

DISSERTATION

THE COLORADO GOLF CARBON PROJECT

Submitted by

Katrina Gillette

Department of Horticulture and Landscape Architecture

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Doctoral Committee:

Advisor: Yaling Qian
Co-Advisor: Ronald Follett

Stephen Delgrosso
Anthony Koski
Rich Conant

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ABSTRACT

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There is concern regarding the rise of greenhouse gas (GHG) emissions and the impending effects of global climate change. Soils are the largest pool of C on earth with small changes having potentially significant effects on atmospheric carbon dioxide (CO_2) concentrations. Soil emits a substantial portion of nitrous oxide (N_2O), and is an important sink for balancing atmospheric methane (CH_4) through microbial oxidation. Anthropogenic management of soil is therefore critical in mitigating the effect of climate change by increasing biological sinks and reducing GHG emissions. Due to recent rapid urban expansion and the common use of turfgrass as ground cover and its associated management, these areas are becoming increasingly important for regional accounting of GHG budgets. Golf courses in particular are important economical green spaces that are intensively managed with common practices that include frequent irrigation, mowing and fertilization. Such management practices increase biogeochemical cycling of C and N in fine quality turfgrass system and may therefore help mitigate atmospheric CO_2 through increase soil organic carbon (SOC) sequestration. However, intensive management of turfgrass may also increase emissions of N_2O and reduce CH_4 oxidation potentials, and therefore it is critical to have a complete account of GHG fluxes in the system.

The objective of this dissertation was to estimate the carbon balance of golf courses using a multifaceted approach that included survey data, ecosystem modelling of C and N dynamics in

turfgrass, and a two year field study measuring trace gas fluxes from a golf course using different urea fertilizers. Survey information was collected from Colorado golf courses regarding energy use from clubhouses, management facilities, and fertilizer and irrigation management, and land use. Further calculations were made from published literature for fertilizer production, N₂O emissions and C offsets through SOC sequestration in regards to land use type. Survey information was also used to evaluate the effects of different management scenarios reported by turfgrass managers in order to simulate SOC accumulation and N₂O fluxes using the DAYCENT biogeochemical model on a near (25 yr) and long (50 yr) term time scale. Finally, soil GHG fluxes were monitored using a modified version of the closed chamber method over the course of a two year field study, where the effects of fertilizer treatment, turfgrass site, and soil drainage potential were evaluated. Soil organic C and N were also measured for future analysis from all field plots. Through these efforts we have encompassed critical components required to calculate an overall C balance of golf course facilities maintained in the state of Colorado.

Energy consumption from clubhouse and maintenance facilities and irrigation pumping stations were the largest sources of emissions, therefore increasing energy efficiency may significantly reduce annual emissions from golf courses. Of the twenty-two golf courses around the state of Colorado that participated in the survey, most had similar areas of managed turfgrass and nearly all maintained alternative land use types apart from turfgrass. Increasing the area of natural grassland and trees that have minimal management inputs is important to offset the C intensive management required to maintain the aesthetics of fine quality turfgrass. Alternative land use types contributed to C offsets through SOC accumulation not only for turf management, but offset approximately 40% of CO₂ emissions from building and irrigation systems. In our second analysis we used the DAYCENT model to make projections of SOC and N₂O emission

over several periods of time; simulations were based on fertilizer rates reported in the survey to evaluate different management scenarios. The model projected rapid SOC sequestration rates when turfgrass was newly established, but these rates decreased and N₂O emissions substantially increased after 25 yr if best management practices were not used. Field trials were the third and final part of our study, and we observed greater N₂O emissions from fairways than from the rough turfgrass sections for all fertilizer treatments; a likely result of taller mowing height that increased plant water transpiration as well as from an increased layer of thatch on the Kentucky Bluegrass rough that partially immobilized N applications. Of the fertilizer treatments, Polyon with advanced coated technology was the most effective in restricting N substrate to control N₂O emissions, especially following summer fertilizer applications. Using fertilizer technologies that reduce the risk of loss is important both economically and environmentally. Soil water and temperature were important abiotic variables affecting N₂O and CH₄ emissions, with emissions increasing as high soil water content depleted soil oxygen and rising summer temperatures reduced C3 turfgrass physiological activity. Observations collected in the field signify important GHG mitigation strategies in managing turf irrigation and fertilizer, as well as effective fertilizer technologies to reduce N₂O emissions. If turfgrass managers are to employ the best GHG mitigation strategies to fine quality turf, there must be a complete understanding of the variables effecting soil GHG emissions that include N substrate availability, soil water and temperature, and plant physiology.

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CHAPTER 1:
CO₂e BALANCE OF COLORADO GOLF COURSES BASED ON REPORTED SURVEY
RESULTS FOR ENERGY AND LAND USE

SYNOPSIS

Carbon dioxide (CO₂) is the primary greenhouse gas (GHG) emitted through fossil fuel combustion, and nitrous oxide (N₂O) is the primary GHG emitted from agricultural soils. Turfgrass is a common and important feature in urban landscapes that can potentially mitigate atmospheric CO₂; however more research is needed to better understand ecosystem functions of urban soils. Golf courses emit GHGs to accommodate golfer amenities and intensive management of fine quality turfgrass, yet alternative land uses such as restored native rangeland and forest help offset emissions. Energy use from facilities and land use and management was compiled from twenty-two Colorado golf courses. We used statistical methods to identify two groups of golf courses based on annual energy consumption. Annual emissions from energy consumption for the low and the high group emitted on average 255 and 512 Mg CO₂e from, respectively. Soil C sequestration from turfgrass and alternative land uses types, such as native and forest area, were important offsets to C intensive management of turfgrass. Land based C sequestration offsets accounted for approximately 40% of CO₂ emission from fossil fuel use, and CO₂ emission intensity from one 18-hole round of golf may be as high a 13 kg CO₂. However, it critical to recognize that these offsets are diminished over time as C pools reach equilibrium; simultaneously as turfgrass age increases indices for greater N losses also increase, making best

management practices critical to environmental stewardship. Increasing energy use efficiency from irrigation systems and buildings will further offset emissions from golf courses.

INTRODUCTION

Carbon dioxide (CO₂) and nitrous oxide (N₂O) are important greenhouse gases (GHG) that have substantially increased since the onset of the industrial era, leading to a strong interest in stabilizing human induced GHG to mitigate the risk of climate change (FAO, 2012). Carbon dioxide is the primary GHG emitted through human activities, accounting for 84% of all U.S. GHG emissions in 2011 (EPA, 2011). Fossil fuel combustion to generate electricity is the most important source of CO₂ emissions, accounting for nearly 40% of all CO₂ emitted in the U.S. (EPA, 2011). Building related energy costs accounts for substantial shares of global energy consumption (EIA, 2010). Land and oceans, however, provide important offsets to fossil fuel combustion by absorbing approximately half of the CO₂ emissions, thereby also slowing the rise of atmospheric CO₂ concentrations (Poulter et al., 2014). However terrestrial biological cycling of C can only offset fossil fuel emissions on a decadal or century time scale (IGBP, 1998).

Soils can act as a net sink or source of CO₂, however unlike CO₂, there are no significant sinks for N₂O. Soil emits over half of the atmospheric N₂O from both natural and managed systems combined (Skiba and Smith, 2000), with being the primary GHG emitted from non-flooded agricultural soils (Del Grosso et al., 2008). In fact, due to unchecked emissions and rapid increase in atmospheric concentration, N₂O has been deemed the single most important ozone depleting emission in the 21st century (Ravishankara, et al., 2009). The production of N₂O is regulated through two soil microbial processes, nitrification and denitrification, that may occur simultaneously or individually in the soil environment. Microbial processes that produce soil

N₂O are primarily controlled through N substrate availability (NH₄⁺ for nitrification and NO₃⁻ for denitrification), and soil temperature and moisture.

Greenhouse gas emissions from agricultural soils in temperate regions have been well documented (Mosier et al., 1991; Dobbie and Smith, 2003; Syakila and Kroeze, 2011). More recently, due to rapid urban expansion, turfgrass systems have been recognized as an important part of regional GHG budgets (Kaye et al., 2004; Bremer, 2006; Zhang et al., 2013). Turfgrass is a common and important landscape feature in urban areas (Bandaranyake et al., 2003) with an estimated 16 Mha of turf in the United States (Milesi et al., 2005). Turfgrass is an excellent ground cover in urban areas because it promotes ground water infiltration and filtration, and dissipates the urban heating effect through plant transpiration (Beard, 1973). Fertilizer and irrigation water inputs accelerate soil biogeochemical processes in turfgrass, thereby accelerating C sequestration rates (Qian and Follett, 2002; Lal, 2004; Huh et al., 2008). In combination with sustained ground cover from its perennial nature, turfgrass systems have potential for long term SOC storage, and have therefore been promoted as a potential CO₂ mitigation strategy (Lal, 2004a; Smith et al. 2007b; Qian and Follett, 2002).

While fertilization and irrigation increase SOC accumulation in turfgrass systems, emissions of other soil GHGs may also be accelerated (Townsend-Small and Czimczik, 2011; Kaye et al., 2004). Understanding the effects of land use management on soil C and N dynamics is a critical part of GHG mitigation, and maximizing benefit of urban green spaces. Nitrogen fertilizer is the most limiting nutrient factor in turfgrass systems (Hull and Lui, 2005) and a critical management component for maintaining aesthetically appealing urban landscapes (Qian et al., 2003). Because of the high N fertilizer and irrigation inputs for fine quality turf, it is a challenge to reduce environmental impacts (Huh et al., 2008).

Golf courses may be an important component in regional C and N biogeochemical cycling. Turf management inputs may equal or exceed agriculture croplands (Law et al., 2004); therefore environmental impacts from management could be substantial. Golf courses maintain some of the finest quality turf in the world, and intensive turf cultural practices are common to maintain the high quality standards required for the game. Golf courses are not only important green spaces in urban communities (Tanner and Gange, 2005), but are also one of the most economically profitable land use types on a per hectare basis, generating billions of \$USD to the international economy (Rodriguez-Diaz et al., 2007).

Nonetheless determining the C cost of golf courses is complicated because the CO₂ balance of the system is not only dependent upon land management inputs, but also the associated energy costs of golfer amenities and other turf management facilities. In order to estimate the scale of the various CO₂ sources and sinks from golf courses, we compiled survey data from twenty-two golf courses in Colorado to quantify annual energy consumption from clubhouse and maintenance facilities, electricity for pumping irrigation water, liquid fuel usage, and annual fertilization rates to greens, tees, fairways and roughs. Other data reported in the survey pertained to the number of 18-hole rounds played per golf course, and the various land use types maintained at golf course allowing estimates of soil organic carbon (SOC) sequestration rates. The objective of our study was to evaluate the CO₂ equivalents (CO₂e) balance of Colorado golf courses through energy consumption and land use management obtained from survey data. This information will not only provide important estimates to land use and potential soil C cycling within the confinements of golf courses, but also allow for better local and regional estimates of CO₂e emission from these facilities. Furthermore we will also be able to calculate the CO₂e emission intensity per round of golf played in Colorado.

MATERIAL AND METHODS

Colorado Golf Course Survey

A survey was collected from golf courses in the state of Colorado for the years 2008 and 2009 using the online survey, Survey Monkey. Twenty-two courses participated in the survey; the names of participants, location, year of construction, golf course type (public or private), total golf course area, and total area of irrigated turf are presented in Table 1. Golf courses reported electric and natural gas use from clubhouse and maintenance facilities, electricity for irrigation, fuel usage, and the number of 18-hole equivalent rounds played per year. Land use and management information regarding fertilization rates per managed section of turf, annual irrigation water use by source, and hectares of alternative land use types such as restored native rangeland, unmaintained, wetlands and forest were also provided.

