the possibility that lower N<sub>2</sub>O fluxes from active treatments (particularly AGW) caused by a higher N<sub>2</sub> to N<sub>2</sub>O ratio resulting from the availability of labile C to heterotrophic denitrifiers, cannot be excluded (Granli and Boeckman, 1994). This possibility had been demonstrated from the results in the laboratory experiments using the same saline-sodic field soil (Chapter 3) which showed that N<sub>2</sub> emissions were significantly greater from active compared to cured amendments and greater N<sub>2</sub> to N<sub>2</sub>O ratios were recorded for AGW alone at all three temperatures throughout the incubation period.

Under unwetted and wetted conditions, WFPS weakly correlated with  $N_2O$ emission rates due to less variability in WFPS measured within each group (Table 4.4). Nitrous oxide was negatively correlated with  $CO_2$  fluxes under unwetted and wetted conditions as increased  $CO_2$  emissions may have driven the conversion of  $N_2O$  to  $N_2$ , thus completing denitrification. This observation is consistent with the findings from

laboratory incubations (Chapters 2 and 3) wherein treatments producing greater  $CO_2$  emissions produced higher  $N_2$  emissions and  $N_2$  to  $N_2O$  ratios with varying salinity levels from 2.8-30.6 dS m<sup>-1</sup> at 25°C and with EC<sub>e</sub> 100 dS m<sup>-1</sup> at 15, 25, and 35°C temperature levels.

To examine the factors governing N<sub>2</sub>O fluxes separately under unwetted and wetted conditions, multiple regression analysis was performed with soil properties such as temperature, moisture, NO<sub>3</sub><sup>-</sup>-N, and CO<sub>2</sub> emission rates. In this study, biophysical factors such as soil temperature, WFPS, NO<sub>3</sub><sup>-</sup>-N, and CO<sub>2</sub> emissions could explain only 66% of the variability in N<sub>2</sub>O emission rates (Table 4.5) suggesting that a combination of other biophysical factors including enzyme activities likely altered by high application rate of organic amendments may be responsible for N<sub>2</sub>O fluxes from these saline-sodic soils.

The high spatial and temporal variability observed in field N<sub>2</sub>O emissions in this study is consistent with findings from other authors (Dalal et al., 2003; Granli and Boeckman, 1994). Parton et al. (2001) attributed this to the complex multiplicative rather than the additive effects of the biophysical factors on N<sub>2</sub>O emissions from soils. Monitoring other additional soil properties such as dissolved organic C, microbial populations, and their enzyme activity may provide a better understanding of the factors that govern N<sub>2</sub>O emissions in highly saline-sodic conditions as observed in this study. The extent of N<sub>2</sub>O dissolution in the soil solution and its rate of diffusion to the soil surface are additional parameters that may explain some of the variability of N<sub>2</sub>O

production rates unaccounted for under field conditions (Jury et al., 1982). Thus, although  $N_2O$  emission rates are regulated by various biophysical properties in soil, close relationship between soil  $N_2O$  production and  $N_2O$  emission rates may rarely be achieved.