In order to calculate a CO₂ balance, CO₂ coefficients were used to convert energy use and land management from the survey into CO₂ equivalents (CO₂e) to estimate sources and sinks (offset). Coefficient conversions for CO₂e sinks and sources are referenced from published journals and defined in Table 2. A CO₂e coefficient of 0.9 kg kWh⁻¹ was used for electricity consumption in Colorado based from the EIA (2001). Coefficient of 5.3 kg CO₂ therm⁻¹ and 1.3 kg CO₂ kg⁻¹ propane were used for CO₂e emissions for natural gas and propane, respectively (EPA, 2012). Unleaded and diesel fuel CO₂e coefficient are estimated at 8.8 and 10.1 kg CO₂ liter⁻¹, respectively (EPA, 2012). Means of 4.8, 0.7, and 0.6 kg CO₂ kg⁻¹ were used for production and transportation costs of nitrogen (N), phosphorus (P), and potassium (K) fertilizers, respectively (Lal, 2004). Soil N₂O emission factors are based from IPCC (2006) emission factors that assume 1.0% of applied fertilizer will be directly emitted as N₂O. Global

warming potential of 298 were estimated for N₂O emissions from Forster et al. (2007) over a 100 year time period. Land based CO₂e sinks from SOC sequestration from greens, tees, and fairways turfgrass were estimated at 3.2 Mg CO₂ ha⁻¹ (Qian and Follett, 2002). A slightly lower SOC sequestration rate of 2.8 Mg CO₂e ha⁻¹ was used for the rough and clubhouse lawns (Zhang et al., 2013). Land base CO₂e sinks from golf course unmaintained were estimated from Derner et al. 1997 who measured SOC sequestration rates from native rangeland in Colorado to be 1.4 Mg CO₂ ha⁻¹. We used a slightly greater number for restored native rangeland of 1.7 Mg CO₂ ha⁻¹ based on estimates from Zirkle et al. (2011) and Lal et al. (2003). Carbon dioxide sinks from wetlands were from assessments made by Euliss Jr. et al. (2005) who estimated 2.9 Mg CO₂ ha⁻¹, and finally, CO₂e sinks from forests were taken from an urban tree density that sequesters an estimated 25 Mg CO₂ ha⁻¹ (Nowak and Crane, 2002).

Statistical analysis

PROC CLUSTER (SAS Institute, 2008, Cary, NC, USA) analysis was used to group golf courses based off specific variables reported in the survey. The Ward clustering method was used in order to base clustering decisions on ANOVA sum of squares which are predicted hierarchically on the data set. Reported values for energy use and land management are based off of the two year mean of data for 2008 and 2009. The first cluster analysis was based on reported energy consumption from clubhouse and maintenance facilities and pumping irrigation. Land management practices were then assessed based on group rankings for energy consumption. By ranking golf course by the major sources of energy consumption first, land based CO₂e sinks (offsets) were then calculated to estimate the total CO₂e balance of our data set. Only sixteen golf courses completed information for energy consumption, therefore our first cluster analysis only includes energy consumption values reported by these courses alone.

Using similar analytical procedures, a second cluster analysis was performed to estimate CO₂e balances from land management alone, with energy consumption from clubhouse and maintenance being excluded. The data set for land management was the most complete, totaling twenty-two golf courses. The second cluster analysis for land management was based on total area of fairway, rough, irrigated turf, wetland, native, and unmaintained, and turf N fertilization rates (tees, greens, fairway and rough). CO₂e emissions from pumping irrigation water, fuel usage, and fertilizer production were also accounted for based on group rankings for land management to further estimate the CO₂e balance of the second cluster analysis.

RESULTS AND DISCUSSION

Golf Course Energy Consumption

PROC Cluster analysis identified two distinct groups of golf courses based on energy consumption from clubhouse and maintenance facilities and pumping irrigation water. In group 1 (G1) there were six golf courses, and in group 2 (G2) there was eight golf courses (two courses were in different group rankings and are discussed further below). Carbon dioxide equivalents emissions from energy consumption in the G1 and G2 group of golf courses are presented in Figure 1. Average CO₂e emissions from energy consumption at clubhouse and maintenance facilities for G1 group totaled 255 Mg CO₂e per year, with clubhouse electricity and natural gas making up 130 ^{+/-}30 and 25 ^{+/-}5 Mg CO₂e of the total, respectively. The only two mountain courses that completed the energy consumption information were also in this smaller CO₂e emission group, and may indicate that mountain courses, because they are opened for shorter periods of time during of the year, have lower annual CO₂e emissions than courses that are opened for longer periods of time, such as those located on the Front Range.

All golf courses that were in the G2 group are located on the Front Range area of Colorado. Average CO₂e emissions from energy consumption were 512 Mg CO₂e for the G2 group of golf courses, nearly double of the first group (G1). Clubhouse electricity and natural gas consumption from golf courses grouped in G2 totaled 288 ^{+/-}46 and 93 ^{+/-}13 Mg CO₂e, respectively. Emissions from unleaded and diesel fuel use was fairly similar between the two groups of golf courses, totaling 20 ^{+/-}3 and 39 ^{+/-}9 Mg CO₂e for G1, and 32 ^{+/-}3 and 38 ^{+/-}8 Mg CO₂e yr⁻¹ for G2, respectively.

Two golf courses were excluded in our statistical model due to significantly greater energy consumption. Total clubhouse electricity and natural gas from the first course was 18348 and 5310 Mg CO₂e yr⁻¹, respectively that is over one-hundred times the consumption of the first two groups. Clubhouse electricity and natural gas consumption at the second golf course was 1015 and 437 Mg CO₂e, respectively (data not shown). Both of these courses maintain spa facilities with lap pools which significantly increased energy use for maintenance and heating. In an energy use analysis of a University in Mexico, Escobedo et al. (2014) suggested using solar panels and electric pumps for heating pool water as an alternative energy sources. Furthermore, electricity for irrigation pumping was nearly five times greater at the second golf course, averaging 586 Mg CO₂e across 2008 and 2009; this is curious because total irrigated turf area was similar to other courses. However, pumping irrigation water is a major source of energy consumption involved in turf maintenance (Schlesinger, 1999). Therefore irrigation audits to improve system efficiency may contribute substantially to CO₂e emissions decreases.

Importantly, reported electricity used in clubhouse may also include electricity used to charge golf carts. Seventy percent of golf courses that participated in the survey reported that

electric golf carts accounted for 100% of their fleet, and only 30% of golf courses reported that golf cart fleets were gas engine or a combination of gas and electric.

Based on group rankings for energy consumption, we evaluated land use types and fertilization rates for the two statistical groups, G1 and G2. The area (ha) of each land use type and N fertilizer applications in which calculations are based on are presented in Table 3. Due to large scale differences between CO₂e sources from energy consumption and land use, we present CO₂e sinks and sources from land use and management separately in Figure 2. Total CO₂e emissions from electricity used to pump irrigation water, fertilizer production, and N₂O emissions were 177 and 206 Mg CO₂e yr⁻¹ for G1 and G2 groups; electricity used for pumping irrigation water was the largest CO₂e cost, totaling 138 and 167 Mg CO₂e yr⁻¹ for G1 and G2, respectively. Carbon dioxide equivalent offsets from land use exceeded emissions from land management for both groups, with land based offsets totaling 191 and 271 Mg CO₂e yr⁻¹ for G1 and G2, respectively. The G1 and G2 groups had a negative net balance of 14 and 69 Mg CO₂e based on sources and sinks associated with land management, offsetting approximately 40% of building related costs, respectively. In Table 4 we present estimates for CO₂e emission intensity for each 18-hole round of golf played based on the CO₂e balance of energy use and SOC offsets, which totaled 8.7 and 13.3 kg CO₂e per round for the G1 and G2, respectively.

There was little difference in fertilization rates between the two statistical groups and emissions from production and transportation of N, P, and K fertilizers totaled 25 Mg CO₂e the two statistical groups. Colorado golf course turf managers reported application rates phosphorus (P) application of 60 kg P ha⁻¹ yr⁻¹. Potassium (K) fertilization rates for G1 and G2 averaged 175^{+/-}31 and 200^{+/-}20 kg K ha⁻¹ yr⁻¹ for turf greens respectively, and 100^{+/-}10 kg K ha⁻¹ yr⁻¹ tees. Production and transportation of N, P, and K fertilizers are sited as producing net CO₂ emissions

(Schlesinger, 1999; Lal, 2004b). Nitrogen fertilizer was the soil amendment applied in the greatest quantities to all sections of managed turf, and is the most C intensive fertilizer input, thereby generating the majority of the CO₂ emissions from fertilizer production. Based on nitrogen fertilization rates, we used the IPCC (2007) emission factor of 1% to estimate N₂O emissions from golf course turfgrass. Managed turfgrass N₂O emissions accounted for 14 Mg CO₂e yr⁻¹ for both statistical groups.

On average, G2 golf courses were 10 hectares larger than courses in the G1 group, therefore land based offsets were more significant. Based on sequestration potentials of 3.2 Mg CO₂e ha⁻¹ yr⁻¹ reported by Qian and Follett (2002), soil organic C sequestration from fairways accounted for 57 and 50 Mg CO₂e offsets for G2 and G1 groups, respectively. Turf SOC sequestration from the roughs was based on Zhang et al. (2013) estimates of 2.7 Mg CO₂e ha⁻¹ yr⁻¹, accounting for a total of 44 and 71 Mg CO₂e offsets for G2 and G1 groups, respectively. Potential CO₂e sinks for land managed as unmaintained areas were estimated at 44 and 47 Mg CO₂e for the G1 and G2 groups, respectively. A slightly greater SOC sequestration rate of 1.7 Mg CO₂e ha⁻¹ was used for restored native rangelands, with estimated sequestration potentials of 33.8 and 44.5 Mg CO₂e for G1 and G2 groups, respectively. Carbon offsets from wetland management are large, sequestering up to 2.9 Mg CO₂e ha⁻¹ yr⁻¹ (Euliss Jr. et al., 2005). Offsets from wetlands were estimated to be 23.0 and 8.2 Mg CO₂e for G1 and G2 groups, respectively; however we recognize that methane emissions from wetlands affect CO₂e but are unaccounted for in our estimates. Due to the large sequestration potential of trees stands, the small area of tree stands (0.45 ha) in the LUG2 group accounted for 41 Mg CO₂e. Carbon dioxide offsets from golf course trees were based on an urban tree density of 25 Mg CO₂e ha⁻¹ (Nowak and Crane, 2001).

Trees on golf courses are excellent C offsets because trees have 10 times greater sequestration potentials than turfgrass (Bartlett and James, 2011).

Golf Course Land Use

Turfgrass nutrient management and area per land use type was the most complete set of data collected in our survey (complete data all twenty-two courses). Therefore we performed a second cluster analysis based on N turf fertilization rates, and area of fairway, rough, total irrigated turf, native, wetland, and unmaintained hectares, and excluded energy use from facilities. Of the twenty-two golf courses, statistical analysis identified two groups of golf course based on the previous land use areas and N fertilization rates. There were fifteen golf courses within the first group (LUG1), and seven golf courses in the second group (LUG2) based on the above variables. Presumably the LUG1 group is the more common scenario for land management for golf courses in Colorado since nearly two-thirds of golf courses were in this cluster group. Also, CO₂e emissions were calculated using similar methods for liquid fuel use, electricity for pumping irrigation water, fertilizer production, and soil N₂O emissions based variables in the second group of clustering variables.

The CO₂e balance for land management and SOC rates is presented in Figure 3. The land use area and fertilization rates used for CO₂e balances are presented in Table 3 for LUG1 and LUG2 groups. Average CO₂e emissions from turfgrass maintenance were similar between the two LUG1 and LUG2 groups, totaling 290 and 232 Mg CO₂e, respectively. Emissions from diesel use totaled 33 and 28 Mg CO₂e for LUG1 and LUG2 groups, and emissions from unleaded fuel use totaled 48 and 34 Mg CO₂e, respectively. Electricity used for golf irrigation

water pumping generated the greatest CO₂e cost and totaled 168 and 138 Mg CO₂e for LUG1 and LUG2 groups, respectively.

CO₂e offsets from turfgrass SOC sequestration compensated for less than half of total emissions from turfgrass management, with total turf SOC sequestration totaling 120 Mg CO₂e for each statistical group. It was only after including SOC sequestration from other land use types (ie native, forest, and unmaintained) that LUG2 golf courses were a net sink for CO₂e emissions, totaling 88 Mg CO₂e (Fig. 3). However, even with other land use types included, the CO₂e balances for golf courses in the LUG1 group were a net source of emissions, totaling 72.5 Mg CO₂e. Calculations for CO₂e intensity based on land use are also presented in Table 4 for LUG1 and LUG2 groups, and are based on the average number of 18-hole rounds played and CO₂e balances for each group. The LUG2 group was the only data set that estimated each round of golf to contribute to CO₂e offsets, with each 18-hole round of golf played contributing to nearly 3 kg CO₂e being sequestered.

The greater area of unmaintained and restored native rangeland increased the average size of golf courses in the LUG2 group by approximately 30% compared to courses in the LUG1 group. However, total CO₂e sinks from turf fairway and rough SOC sequestration were fairly similar between the two groups, with an estimated 45 Mg and 63 Mg CO₂e offsets for LUG1 group, and 52 and 58 Mg CO₂e for LUG2 group, respectively. Carbon dioxide equivalent balances were further affected by fertilizer rates, where LUG1 had slightly lower N fertilization rates for greens and tees, and the second group, LUG2, had lower N fertilization rates on fairways and roughs. Because fairways and roughs have substantially larger areas than greens and tees, the lower N applications not only reduced the CO₂e emissions from fertilizer production but also slightly reduced N₂O emissions for the LUG2 group.

Ultimately, it was the greater area of unmaintained, native, and wetland areas that allowed LUG2 courses to be a net sink for atmospheric CO₂ based on land management. The LUG2 group had nearly three times the area of unmaintained and native areas as the LUG1 group of golf courses. Bartlett and James (2011) identified non-playing areas of golf courses, such as unmanaged areas and trees stands, to be important C offsets to intensive turfgrass management. However it is important to remember that SOC sequestration follows a sigmoidal curve (Lal, 2004), and is only sustained until the soil reaches an equilibrium, typically within the first 20 to 50 yr (Sauerbeck, 2001). As for turfgrass systems specifically, accumulation of SOC is the most rapid after initially establishment, with variable decomposition rates depending on nitrogen and irrigation inputs (Qian and Follett, 2002). On average, golf courses in our study were less than 30 years old, therefore justifying using a high sequestration rate, but these potential SOC rates diminish as soils reach equilibrium. Nonetheless, it may be best to view terrestrial sinks as significant but provisional reservoirs because the C which is initially sequestered may be vulnerable to return to the atmosphere in less than a century and therefore may not be permanent (IGBP, 1998).

We would like to complete our discussion on soil GHG emissions by briefly comparing measured N₂O emissions from turfgrass and the emission factors used by the IPCC (2006). The IPCC (2006) report assumes that 1.0% of applied fertilizer will be directly emitted as N₂O, however this value does not take into account land use, soil type, or precipitation gradients (Lesschen et al., 2011). Annual N₂O emissions reported from turfgrass field studies have a fairly wide range of variability, measuring from 2.5 to 6.4 kg N₂O-N ha⁻¹ yr⁻¹ (Kaye et al., 2004; Guilbault and Mathias, 1998). Soil N₂O emissions from turf depend on turfgrass age, soil water status, and fertilization practices (Mancino et al., 1988; Qian et al., 2003; Zhang et al. 2013).

Zhang et al. (2013) demonstrated with the DAYCENT ecosystem model that in as little time as ten yr following turfgrass establishment N₂O emissions may double if best turf grass management practices are not followed. Turfgrass age is an important factor that determines the fate of applied N due to the high internal N cycling (Bouldin and Lathwell, 1998; Qian et al., 2003; Frank et al., 2006). Nitrogen fertilization should be reduced as the age of the grass stand increases when clippings are returned (Qian et al., 2003), or the chances of losing N from the system are greatly increased (Porter et al., 1980; Petrovic, 1990) from gaseous losses or leaching.

Golf Course Water Sources and Use

Golf courses also reported water used for irrigation by source (well, potable surface or reuse effluent). Total irrigation water use was averaged for the years 2008 and 2009, of this, 9.5, 19.5, 44.2, and 26.8% was drawn from potable, well, surface, and effluent water sources, respectively. Total irrigated area of turf was similar for LUG1 and LUG2 golf course groups, averaging 39 ^{+/-} 2.8 ha. According to reported annual water use for irrigation and total irrigated hectares of turfgrass, an average of 82 cm of irrigation water per hectare of turfgrass was applied to golf courses in Colorado. However the reported amount of total water used for irrigation was probably not all used for turfgrass, but also cleaning maintenance facilities and equipment. Regardless, globally irrigation is responsible for approximately 70% of anthropogenic water consumption (FAO, 2010). Water demand from turfgrass varies by region, and the semi-arid environment in Colorado increases plant water use through high evapotranspiration rates. There is a large interest in conserving water use in turfgrass systems. Batug and Buyuktas (2002) demonstrated that high quality turfgrass can be obtained with irrigation water inputs that equal 75% ET, with no difference in turf quality when irrigation water was applied at 100% ET.

Reducing water application rates to meet lower ET demands coupled with precipitation accounting could potentially reduce water use from golf courses in Colorado.

Additionally, energy intensity for turf irrigation is substantially greater than previous estimates for irrigated agriculture (Follett 2011; Schlesinger, 1999). Based on electricity used for pumping irrigation water and total irrigated hectares, energy consumed per irrigated hectare of turfgrass equates to 4.4 and 3.6 Mg CO₂e ha⁻¹ for LUG1 and LUG2 groups, respectively. Our survey results concluded that electricity was the only source used to generate energy for pumping irrigation. West and Marland (2002) determined that when electricity was the primary source of energy pumping irrigation water produced 0.95 Mg ha⁻¹ yr⁻¹. Follett (2001) calculated 0.72 Mg CO₂e ha⁻¹ of energy required for the 15.5 Mha of US irrigated agricultural land from pumping irrigation, but his calculations were based on a mix of energy sources, with only 52.6% of electricity from coal fired sources. Regardless, due to the C intensity of pumping irrigation water, increased efficiency in irrigation systems and power sources could help to substantially offset CO₂e emissions from pumping irrigation water.

CONCLUSION

Electricity consumed at clubhouses facilities and pumping irrigation water were major sources of CO₂e emissions from Colorado golf courses, with natural gas and fuel use making up other important CO₂e emission sources. Soil organic sequestration from fairway and rough turfgrass together with other alternative land use types such as native and forests areas were important sinks that offset C intensive land management at golf courses. However it is important to recognize spatial and temporal variability of SOC, and that SOC reaches equilibrium over time, diminishing CO₂ offsets from sequestration. As SOC levels reach equilibrium as the age of

the turfgrass stand increases, N inputs should also be adjusted to avoid losses to the environment. Contrary to SOC sequestration, CO₂e emissions from anthropogenic energy consumption will steadily continue every year. This gives our CO₂e balance estimates for golf courses a fairly high degree of uncertainty because calculations for land based CO₂e offsets greatly depend on baseline soil C pools, longevity and vegetation type, land management practices, fertilizer and irrigation inputs, soil texture, and climatic factors. Increasing energy use efficiency at clubhouses and irrigation pumping systems will greatly contribute to mitigating CO₂e emission from golf course facilities, along with land management practices that include best turfgrass practices and increasing areas that have low inputs costs and a high potential to sequester atmospheric CO₂, such as forests and/or restored native rangeland.

TABLES AND FIGURES

Table 1.1. List of Colorado golf courses that participated in the survey, year of construction, course type (public, private or semi-private), and region of the state where they are located. Total hectares (ha) and total area of maintained turfgrass are also provided.

Golf course name	Year Constructed	Type	Colorado region	Total area (ha)	Irrigated turf (ha)
Glacier Golf Club	1970	Private	Southern Mountains	60	36
Haymaker Golf Course	1997	Public	Northern Mountains	96	31
Beaver Creek Golf Club	1981	Semi-Private	Central Mountains	32	26
Tiara Rado Golf Course	1975	Public	Western Slope	72	35
Ironbridge Golf Club	2003	Semi-Private	Western Slope	95	40
Ptarmigan Country Club	1988	Private	Front Range	64	49
Legacy Ridge Golf Course	1993	Public	Front Range	69	40
Heather Gardens Golf Course	1972	Semi-Private	Front Range	16	14
Denver Country Club	1901	Private	Front Range	41	36
Lone Tree Golf and Hotel	1985	Public	Front Range	112	56
West Woods Golf Club	1992	Public	Front Range	85	44
Heritage at Westmoor Golf Course	1998	Public	Front Range	86	34
Murphy Creek Golf Course	1999	Public	Front Range	92	65
Lakewood Country Club	1908	Private	Front Range	42	42
Lake Arbor Golf Course	1973	Public	Front Range	38	31
The Meadows Golf Club	1983	Public	Front Range	41	17
The Homestead Golf Course	2001	Public	Front Range	48	32
The Broadlands Golf Course	1998	Private	Front Range	82	36
Shadow Creek	1995	Private	Front Range	12	2
Saddle Rock Golf Course	1996	Semi-Private	Front Range	96	42
The Club at Flying Horse	2005	Private	Front Range	84	36
Common Ground Golf Course	2007	Public	Front Range	141	52

Table 1.2. Estimates for carbon dioxide (CO₂) emissions: electric kilogram (kg) of CO₂ per kilowatt hour (kwh); natural gas kg CO₂ per thermal unit (therm); and propane kg CO₂ per kg. Emissions caused by the manufacturing and transportation of nitrogen (N), phosphorus (P) and potassium (K) fertilizers in kg CO₂ per kg of fertilizer. Estimates of soil carbon (C) sequestration are measured in megagrams of CO₂ per hectare (ha).

Parameter description	Value	Units	Reference
Electricity	0.9	kg CO ₂ kwh ⁻¹	U.S. EIA, 2001
Natural gas	5.3	kg CO ₂ therm ⁻¹	U.S. EPA, 2012
Propane	1.3	kg CO ₂ kg ⁻¹	U.S. EPA, 2012
Diesel fuel	10.1	kg CO ₂ liter ⁻¹	U.S. EPA, 2012
Unleaded fuel	8.8	kg CO ₂ liter ⁻¹	U.S. EPA, 2012
Nitrogen fertilizer production	4.8 ^{+/-} 5.9	kg CO ₂ kg ⁻¹ N	Lal, 2004
Phosphorus fertilizer production	0.7 ^{+/-} 1.3	kg CO ₂ kg ⁻¹ P	Lal, 2004
Potassium fertilizer production	0.6 ^{+/-} 0.6	kg CO ₂ kg ⁻¹ K	Lal, 2004
Soil N ₂ O emission factor	1.0	% of fertilizer applied	IPCC, 2006_Direct emissions
N ₂ O global warming potential (GWP)	298	CO ₂ GWP	Forster et al., 2007
Greens, tees, fairway turfgrass soil C sequestration	3.2 ^{+/-} 1.8	Mg CO ₂ ha ⁻¹	Qian and Follett, 2002
Rough turfgrass SOC sequestration	2.7	Mg CO ₂ ha ⁻¹	Zhang et al., 2013
Restored native grassland SOC sequestration	0.48	Mg CO ₂ ha ⁻¹	Zirkle et., 2011; Lal et al., 2003
Unmaintained SOC sequestration	0.4	Mg CO ₂ ha ⁻¹	Derner et al., 1997
Wetland soil C sequestration	2.9	Mg CO ₂ ha ⁻¹	Euliss Jr. et al., 2005
Forest soil C sequestration	25 ^{+/-} 21	Mg CO ₂ ha ⁻¹	Nowak and Crane, 2002

Table 1.3. Hectares (ha) of each land use type and N fertilizer application rate (kg N ha⁻¹) for the two energy statistical groups (G1 and G2), and the two Land Use statistical groups (LUG1 and LUG2).

	G1	G2	LUG1	LUG2
Total ha	68	84	67	98
Green ha	1	1	1	1
Tees ha	1	2	1	1
Fairway ha	17	15	14	15
Rough ha	15	25	23	21
Native ha	20	32	12	38
Unmaintained ha	31	43	18	46
Wetland ha	2	3	2	6
Forest ha	0	0.5	0.6	0.6
Green kg N ha ⁻¹	200	210	195	230
Tees kg N ha ⁻¹	180	200	175	220
Fairway kg N ha ⁻¹	150	135	160	110
Rough kg N ha ⁻¹	115	90	110	80

*G1 and G2 groups are based on 16 golf courses that provided information building energy use; LUG1 and LUG2 are based on land management only.