## Conclusions

Incorporation of different organic amendments to saline-sodic soils significantly affected soil N<sub>2</sub>O and CO<sub>2</sub> emissions. The amount and quality of organic C they supplied controlled the production of N<sub>2</sub>O and CO<sub>2</sub> by regulating the soil C and N dynamics. Dairy manure applications to soil in both active and cured forms released significantly higher amounts of mineral N than the greenwaste treatments which was either accumulated as  $NH_4^+$ -N or converted to  $NO_3^-$ -N in the soil causing ADM and CDM to increase N<sub>2</sub>O emissions compared to the AGW and CGW treatments. Compared to the dairy manure treatments, approximately 34-64% reduction in average daily N<sub>2</sub>O emissions was achieved with greenwaste amendments even at an application rate of 100 Mg ha<sup>-1</sup>and their average daily N<sub>2</sub>O emission fractions ranged from 0.01-0.03 g kg<sup>-1</sup>. Additionally, soil moisture, NO<sub>3</sub><sup>-</sup>-N, and CO<sub>2</sub> emissions explained 66% of the variations in daily N<sub>2</sub>O fluxes. I conclude that active amendments, particularly AGW, proved to be efficient in reducing N<sub>2</sub>O emissions compared to the cured treatments. Results from this study confirm the findings of the 60-day laboratory incubations at varying temperatures suggesting that remediation with greenwaste amendments seems to be a valuable substitute for dairy manure treatments because of a low average daily emission fraction as well as low soil NO<sub>3</sub><sup>-</sup> concentrations. Based on the findings from Chapter 2, I also contend that organic amendment induced N<sub>2</sub>O emissions will be lower from salt-affected soils with low electrical conductivity values than those observed in this study representing extreme saline-sodic conditions. However, a more comprehensive long-term evaluation on the effect of these amendments on remediating salt-affected soils needs to be considered. Further site-specific research is also needed to accurately compare the tested treatments under varying salinity conditions with extended flux measurements to include long-term impacts on associated greenhouse gas emissions.

Parameter	Value
Sand (%)	43.12
Silt (%)	37.43
Clay (%)	19.45
Bulk Density (g cm <sup>-3</sup> )	1.33
$EC_e (dS m^{-1})$	107.61
рН	8.14
Total C (%)	1.27
Organic C (%)	0.92
Total N (%)	0.08
$NO_3$ -N (mg kg <sup>-1</sup> )	198.28
$NH_4^+$ -N (mg kg <sup>-1</sup> )	1.46
Sodium Adsorption Ratio	148.36

Table 4.1: Physical and chemical properties of soil (0-25 cm)

Parameter	AGW	CGW	ADM	CDM		
Total C (%)	33.41	30.54	26.63	18.10		
Total N (%)	0.78	1.10	1.72	1.34		
C:N	42.91	27.81	15.59	13.62		
$NO_3^{-}-N (mg kg^{-1})$	2.36	6.03	12.56	33.11		
$NH_4^+ - N (mg kg^{-1})$	15.02	28.61	132.81	85.67		
Organic Matter (%)	73.64	65.05	62.24	37.98		
Stability Index (mg CO <sub>2</sub> -C g OM <sup>-1</sup> day <sup>-1</sup> )	5.33	2.15	4.92	1.87		
Particle Size Distribution		% by Weight				
> 15.8 mm	18.40					
9.5-15.8 mm	19.24					
6.3-9.5 mm	12.31		10.78			
4.0-6.3 mm	15.33	100	89.22	100		
2.0-4.0 mm	10.83					
< 2.0 mm	23.34					

Table 4.2: Composition of organic amendments expressed on a dry weight basis.

Table 4.3. Nitrogen applied, average soil  $NH_4^+$ -N and  $NO_3^-$ -N (0-10 cm) concentration, average daily gaseous fluxes, and average daily N<sub>2</sub>O emission fractions (mean ± std. error) for different organic amendments applied at 100 Mg ha<sup>-1</sup> to an extreme saline-sodic soil.

Treatment	N Applied (kg ha <sup>-1</sup> )	Average NH4 <sup>+</sup> -N (kg ha <sup>-1</sup> )	Average NO <sub>3</sub> <sup>-</sup> -N (kg ha <sup>-1</sup> )	Average Daily CO <sub>2</sub> -C (kg ha <sup>-1</sup> )	Average Daily N <sub>2</sub> O-N (g ha <sup>-1</sup> )	Average Daily N <sub>2</sub> O Emission Fraction (g kg <sup>-1</sup> )
Control	0	$0.36 \pm 0.23$ a	138.92 ± 25.39 a	$1.69 \pm 0.14$ a	$1.37 \pm 0.21$ a	-
AGW	780	$1.64\pm0.61~\text{b}$	$236.87\pm38.66~\text{b}$	$12.81 \pm 1.02 \text{ d}$	$10.77\pm0.94~b$	$0.012 \pm 0.02$ a
CGW	1100	$1.88\pm0.97~b$	267.33 ± 31.54 c	$9.04\pm0.83\ c$	$25.73 \pm 5.03$ c	$0.022\pm0.06~b$
ADM	1720	$5.26 \pm 1.11 \text{ c}$	$306.51 \pm 30.92 \text{ d}$	$9.95\pm0.95\ c$	$30.28 \pm 2.67$ c	$0.017\pm0.04~ab$
CDM	1340	$8.08 \pm 1.53 \text{ c}$	336.39 ± 42.86 e	$6.13 \pm 1.08 \text{ b}$	$38.82\pm6.24~d$	$0.028\pm0.07~c$