Table 1.4. Energy intensity (kg CO₂e per round) calculated from the average annual number of rounds played and total CO₂e balance (Megagrams CO₂e) for the energy statistical groups (G1 and G2) and the land use statistical groups (LUG1 and LUG2).

Group	Rounds Played (18 hole equivalent)	CO ₂ e Balance Mg CO ₂ e	Intensity kg CO ₂ e per round
G1	27839	241	8.7
G2	33337	443	13.3
LUG1	26931	72	2.7
LUG2	29724	-88	-3.0

*Calculations for G1 and G2 groups are include emission from energy use and land use for 16 golf courses; calculations for LUG1 and LUG2 are for land use only and include 22 golf courses.

Energy Use

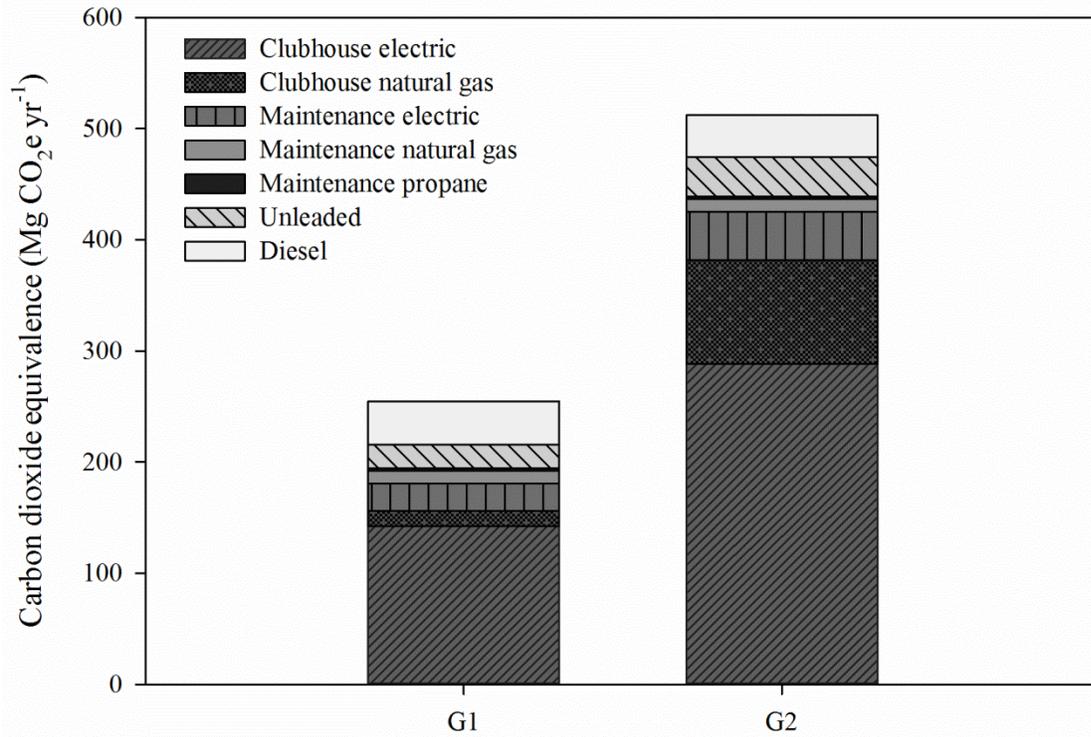


Figure 1.1. Carbon dioxide equivalents (CO₂e) emissions from fossil fuel combustion for clubhouse and maintenance building electricity and natural gas use, and diesel and unleaded fuel measured in megagrams (Mg) of CO₂e per year (yr) for two statistical groups of golf courses G1 and G2.

Land Management CO₂e Balance

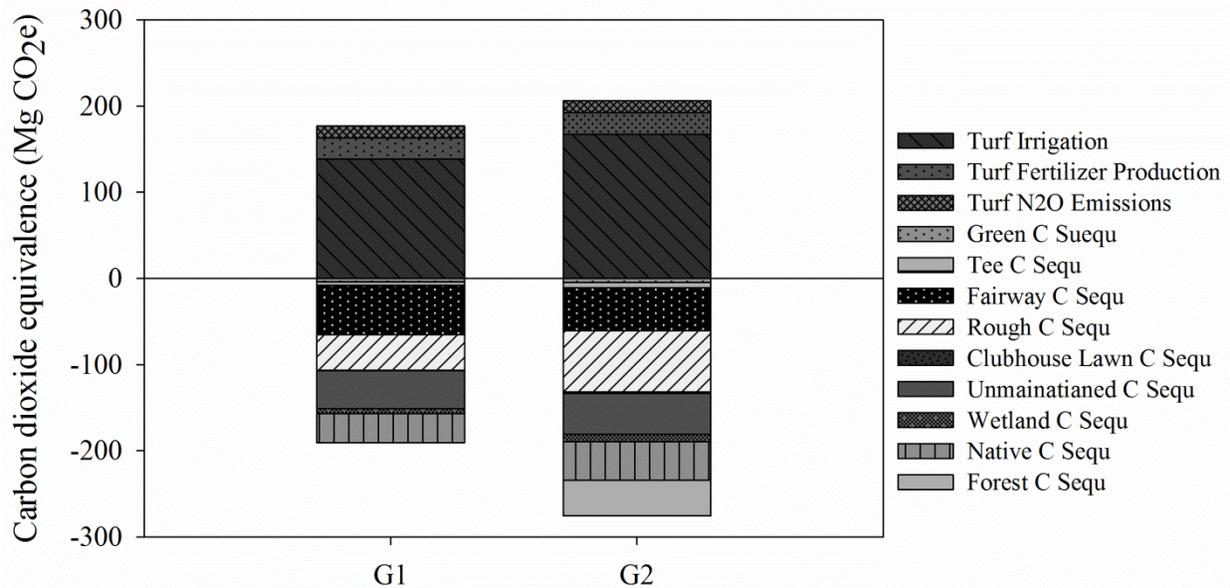


Figure 1.2. Carbon dioxide equivalents emissions for turf maintenance and land management based on two statistical groups G1 and G2 for energy consumption. Positive emissions represent estimates from land management inputs such as turf irrigation, turf fertilization (N, P, and K), and soil nitrous oxide (N₂O) emissions. Negative values represent estimates for carbon dioxide equivalents offsets from land carbon (C) sequestration (sequ) for the various land use types reportedly maintained at golf courses.

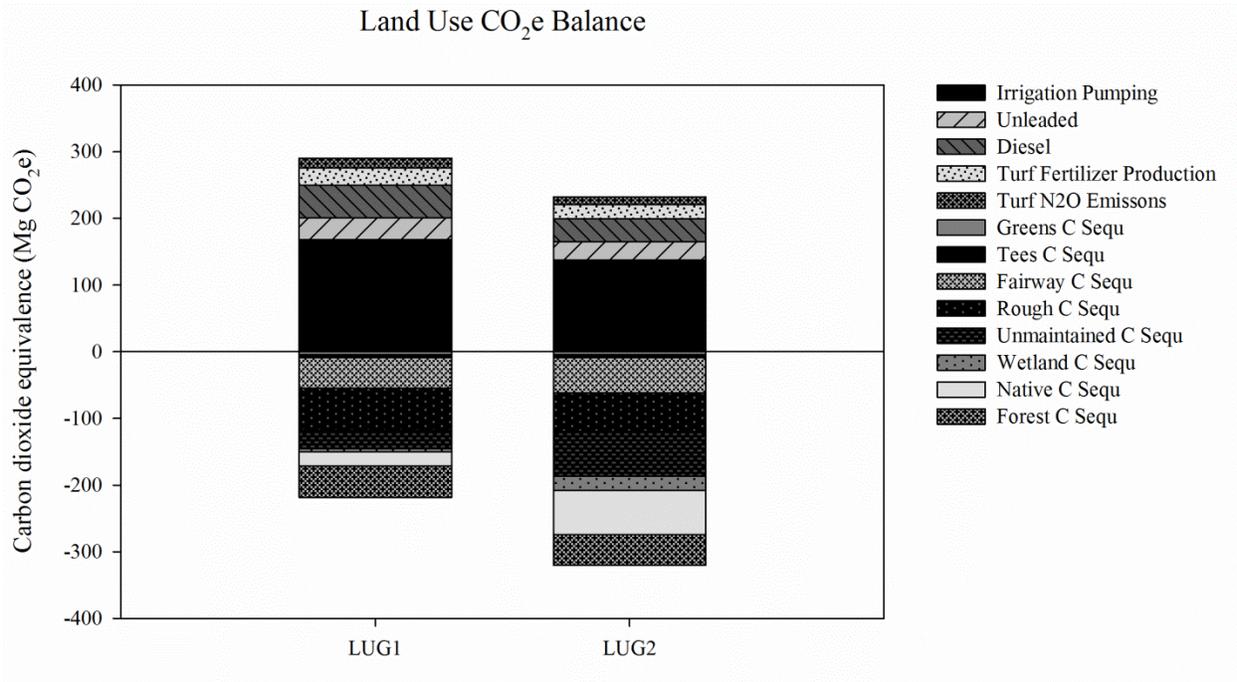


Figure 1.3. Carbon dioxide equivalents (CO₂e) balance for the second cluster analysis based on land management and land use type only. Positive values represent emissions from irrigation water pumping, fuel use, turf fertilization (total of N, P, and K) production, and soil nitrous oxide (N₂O) emissions. Negative values represent estimated carbon dioxide equivalents offsets from soil carbon (C) sequestration (sequ) for the various land use types at golf courses.

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CHAPTER 2:

DAYCENT MODEL EVALUATION OF MANAGEMENT IMPACTS ON SOIL CARBON AND NITROGEN ON TURFGRASS

SYNOPSIS

Rising greenhouse gas emissions are of great concern due to the associated impacts of global climate change. It is important to further assess C and N dynamic in urban areas due to rapid expansion and the associated land cover of turfgrass systems that often require nitrogen and irrigation management to maintain aesthetic quality. Unfortunately it is impossible to directly measure changes in SOC or soil trace gas emissions from turfgrass on a regional or national scale. Therefore process based models such DAYCENT are useful tools to help estimate these changes and their associated uncertainties. DAYCENT has been validated for turfgrass systems and was used to simulate soil C and N for one golf course that participated in the survey. In order to simulate typical management scenarios of fairway, rough and greens, survey information was collected from eighteen golf courses on the Front Range of Colorado. Model outputs of soil C, nitrous oxide, and N leaching were converted to CO₂ equivalents (CO₂e). CO₂e associated costs of irrigation and fertilizer production were also used to generate an overall CO₂e balance for each section of turf. The model simulated rapid SOC accumulation and increased N₂O emissions from turf fairway and rough shortly after turf establishment. Model outputs for leaching were only significant for treatments that were over watered. Simulations of N₂O emissions from putting greens remained steady, but leaching was high. Total CO₂e balances were a net source of emissions for all sections of turfgrass, averaging 1.6, 0.95, and 2.1 Mg CO₂e ha⁻¹ yr⁻¹ from the

fairway, rough and greens, respectively, after 50 yr of turfgrass establishment. Reducing N inputs after turf is established and increasing irrigation system energy use efficiency could substantially decrease emissions from highly managed turf.

INTRODUCTION

Rising atmospheric concentration of greenhouse gases are caused by anthropogenic activity and increase the risk associated with global climate change. Nitrous oxide (N₂O) is one of the most important ozone depleting emission in the 21st century (Ravishankara, et al., 2009), because of its high global warming potential of 298 and the lack of natural sinks to mitigate concentration (Forster et al., 2007). Nitrous oxide is the primary GHG emitted from agricultural soils (Del Grosso et al., 2008), with both natural and managed soils combined emitting over half of the total atmospheric N₂O (Skiba and Smith, 2000). The production of soil N₂O is regulated through two soil microbial processes, nitrification and denitrification. Microbial processes that produce soil N₂O are primarily controlled through N substrate availability (NH₄⁺ for nitrification and NO₃⁻ for denitrification), and soil temperature and moisture.

Land and oceans, provide important offsets to fossil fuel combustion by absorbing approximately half of the CO₂ emissions, thereby also slowing the rise of atmospheric CO₂ concentrations (Poulter et al., 2014). Changes in soil C could therefore have a significant impact on atmospheric CO₂ concentrations. Conversion from natural systems to agricultural tends to decrease soil organic carbon (SOC) pools (Lal and Bruce, 1999), but soil restoration through conversion to grassland combined with intensive management can greatly increase SOC pools of that were once depleted in soils (Conant, 2001). However terrestrial biological cycling of C may only offset fossil fuel emission on a decadal or century time scale (IGBP, 1998). Furthermore, C

accumulation may only be sustained as long as management practices are maintained (Smith, 2004), but if SOC enhancing activity is terminated C accumulated during enhanced management may be subject to rapid loss (Smith et al., 1996).

Due to rapid urban expansion, turfgrass systems have been recognized as an important part of regional GHG budgets (Kaye et al., 2004; Bremer, 2006; Zhang et al., 2013). Turfgrass is a common landscape urban areas (Bandaranyake et al., 2003; Milesi et al., 2005) that provides a suite of benefits that include urban heat dissipation and increased ground infiltration and filtration (Beard, 1973). Fertilizer and irrigation water inputs accelerate soil biogeochemical processes in turfgrass, thereby accelerating C sequestration rates (Qian and Follett, 2002; Lal, 2004; Huh et al., 2008). The rapid increase in SOC level in turfgrass systems has potential for long term SOC storage, and has therefore been promoted as a potential CO₂ mitigation strategy (Lal, 2004a; Smith et al. 2007b; Qian and Follett, 2002). However it is important to recognize the sustained C cost of managing turf with N fertilizer and irrigation. Furthermore, while fertilization and irrigation increase SOC accumulation in turfgrass systems, emissions of other soil GHGs may also be accelerated (Townsend-Small and Czimczik, 2011; Kaye et al., 2004). Therefore it is critical to assess the effects of land use management on soil C and N dynamics and the impact of GHG sinks and sources, in doing so the benefits of urban green spaces can be maximized.

A better understanding of the ecosystem functioning from turfgrass management is needed (Racitti, et al., 2009; Pouyat et al., 2009), yet it is impossible to directly measure changes in SOC or soil trace gas emissions from turfgrass on a regional or national scale. Therefore process based models such as CENTURY or DAYCENT are useful tools to help estimate these changes and their associated uncertainties. CENTURY is a multi-compartmental ecosystem model developed to simulate long term SOC sequestration through soil organic carbon and

nitrogen dynamics, nutrient cycling and plant production (Parton et al., 1987; Parton et al., 1993), and has been well validated for a variety of ecosystems (Parton et al., 1993; Parton and Rasmussen, 1994) including turfgrass systems (Qian et al., 2003; Bandaranayake et al., 2003). More recently, an improved daily version of the model, DAYCENT, was developed and validated for various ecosystems (Del Grosso, et al., 2002; Del Grosso et al., 2005; Del Grosso et al., 2006; Li et al., al 2006; Del Grosso et al., 2008). Like the previous version, DAYCENT uses nutrient availability, land management practices, specific soil properties and daily weather information as key drivers to the biogeochemical model. DAYCENT allows daily outputs of terrestrial and atmospheric C and N exchanges, allowing an opportunity to evaluate daily fluxes of soil trace gas emissions in turf ecosystems (Zhang et al., 2013; Zhang et al., 2013).

Turf management inputs may equal or exceed agriculture croplands (Law et al., 2004). Finely managed turfgrass at golf courses requires C intensive management; therefore environmental impacts from management could be substantial. Importantly, in semi-arid environments such as Colorado, turf systems are limited by water availability and irrigation may pose a substantial cost to production. The objective of our study was to simulate soil C and N dynamics of fairways, greens, and rough at golf course using the biogeochemical model DAYCENT under different management scenarios. In order to get the most realistic management practices used by turf managers we gathered information using a survey collected from 18 golf courses on the Front Range of Colorado. DAYCENT simulations were carried for different management scenarios and model outputs of SOC sequestration, N₂O emission, and N leaching were used to calculate CO₂ equivalents for near term (25yr) and long term (50 yr) periods. We also used other published data to estimate the CO₂e emissions of pumping irrigation water and producing fertilizer. This research will provide information for typical turf management practices

used on highly managed golf courses and provide estimates of CO₂e emissions of turfgrass in this region of Colorado based on near term and long term ecosystem model simulations.

MATERIAL AND METHODS

DAYCENT Model Simulation for Saddle Rock Golf Course

The 4.2 version of DAYCENT was used to simulate long term SOC and soil N dynamics from Saddle Rock Golf Course. DAYCENT uses nutrient flows, soil water and temperature on a daily time scale. Information on soil texture, and soil mineral fractions (% sand, clay and silt), daily weather of minimum and maximum air temperatures, plant type, monthly precipitation and irrigation, and management inputs are needed to run the model. Further details on DAYCENT model are offered by Del Grosso et al. (2008). Turfgrass parameters were based from previous studies (Qian et al., 2003; Bandaranayake et al., 2003; Zhang et al., 2013) that included above and belowground C allocation, lignin content, and thatch damping factors.

In order to have information on specific historic land information, management practices, and weather data, we collected detailed information from one golf course that participated in the golf course survey. Daily weather information for years 1980 to 2012 was obtained from DayMet weather station near Saddle Rock Golf Course, CO (39.35°N, 104.44°W). Soil bulk density for the fairways and rough was 1.15 g cm⁻³. Similar soil minerals fractions were used for the fairway and rough, with estimates of 35, 15, and 50 % of sand, silt and clay, respectively, and 1% organic matter in the 0-20 cm. Soil bulk density was estimated at 1.7 g cm⁻³ for putting greens. Soil fraction estimates for the greens were 80.0, 10.0, 10.0 % for sand, silt, and clay, respectively, and 1.0% organic matter.

Model outputs are influenced by SOC and mineral N levels; therefore historic land management was obtained from Saddle Rock Golf course. In order to establish the initial soil C baseline prior to golf course establishment, simulations were ran from year 1 to year 1993 using three successive land use scenarios of undisturbed native range, grazing land, and dryland wheat. Initially, all baseline simulations began with undisturbed native range that had a mix of 50% cool and warm-season grass vegetation. Native range was converted to agricultural or pasture in 1960. Agriculture consisted of a dryland wheat fallow system that used $120 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ and low yielding wheat until 1982; higher yielding wheat was simulated starting in 1983 with fertilization increased to $165 \text{ kg N ha}^{-1} \text{ yr}^{-1}$; this system was maintained until it was converted into golf course turfgrass. Pasture land was simulated using a dryland system with 50% cool and warm-season grasses, that was moderately grazed and an annual fertilization rate of $50 \text{ kg N ha}^{-1} \text{ yr}^{-1}$. Upon turfgrass establishment starting in 1994, simulated levels of active, passive and slow SOC pools were 0.2, 10.6, and 19.2 Mg ha^{-1} , respectively, at the fairway and rough. Restored native sections were converted to 75% warm season and 25% cool-season grasses in 1994 during golf construction. Simulated levels of active, passive and slow SOC pools were 0.2, 10.6, and 19.2 Mg ha^{-1} , respectively, at the restored native.

Since golf course putting greens are typically constructed on an artificial soil series, a different soil series was considered for simulations of the greens. The top 30 cm soil of the greens soil profile had sand, silt and clay mineral fractions of 75, 0.5, and 15%, respectively, and organic matter levels of 1%. We based soil organic matter pools for putting greens from Century model simulation performed by Bandaranayake et al. (2003). The previous study arrived at proportions of slow, active and passive SOC pools from peatland simulations performed by

Chimmer et al. (2002). For this study, simulated levels of slow, active and passive SOC pools at the time of turf green establishment were 0.59, 0.55 and 11.3 Mg ha⁻¹, respectively.

In 1994 land preparation began for turf where there was a break and change in vegetation. Three turf cultivation options in DAYCENT (turf sweeping, cultivation, and drilling) were simulated for top soil stripping and land grading during golf course construction. Turf establishment was simulated for one year, in which fertilization rates were 120 kg N ha⁻¹ and irrigation water was applied at 100% ET from May until September. Upon turfgrass establishment, different scenarios of N fertilizer management and irrigation levels were used for model inputs for the fairway, rough and greens. Each of the N application rates was based on survey results of the eighteen golf courses that participated in our study and are presented in Table 1 for each section of turf grass. Regardless of fertilizer rate for each scenario, N applications occurred throughout the growing season starting in April and ending in October for each turfgrass section. The timing of N fertilizer applications was based on management reported by Saddle Rock golf course, and other publications describing turfgrass DAYCENT model simulations (Bandaranayanke et al., 2003).

Turfgrass Management Scenarios

Annual aerification was simulated every spring to the greens, fairway and rough to relieve compaction. Turfgrass damping factor was maintained at 0.003 on the greens and fairway due to shorter mowing height and cultural practices to control thatch. However, due to taller mowing height on the rough which allows for an increase of thatch accumulation on Kentucky bluegrass, the damping factor was increased to 0.0045 as cited by Zhang et al. (2013).

Fairway, rough and greens fertilizer management was collected from 18 golf courses on the Front Range of Colorado for the years 2008 and 2009 through the online survey, Survey Monkey. Reported survey nitrogen (N), phosphorus (P), and potassium (K) fertilizers application rates to fairway, rough and greens are shown in Table 1. Fertilizer rates reported in the survey, then used as five management scenarios in DAYCENT for the fairway and rough, and four scenarios for the greens, which are also presented in Table . Model inputs for fairway N application rates were 135, 100, 150, and 180 kg N ha⁻¹ yr⁻¹ for the Saddle Rock (SR), low N (LN), medium N (MN), and high N (HN_75ET) management scenarios, respectively. The model was also used to evaluate how a modification to the SR management scenario would affect SOC and N₂O by reducing N fertilizer inputs by 50% after the first 25 yr of turf establishment (abbreviated as SR_25-50); fertilizer rates for this management scenario on the rough (SR_25-50) were 65 kg N ha⁻¹ yr⁻¹. Model inputs for nitrogen fertilizer rates on the rough were 105, 70, 90, and 130 kg N ha⁻¹ yr⁻¹ for the SR, LN, MN, and HN scenarios, respectively. Management scenarios for N fertilizer rates on the greens section of turf were 150 and 180 kg N ha⁻¹ yr⁻¹ for the GRN_150 and GRN_180, respectively.

Growing season irrigation water applications were reported by Saddle Golf Course began in April and ended in October, with irrigation applications meeting approximately 75 and 50% of evapotranspiration (ET) demand on the fairway and rough. In the model, irrigation water applications were scheduled when soil water content was depleted to 25 and 50% of soil water holding capacity on the fairway and rough, respectively, and used for the SR, LN, MN, HN_50ET (rough), and HN_75ET (fairway) treatments. Using these two irrigation rates for the fairway and rough, the 50 year average was approximately 43.5 and 25 cm of irrigation water per year, respectively. For the high N and irrigation scenarios on the fairway (HN_100ET) and rough

(HN_75ET), irrigation rates were simulated to meet 100 and 75%, respectively. The model predicted that on average 47 and 42 cm of irrigation water applied per year over the 50 yr simulation period in order to meet 100 and 75% ET demand, respectively. Also based on Saddle Rock irrigation management on turfgrass managed as the green, irrigation water applications were simulated to meet approximately 75% ET demand for the GRN_150 and GRN_180 treatments. In the model, irrigation was applied to the greens when soil water content was depleted to 25% of soil water holding capacity. A second irrigation rate was also used to 100% ET for the GRN_150_Irri and GRN_150_Irri management scenarios. Over the 50 yr simulation period the model predicted that in order to meet 75 and 100% ET demand that 30 and 35 cm of irrigation water was needed, respectively.