Note: Different letters within the same column denote significant (P < 0.05) differences between treatments.

Treatment	n	CO <sub>2</sub> -C	NO <sub>3</sub> <sup>-</sup> -N	WFPS	Soil Temperature
Active Amendments	168	0.59**	0.37**	0.79**	-0.43*
Cured Amendments	168	0.44**	0.35**	0.85**	-0.31*
Unwetted Conditions	168	-0.22*	0.37*	$0.42^{*}$	$-0.28^{*}$
Wetted Conditions	168	-0.23*	$0.49^{*}$	$0.47^{*}$	ns
Combined Data	336	$0.42^{**}$	0.39*	0.75**	ns

Table 4.4: Pearson correlation coefficients between daily N<sub>2</sub>O emission rates and soil properties.

Note: ns, \*, \*\* represent non-significant and significant correlation at P < 0.01 and P < 0.05, respectively.

Treatment	Regression E	quation	Combined r <sup>2</sup> (adj)	P-Value
Active Amendments	- 7.764 + 2.853 Ln NO <sub>3</sub> <sup>-</sup> + 0.1	58 CO <sub>2</sub>	0.480	< 0.01
Cured Amendments	$1.484 + 1.465 \text{ Ln NO}_3^- + 0.03$	86 CO <sub>2</sub>	0.319	< 0.05
Unwetted Conditions	$-1.226 + 1.712 \text{ Ln NO}_3^ 0.20$	07 CO <sub>2</sub> + 7.637 WFPS	0.317	< 0.01
Wetted Conditions	5.957 + 0.701 Ln NO <sub>3</sub> <sup>-</sup>	+ 1.34 WFPS	0.301	< 0.01
Combined Data	-2.478 + 1.706 Ln NO <sub>3</sub> <sup>-</sup>	+ 5.738 WFPS	0.665	< 0.05

Table 4.5: Stepwise regression analysis of daily N<sub>2</sub>O emission rates with soil properties.

Note: Units for selected variables are reported as: Soil  $NO_3^-$  concentrations (mg N kg<sup>-1</sup>), daily  $CO_2$  emission rates (kg C ha<sup>-1</sup> day<sup>-1</sup>) and water-filled pore space (%).



Fig. 4.1. Average Air Temperature, Precipitation and Irrigation at the field site from April 2012 through July 2013.



Fig. 4.2. Soil Temperature, Water-Filled Pore Space, and Irrigation or Precipitation corresponding to gas sampling events.



Fig. 4.3. Daily CO<sub>2</sub> fluxes from organic amendments incorporated into a saline-sodic soil.



Fig.4.4. Daily N<sub>2</sub>O fluxes from organic amendments incorporated into a saline-sodic soil.

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## 5. CONCLUSIONS

The purpose of this dissertation was to examine the influence of soil salinization and properties of organic amendments on greenhouse gas emissions. In summary, CO<sub>2</sub>, N<sub>2</sub>O, and N<sub>2</sub> emissions were significantly affected by soil salinity, temperature, type of feedstock, and C availability from organic amendments. Soil respiration and mineralization were decreased with increases in salinity from 2.8 to 30.6 dS m<sup>-1</sup>. The general decrease in CO<sub>2</sub> production and soil NO<sub>3</sub><sup>-</sup>-N content with increasing soil EC may have been due to direct influence of osmotic stress on microbially driven biogeochemical processes. Increases in soil EC<sub>e</sub> enhanced N<sub>2</sub>O emissions but decreased N<sub>2</sub> emissions suggesting the possibility of deactivation of N<sub>2</sub>O reductase enzyme responsible for the conversion of N<sub>2</sub>O to N<sub>2</sub>, the final product of denitrification. Also, increases in temperature significantly increased greenhouse gas emissions and soil NO<sub>3</sub><sup>-</sup>-N concentrations. Production of N<sub>2</sub>O, N<sub>2</sub>, and N<sub>2</sub> to N<sub>2</sub>O-N ratios increased at elevated temperatures of 25 and 35°C compared to 15°C as did the CO<sub>2</sub> production associated with improved microbial activity at higher temperatures.

As expected cumulative  $CO_2$ -C emissions were highest from active organic amendments (AGW and ADM) due to the presence of high amounts of labile C that is more easily decomposed. In addition, cumulative N<sub>2</sub>O emissions increased from soils treated with dairy manure amendments compared to greenwaste materials. This was most likely associated with lower C:N ratios of dairy manure amendments that resulted in faster mineralization and nitrification resulting in availability of NO<sub>3</sub><sup>-</sup>as substrate for denitrification. Soil NO<sub>3</sub><sup>-</sup> concentrations in soils treated with greenwaste amendments, particularly AGW, were significantly lower than other treatments including unamended controls indicating that N immobilization was responsible for reduced N<sub>2</sub>O emissions. However, regardless of soil EC<sub>e</sub> and temperature levels, AGW also resulted in greater CO<sub>2</sub> emissions and N<sub>2</sub> to N<sub>2</sub>O-N ratios. This is likely due to the presence of large amounts of labile C in AGW which may be responsible for the conversion of N<sub>2</sub>O to N<sub>2</sub>. This was most evident with a strong correlation between CO<sub>2</sub> and N<sub>2</sub> emissions.

In the field, patterns from the laboratory experiments were verified under unwetted and artificially wetted conditions. Under unwetted conditions,  $CO_2$  and  $N_2O$ fluxes were generally low compared to artificially wetted scenarios. Regardless of soil water content, lower daily  $N_2O$  fluxes were consistently observed from AGW alone. In contrast, significantly higher  $CO_2$  fluxes were recorded for both AGW and ADM treatments. Within the 14-month study period, mineral N content from greenwaste treatments applied in both active and cured forms was significantly lower than from the dairy manure amendments. Active materials incorporated in the form of greenwaste reduced average daily  $N_2O$  emissions by 64% compared to dairy manure amended plots. Average daily emission fractions (AEF) of  $N_2O$  ranged from 0.01-0.03 g kg<sup>-1</sup> from all organic amendments used in this study. In addition, AEF's from active treatments were on an average 42% lower than cured amendments. The laboratory and field studies examined the influence of soil and environmental factors that regulate N<sub>2</sub>O emissions following the incorporation of organic amendments. These studies found evidence to support: 1) higher soil salinity levels enhanced N<sub>2</sub>O emissions regardless of the type and stage of organic amendment incorporated; 2) increased CO<sub>2</sub> and N<sub>2</sub> emissions in response to elevated temperatures and addition of labile C source in the form of active organic amendments; and 3) reduced cumulative N<sub>2</sub>O emissions from greenwaste treatments relative to those that were treated with dairy manure amendments. These findings suggest that greenwaste materials, due to their effectiveness in reducing N<sub>2</sub>O emissions, can be used to substitute dairy manure amendments for remediation of salt-affected soils. Furthermore, results from this work also demonstrate the existence of complex interactions between abiotic and biotic factors in the soil (*e.g.*, electrical conductivity, temperature, soil moisture, and microbial respiration) that serve as important regulators for biologically driven denitrification process and associated N<sub>2</sub>O and N<sub>2</sub> emissions.