CO₂ Equivalent Coefficients

DAYCENT model output of near term (25yr) and long term (50 yr) changes in SOC (Delta_Carbon, ΔC), N₂O emissions, and N leaching were converted to carbon dioxide equivalents (CO₂e). Means of 4.8, 0.7, and 0.6 kg CO₂ kg⁻¹ were used for production and transportation costs of N, P, and K fertilizers, respectively (Lal, 2004). Pumping irrigation water was cited as producing 0.95 Mg ha⁻¹ yr⁻¹ when electricity was the primary source of energy (West and Marland, 2002). Global warming potential of 298 were estimated for N₂O emissions from Forster et al. (2007) over a 100 year time period. In order to compare DAYCENT model outputs to IPCC emission factors we also calculated soil N₂O emission factors based from IPCC (2006) report that assume 1.0% of applied fertilizer will be directly emitted as N₂O. The IPCC (2006) report further describes that 0.75% of leachates will be indirectly emitted as N₂O.

Statistical Methods

Statistical analysis using SAS program PROC CLUSTER (SAS v. 9.2, North Carolina) was used to group golf according to fairway and rough N fertilizer rates. Briefly, we used the Ward method in PROC CLUSTER which bases clustering decisions on similarities and are predicted hierarchically from ANOVA sum of squares. Also there was greater variability in application rates for the fairway and rough turfgrass compared to application rates to the greens, therefore allowing for more distinct groups to be identified in the data set.

RESULTS AND DISCUSSION

DAYCENT SOC Simulations of Golf Course Turf

At the time of turfgrass establishment, simulated SOC for historic land use was reaching equilibrium, having between 30.3 to 30.5 Mg C ha⁻¹. Preparation and establishment of turf did not have a major effect on SOC, and levels remained between 30.0 and 30.1 Mg SOC ha⁻¹ for the fairway and rough. After establishment SOC levels began to increase with the onset of N and irrigation applications. The predicted annual aboveground net primary productivity (ANPP) from DAYCENT is presented in Table 1 for the greens, fairway, and rough were approximately 2800, 2500, and 2000 kg C ha⁻¹ yr⁻¹, respectively. Our values closely match field measurements of 1800 kg C ha⁻¹ yr⁻¹ (Kaye et al., 2005) for medium quality turf, and 2800 kg C ha⁻¹ yr⁻¹ (Qian et al., 2003) for fine quality turf. Koski and Skinner (2011) estimated that in order to meet turfgrass N requirements for a medium quality lawn that 90 kg N ha⁻¹ would have to be applied annually.

The average age of the golf courses that participated in the survey was thirty-one years, but there was fairly large variation, with year of construction ranging between the years 1901 and 2007. There was also a large variation in turfgrass fertilizer application rates to the fairway and

rough section between courses. Nitrogen application rates ranged between 200 and 100 kg N ha⁻¹ yr⁻¹ for fairways and between 110 and 50 kg N ha⁻¹ yr⁻¹ on the roughs.

Simulations were carried for 50 yrs, and total SOC in the top 20 cm of soil was between 52 and 54 for fairway scenarios, and 48 and 49 Mg C ha⁻¹ for rough scenarios. The DAYCENT model predicted rapid SOC accumulation in the first 25 yr of turf establishment, with maximum C sequestration rates reaching 0.58 and 0.62 Mg C ha⁻¹yr⁻¹ on the fairway, and 0.46 and 0.48 Mg C ha⁻¹ yr⁻¹ on the rough. Simulations of SOC sequestration on putting greens was also rapid reaching 32.5 and 33.1 Mg C ha⁻¹ after 50 yr of establishment. Maximum putting green SOC sequestration rates were calculated at 0.55 and 0.66 Mg C ha⁻¹ occurring after 25 yr of turf establishment. Simulated C sequestration rates on the fairways did not reach maximum potentials as reported by Qian and Follett (2002) who measured 0.9 Mg C ha⁻¹ yr⁻¹ from other Colorado golf course fairways. Simulated SOC accumulations of this current study are low but still within range of estimates made by Bandaranayake et al. (2003) who compared simulated and measured SOC sequestration rates using the CENTURY model from Colorado golf course fairways and greens over a 100 year time period. Fairway simulations in the previous study totaled 58 to 80 Mg SOC, and putting greens reached a total of 31 to 36 Mg SOC. The model is sensitive to soil parameters such as bulk density and sand and clay content, and simulations we present in this study may reflect the variability of C sequestration rates for different soil types.

DAYCENT model predictions for N₂O emissions were between 1.1 and 5.9 kg N₂O-N ha⁻¹ yr⁻¹ for the 25 and 50 yr simulation periods on the fairway, and 0.75 and 5.3 kg N₂O-N ha⁻¹ yr⁻¹ during the same time periods on the rough. There was less variation for the near and long term time periods in terms of N₂O emissions on the greens which ranged between 1.0 and 1.2 kg N₂O-N ha⁻¹ yr⁻¹. Emissions from our analysis are within the range of annual N₂O emissions measured

from turfgrass in the field that range between 0.5 and 6.4 kg N₂O-N ha⁻¹ yr⁻¹ (Guilbault and Mathias, 1998; Kaye et al., 2004; Groffman et al., 2009).

Turfgrass CO₂e Balances from DAYCENT Model Simulations

Due to the dynamic changes in soil C and N during the first 25yr of establishment, we based our CO₂e calculations on near term (first 25yr) and long term (50yr) averages for turf management scenarios; each scenario is described in Table 1. The CO₂e calculations based on DAYCENT model results for the ΔC and N₂O emissions are presented for each turf management scenario in Figure 1; included in the CO₂e balances are the CO₂e costs of fertilizers (N,P, and K) (Lal, 2004) and electricity used for pumping irrigation water (West and Marland, 2002). Simulated SOC accumulation was the most rapid in the first 25 years after establishment, and gradually declined over time. Qian and Follett (2002) estimated that SOM reached equilibrium with 25yrs following establishment on Colorado turfgrass maintained as fairways. The first 25yr after turf establishment DAYCENT predicted ΔC between 2.2, 2.0 and 1.7 Mg CO₂e ha⁻¹ yr⁻¹ for the greens, fairway and rough, but the 50 yr ΔC was reduced to 1.5, 1.6 and 1.4 Mg CO₂e ha⁻¹ yr⁻¹ for the respective turf sections.

Simulations of SOC carried out for this study for in the near term (25yr) period are lower than other measured and simulated SOC accumulation which range between 2.4 and 3.4 Mg CO₂e ha⁻¹ yr⁻¹ (Qian and Follett, 2002; Huh et al., 2008; Zhang et al., 2013). However the previous studies reported maximum rates of SOC accumulation which likely occur earlier on (10 yr) prior to SOC saturation, whereas simulations for this report include both the maximum and the slowed rates. Smith (2004) notes that C sequestration rates may greatly decrease after only a few years the soil C enhancing management practices are implemented. Smith et al (1996) goes

onto to establish that if C enhancing management practices are not sustained, the C sequestered in subject to rapid loss, posing a question of permanency.

N₂O emissions simulated in DAYCENT were calculated into CO₂e emissions for the near and long term time periods. During the first 25yr emissions were the greatest from high fertilization rates (HN) on the fairway, ranging between 1.5 and 1.6 Mg CO₂e ha⁻¹ yr⁻¹, but the SR, LN, and MD scenarios did not exceed 1.1, 1.2 and 1.25 Mg CO₂e ha⁻¹ yr⁻¹, respectively. CO₂e emissions from N₂O increased on the fairway to 1.7 and 2.4 Mg CO₂e ha⁻¹ yr⁻¹ for the HN and HN_100ET management scenarios for the long term (50yr) simulation period, respectively, but emissions were similar for the SR, LN, and MN scenarios, emitting 1.3 Mg CO₂e ha⁻¹ yr⁻¹. Emissions during the first 25 yr of establishment for management scenarios on the rough were typically below 1.1 Mg CO₂e ha⁻¹ yr⁻¹, except for the HN_75ET where emissions averaged 1.4 Mg CO₂e ha⁻¹ yr⁻¹. The 50 yr average of emissions were typically below 1.3 Mg CO₂e ha⁻¹ yr⁻¹ for most management scenarios on the rough, except for the HN_75ET treatment which averaged 1.6 Mg CO₂e ha⁻¹ yr⁻¹. Turf simulated as the greens were unique in the sense that emissions did not increase from the 25 to 50 yr simulation period, but remained steady, averaging between 1.1 and 1.2 for all treatment scenarios.

Long term DAYCENT model predictions of N₂O emissions increased on the fairway and rough using a constant of fertilizer rate, with emission increases being dependent on N fertilizer rates. Nitrous oxide fluxes from biological sources are dependent upon soil mineral N concentrations, soil water content and temperature, and texture (Del Grosso et al., 2001a; Parton 2001; Del Grosso et al., 2008). DAYCENT is highly sensitive to N inputs (Del Grosso, et al., 2006), and N₂O emission increases simulated on the fairway and rough turfgrass may be a result of that sensitivity. By using different management scenarios, DAYCENT model simulations

demonstrated greater variability in N₂O emissions than over all SOC sequestration rates which had important impacts on CO₂e balances calculated for the fairway and rough.

The net CO₂e balance for all turfgrass management scenarios is presented in Figure 2. Due to the strong global warming potential of N₂O, increases emissions over time significantly affected CO₂e balances. Including CO₂e emissions from pumping irrigation water all management scenarios had a net positive CO₂e balance. The fairway LN treatment had the smallest CO₂e balance of 0.55 Mg CO₂e ha⁻¹ yr⁻¹ after 25 yr of turf establishment, while other management scenarios emitted between 0.8 and 1.45 Mg CO₂e ha⁻¹ yr⁻¹. The HN_100ET treatment on the fairway had the greatest CO₂e balance after 50yr of establishment than all management scenarios, with a net balance of 2.1 Mg CO₂e ha⁻¹ yr⁻¹. The SR_25-50 management scenario, in which fertilizer and irrigation rates were reduced by half after 25 yr of turf establishment, had the lowest CO₂e balance on the fairway after 50 yr of establishment of 0.99 Mg CO₂e ha⁻¹ yr⁻¹. This management scenario on the rough however had a balance of 1.2 Mg CO₂e ha⁻¹ yr⁻¹, and the LN treatment on the rough had the smallest balance of 0.86 Mg CO₂e ha⁻¹ yr⁻¹. There was less variability in the CO₂e balances for the different management scenarios on the greens after 50 yr of turf establishment, with total CO₂e emission ranging between 1.6 and 1.8 Mg CO₂e ha⁻¹ yr⁻¹.

The model predicted soil mineral N leaching rates to be negligible on the fairway and rough using irrigation management scenarios that did not over apply water (50-75% ET). However simulations on fairway where irrigation was applied to meet approximately 100% ET, leaching rates averaged 80 kg N ha⁻¹ yr⁻¹ over the 50 yr simulation period. There have been many published works on N leaching from turfgrass systems, and most studies conclude that turf systems pose little risk of N leaching (Star and DeRoo, 1981; Miltner et al., 1996; Kopp and

Guillars, 2004; Groffman et al., 2009). However in a review on N leaching rates in turfgrass systems, Petrovic (1990) notes a high degree of variability caused by site specific abiotic factors, such as soil texture, precipitation turf N fertilization and irrigation management practices. Frank et al. (2006) refers to turfgrass age as an important consideration when assessing the risk of over fertilization, and concluded that rates of as low as 50 kg N ha⁻¹ to mature turfgrass stands (>25 yr) increase the potential of N leaching. Along with fertilization, risk of N leaching are increased when turf is over watered. When irrigation is closely monitored to meet actual turf demand the risk of leaching is greatly reduced.

Due to the greater porosity from increased sand content in the top 30 cm of soil there was no increase of N₂O emissions on the greens as there was on the fairway and rough using a constant fertilization rate over time. After 5yr of putting green establishment N₂O emissions doubled, but after this, emissions remained fairly steady for the duration of the simulation. However, because of the sand based root zone on the green DAYCENT predicted much greater leaching rates using all irrigation levels than compared to the fairways and roughs. Nitrous oxide emissions are often lower for coarse textured soils, while indirect emissions may be much greater (Alder et al., 2012). Leaching causes offsite denitrification, thereby indirectly contributing to atmospheric loading of N₂O concentrations (Cavigelli et al., 2012). Offsite movement of N fertilizer increases indirect N₂O emissions when N fertilizer is denitrified downstream (David et al., 2011).

DAYCENT and IPCC Emission Factors

The current methodology used by the IPCC (2006) estimates 1.0% of applied fertilizer will be emitted as N₂O, yet there has been much criticism of this emission factor because it does

not take into account land use, soil type, or precipitation gradients (Lesschen et al., 2011). Nitrogen can be stored and cycled in the plant soil system for many years prior to harvest, or can be lost through other pathways such as gaseous emissions or leaching (Follett, 2001a). An important feature of the DAYCENT is that it accounts for legacy effects of N fertilizer additions, allowing fertilizer to be internally cycled for multiple years (Del Grosso et al., 2005). The age of the turfgrass stand is an important factor in determining the fate of applied N (Frank et al., 2006), and the ability of turf to retain organic N under constant management is reduced as the age of the stand increases (Bouldin and Lathwell, 1998; Qian et al., 2003; Frank et al. 2006).

Turfgrass has high internal N cycling rates, and when clippings are returned to the system N fertilization should be reduced as the age of the grass stand increases (Qian et al., 2003). Therefore there is a high risk of over fertilizing turfgrass stands that have been established for over 10 yr due to the incapacity of soil to store organic N once equilibrium of SOC matter and net N immobilization are reached (Porter et al., 1980; Petrovic, 1990; Frank et al., 2006). Using the DAYCENT model and fertilization rates of $150 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ and irrigation applications of 60 to 100% potential ET, DAYCENT simulations of N_2O emissions from turfgrass by Zhang et al. (2013) dramatically increased within the first 15 yr of turfgrass establishment, reaching maximum N_2O emissions of $6.1 \text{ kg N}_2\text{O-N ha}^{-1} \text{ yr}^{-1}$ after 46 yr.

We compared the 25yr average of N_2O emissions from DAYCENT simulations to the IPCC emission factor of 1% in Figure 3. DAYCENT model predictions of N_2O emission exceeded IPCC emissions by 25 to 100% on fairway, 20 to 45% on the rough, and 50% on the greens for all management scenarios. DAYCENT model simulations from turf have been found to closely match emissions measured in the field (Zhang et al., 2013; Kaye et al., 2004).

However due to the moderate complexity of the model, simulated N₂O fluxes may not exhibit very high accuracy and may need further improvement (Delgrosso et al., 2008).

CONCLUSION

The DAYCENT model predicted rapid SOC sequestration rates in the first 25 yr of turf establishment, with fairways having greater rates than roughs due to greater N fertilizer and irrigation water applications. Rapid SOC sequestration was also predicted on the greens, but reached equilibrium faster due to the sand based root zone. DAYCENT simulations predicted greater N₂O emission after 25yr of turfgrass establishment to the fairway and rough, indicating a need to decrease nitrogen fertilizer inputs. The average age of golf courses that participated in the survey was approximately 30 years, and yet fertilization rates of 180 kg N ha⁻¹ yr⁻¹ were reported for fairways, indicating that N₂O emissions from Colorado golf course turfgrass may exceed IPCC emission factor of 1%. Simulated N leaching on the fairway and rough is in agreement with other published work, indicating that under proper management risk is minimized, yet over watering can greatly increases leaching. However leaching rates from greens were greater than any other documented studies, indicating that the DAYCENT model is highly sensitive to sand content or may not be fully capable of capturing the dynamic interactions of highly managed turf such as those maintained as golf course greens. According to DAYCENT model simulations, at best CO₂e balances of golf course turf can be C neutral, but are more likely sources of CO₂e emission.

TABLES AND FIGURES

Table 2.1. Fairway, rough and greens management scenarios simulated in DAYCENT fairway and rough management scenarios include Saddle Rock (SR), 50% reduction in N (SR_25-50) (50 yrs only), low nitrogen (LN), medium nitrogen (MN), high nitrogen (HN), and high nitrogen and irrigation (HN_Irri) for the fairway and rough. Four management scenarios of 150 and 180 kg Nha-1 yr-1 (GRN_150 and GRN180) and 150 and 180 kg Nha-1 yr-1 with high irrigation (GRN_150_Irri and GRN_180_Irri) are presented for the greens.

Turfgrass section	Management Scenario	Nitrogen fertilizer rate kg ha ⁻¹ yr ⁻¹	Phosphorus fertilizer rate kg ha ⁻¹ yr ⁻¹	Potassium fertilizer rate kg ha ⁻¹ yr ⁻¹	Irrigation (%ET)	Clipping yield (ANPP)* kg ha ⁻¹ yr ⁻¹	Leaching kg ha ⁻¹ yr ⁻¹
Fairway	SR	135	10	58	75	2450	NA
	SR_25-50	65	10	58	50	2350	NA
	Low	100	10	58	75	2300	NA
	Med	150	10	58	75	2500	NA
	High	180	50	100	100	2500	NA
	High N _ Irri	180	50	100	100	2550	80
Rough	SR	105	10	25	50	2000	NA
	SR_25-50	50	10	25	50	2000	NA
	Low	70	10	25	50	1950	NA
	Med	90	30	25	50	2100	NA
	High	130	30	60	50	2100	NA
	High N_Irri	130	30	60	75	2200	NA
GREEN	GRN_150	150	50	180	75	2750	60
	GRN_150	150	50	180	100	2700	80
	GRN_180	180	65	210	75	2800	80
	GRN_180_100ET	180	65	209	100	2850	98

*above ground net primary productivity (ANPP); not applicable (N/A)

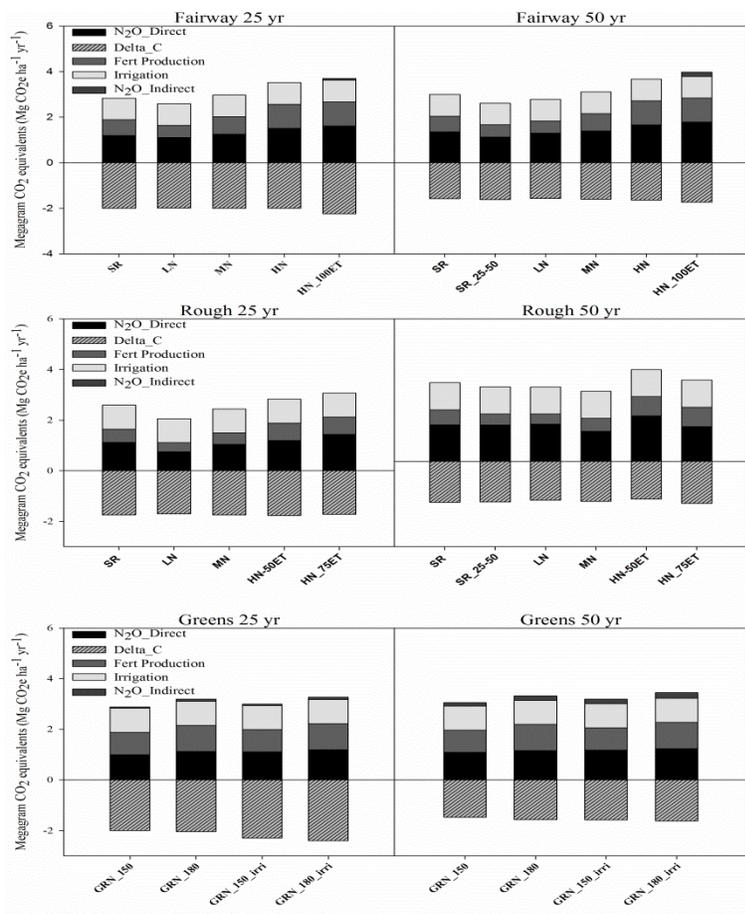


Figure 2.1. The carbon dioxide equivalent (CO₂e) balance of for the fairway, rough and green after 25 yr and 50 yr of turfgrass establishment based on direct N₂O emissions (N₂O_direct), change in soil organic carbon sequestration (Delta_Carbon), fertilizer production, and indirect N₂O emissions from leaching (N₂O_indirect). CO₂e balances are calculated for four and five management scenarios for first 25yr and 50yr of turfgrass establishment for Saddle Rock (SR), 50% reduction in N (SR_25-50) (50 yrs only), low nitrogen (LN), medium nitrogen (MN), high nitrogen (HN), and high nitrogen and irrigation (HN_Irri) for the fairway and rough. Four management scenarios of 150 and 180 kg Nha-1 yr-1 (GRN_150 and GRN180) and 150 and 180 kg Nha-1 yr-1 with high irrigation (GRN_150_Irri and GRN_180_Irri) are presented for the greens.

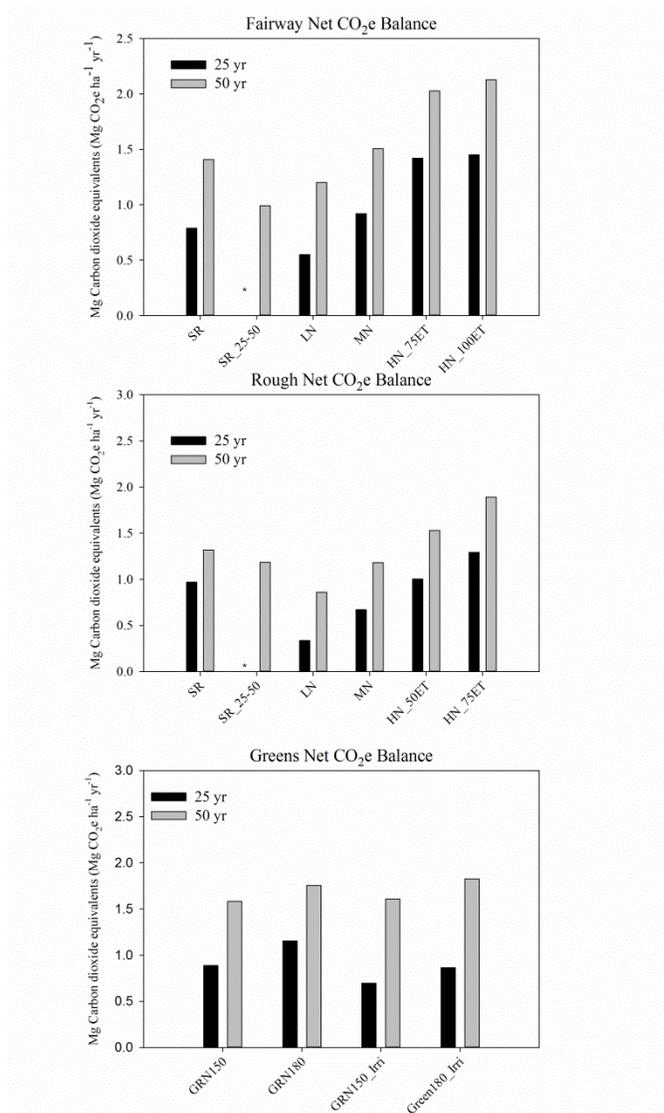


Figure 2.2. The net CO₂ equivalent (CO₂e) balance of fairway rough and greens following 25 yr and 50 yr of turfgrass establishment. (* for the 25 yr time period for management scenario SR_25-50 for the fairway and rough are the same for the SR treatment).

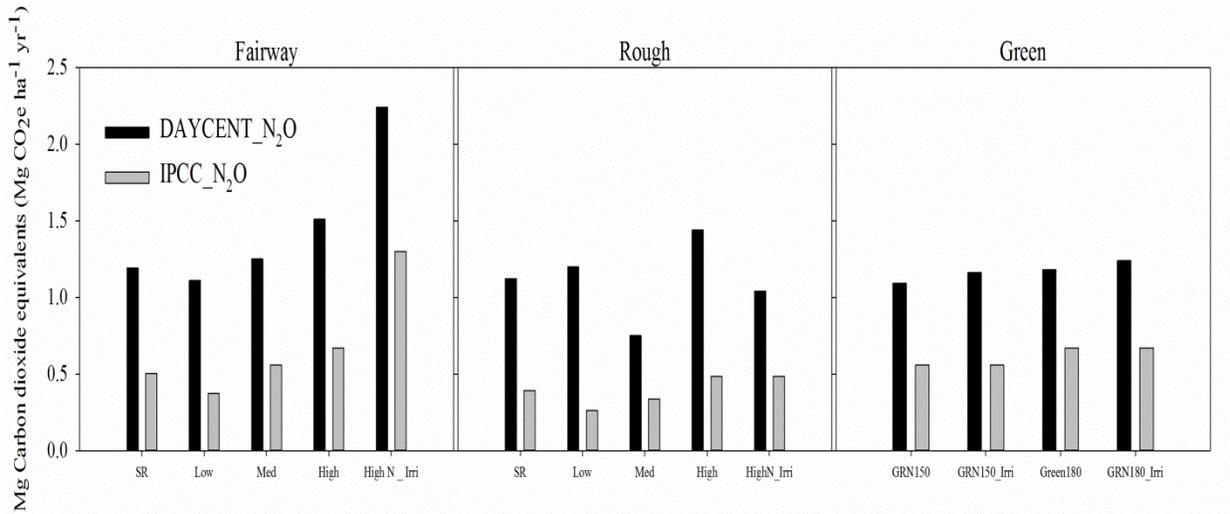


Figure 2.3. Nitrous oxide emissions calculated as carbon dioxide equivalents (CO₂e) based on DAYCENT model output and IPCC emission factor of 1% for the four management scenarios on the fairways, rough and greens section of turfgrass. Fairway and rough management scenarios include Saddle Rock (SR), low nitrogen (Low), medium nitrogen (Med), high nitrogen (High), and high nitrogen and irrigation (HighN_Irri). Management scenarios on the greens include 150 and 180 kg Nha⁻¹ yr⁻¹ (GRN_150 and GRN180) and 150 and 180 kg Nha⁻¹ yr⁻¹ with high irrigation (GRN_150_Irri and GRN_180_Irri) are presented for the greens.

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CHAPTER 3:

NITROUS OXIDE EMISSIONS FROM A COLORADO GOLF COURSE USING DIFFERENT NITROGEN RELEASE MECHANISMS

SYNOPSIS

Urban areas are expanding, but few studies have quantified nitrous oxide (N_2O) emissions from turf systems, especially those that are intensively managed such as golf courses. UMaxx[®], Polyon[®], and BCMU[®] three fertilizer treatments that utilize different mechanisms of controlling N release, were applied to a Front Range Colorado golf course fairway and rough three times during the 2011 growing season at a rate of 50 kg N ha^{-1} per application. The vented chamber method was used to measure turf-soil-atmospheric trace gas exchange. Cumulative emissions from fairway UMaxx, Polyon, and BCMU treatments totaled 6.5, 1.9, and 7.6 $\text{kg N}_2\text{O-N ha}^{-1} \text{ yr}^{-1}$, representing a 4.0, 1.2 and 4.7% loss, respectively. The summer fairway fertilization produced the greatest N_2O fluxes, but was most significant for plots treated with UMaxx and BCMU materials. Rapid fluxes during the summer were likely related to low physiological activity in cool-season turfgrass, and warm, wet soil conditions that increased denitrification rates. However, Polyon treatments applied to the fairway were more resistant to N_2O losses than other fertilizer treatments. Fertilizer treatments applied to the rough had cumulative emissions of 2.4, 1.5, and 1.5 $\text{kg N}_2\text{O-N ha}^{-1}$ from UMaxx, Polyon, and BCMU treatments, and corresponds to a 1.3, 0.6, and 0.6% loss of total N applied, respectively. Differences in turf management played a significant role on N_2O emission rates. Therefore, understanding variables that affect

such emissions from golf course turfgrass will help decrease nitrogen losses and maximize benefits of urban green spaces.

INTRODUCTION

Increased greenhouse gases (GHGs), e.g. carbon dioxide (CO₂), methane (CH₄), and nitrous oxide (N₂O) have contributed to climatic warming and destruction of atmospheric ozone (Cicerone, 1989). Anthropogenic N₂O emissions make up 60% of the global budget, with the remainder coming from natural sources (Syakila and Kroeze, 2011). Nitrous oxide has much greater global warming potential than CO₂ (Syakila and Kroeze, 2011), and stays chemically active in the atmosphere for approximately 114 years (Albritton and Mira-Filho, 2001). Since the onset of the industrial era, the 20% increase of N₂O concentration has been almost linear over time (Forster et al., 2007), and now exceeds 320 ppbv (Smith et al., 2012). This increase signals the impact humans have had on the global nitrogen (N) cycle from the transfer of unreactive atmospheric gas (N₂), to biological terrestrial and aquatic systems. Combining future predictions of urbanization, population growth, and energy and food demands, anthropogenic N₂O emissions are likely to continue to have ecological impacts for decades to come (Vitousek et al. 1997; Ravishankara et al. 2009, Chu and Manjumbar, 2011).

While specific sources and quantities of N₂O emissions are uncertain, it is clear that soil management practices from legume cropping, and fertilizer and manure applications are primary sources of U.S. agricultural N₂O emissions (US EPA, 2011). Nitrous oxide is released as a side product of soil microbial nitrification and denitrification. The rate of nitrous oxide emissions from soils is a function of soil temperature and moisture, top soil N substrate availability, as well as labile C substrates for denitrification (Granli and Bøckman, 1994; Skiba and Smith, 2000; Conen et al., 2000). As a result, environmental conditions and soil management practices that

affect soil moisture, temperature and nitrogen substrate, significantly impact the amount of soil N₂O released (Skiba and Smith, 2000; Bremer, 2006; Clayton et al. 2007).

Rapid urbanization has occurred in the past 25 years worldwide, and turfgrass is a common feature in urban landscapes (Yao and Shi, 2010; Dell et al., 2010; Bandaranayake et al., 2003). Turfgrass ecosystems are highly managed, and one of the most extensively irrigated crops in the United States (Milesi et al., 2005). Recent research (Qian and Follett, 2002; Zirkle et al., 2011) has described turfgrass systems as contributors to atmospheric CO₂ mitigation through rapid SOC sequestration as a result of nutrient input management and sustained soil cover due to the perennial nature of turfgrass. However, without comprehensive accounting of total GHG emissions in managed systems, a complete understanding of the carbon (C) and (N) nitrogen cycle through ecosystem functions cannot be possible (Robertson and Grace, 2004; Del Grosso et al., 2005; Townsend and Czimick, 2010). Research has only recently begun to evaluate the important human-environmental interactions in residential landscapes (Byrne and Grewal, 2008). In particular, N cycling in turfgrass systems has not been as rigorously studied as in agricultural systems (Groffman et al., 2009), leaving environmental impacts of these fertilized and irrigated areas uncertain (Kaye et al., 2004; Zhang et al. 2013).

Although N₂O emissions tend to directly increase with N fertilizer application (Granli and Bøckman 1994; Maggiotto et al., 2000; Lokupitiya and Paustian, 2006), the amount of N₂O released per kg of N applied can vary (Van Groenigen et al. 2010; Lesschen et al. 2011). Recent advancements in fertilizer technology that alter interactions between N additions and the soil environment may decrease N₂O emissions by reducing environmental losses and increasing plant nutrient availability compared to conventional types (Shuman 2006; Olson-Rutz et al., 2009). There are several mechanisms by which N fertilizer technology may alter the release of nitrogen.

Blaylock et al. (2004) characterized controlled release fertilizers, as inorganic N compounds that have low solubility and release rates intended to match plant demand. Stabilized or slow release N fertilizers, inhibit microbial or enzyme activity, decreasing denitrification by maintaining N substrate in the more stable form of ammonium (Halvorson et al., 2013). Quantifying how the relationship changes for different types of fertilizer is a primary focus of current research (e.g., Halvorson et al., 2013), but more research is needed to assess how different mechanisms of fertilizer release are affected under a variety of conditions.

Today, golf courses are a common landscape feature around the world, with an estimate of 32,000 courses globally (Tanner and Gange, 2005), that are typically 60-80 ha in size (EPA, 2010). There is limited research on turf-atmospheric exchanges of trace gases (Guilbault and Matthias, 1998), especially those that address the impact of intensive management practices unique to golf courses, such as frequent fertilization, mowing, and irrigation events. The purpose of this research was to quantify N₂O emissions from a Colorado golf course fairway and rough using three urea fertilizers with different mechanisms that control N release. Fertilizers were applied multiple times to each fairway and rough throughout the growing season to determine when N₂O losses were the greatest from the two turfgrass sites.

MATERIAL AND METHODS

Site Description and Fertilizer Applications

This study was conducted on the Front Range of Colorado, USA, in a region where urban sprawl has changed primary land use from rural to suburban. The club was opened to golfers in 2007, but the historical land use for the site was a 100 year old alfalfa and sheep farm. The soil is classified as 67.4% Larim gravelly sandy clay loam, and 32.6% Ascalon sandy clay loam. The

soil is calcareous with a pH of 7.5, with a sandy clay loam texture from 1-5 cm, and the soil texture below (5-90 cm) is sandy clay. Soil mineral fractions of sand, silt and clay, bulk density and soil organic carbon and nitrogen in the 0-5 cm of the soil profile are presented in Table 1. Mean air temperature during the study period, June 2011 to May 2012, was 10.1 °C, 1.2 °C above the 20 year average. There was a total of 124 mm of precipitation during the study period, about half of the 20 year average.

In 2006 Perennial ryegrass (*Lolium perenne*) was seeded to fairways, and Kentucky bluegrass (*Poa pratensis* L.) was sodded to roughs. Fairways are mowed three times per week at 1.9 cm height. Roughs are mowed one or two times per week at 6.35 cm height. Irrigation water is applied every day starting in March and ending in October at approximately 100% evapotranspiration on the fairway and rough sites. Prior to the experimental plot establishment, the last fertilizer application occurred in May and July of 2010, and totaled 250 and 175 kg N ha⁻¹ of POLYON[®] on the fairway and rough, respectively.

Turfgrass fairway and rough study plots were selected in early May of 2011 (Julian day of year (DOY) 122) at a golf club near Fort Collins, CO. Global positioning systems located the exact field sites to be 32.066°N, 57.65°W on the fairway and 32.064°N, 57.69°W on the rough. Turfgrass plots were selected on the back-nine of the golf course where there was minimal soil disturbance during golf course construction. The primary factors investigated were fertilizer treatments and turfgrass sites (fairway versus rough). A randomized complete block design was established on the fairway and rough in order to accommodate three replications and four treatments which included three EEN fertilizers and one control (zero fertilizer). Each block was divided into 12 plots, with each plot measuring 1.5 m² in size, and 60 cm borders separating replications, to accommodate the four treatments (control, UMaxx, Polyon and BCMU).

The three granular urea fertilizer sources evaluated were as follows: UMaxx[®] (47% N) (Koch Agronomic Services, LLC, Wichita, KS), and two Agrium Advanced Technologies fertilizers Polyon[®] (42% N) and balance chain methylene urea BCMU[®] (21% N) (Loveland, CO). UMaxx[®] uses an soil enzyme inhibitors nitrification dicyandiamide (DCD) and urease thiophosphoric triamide (TPT) as a slow release mechanism; Polyon[®] is a polymer coated controlled release urea fertilizer; and BCMU[®], is an uncoated balanced methylene urea chain, that requires biological degradation, much like urea. Fertilizers were applied three times during the growing season, on Julian DOY 165, 210, and 259 of 2011 during the months of June, July, and September (from here on fertilizations will be referred to as F1, F2, and F3, respectively). A total of 150 kg N ha⁻¹ of each fertilizer treatment was split into three applications, with 50 kg N ha⁻¹ applied per fertilization. Fertilizer was mixed with approximately 50 g of sand and applied by hand for an even distribution across each treatment plot. After fertilization 8-10 mm of irrigation water was applied through an in-ground sprinkler irrigation system to all fertilized plots.

Soil Processing

Baseline soil samples were collected during the spring of 2011 (DOY 122) using techniques highlighted by Follett (2009). Briefly, by under cutting with a flat bladed shovel, one 25 cm³ square of whole intact soil was extracted from the top 0-5, 5-10, and 10-30 cm of the soil profile from one of the four corners of the randomized block. Upon extraction each sample was immediately and carefully placed in plastic bags to preserve field soil moisture and soil structure. Soil samples at 30-60 cm and 60-90 cm in the first replication of samples were extracted using a metal soil core of a known volume and handled accordingly. On the following three replications

of soil samples, only the top 0-5 and 5-10 cm of soil were extracted by under cutting with the shovel blade, and the remaining three depths were extracted using soil cores.

Soils were transported to the USDA-ARS laboratories and stored until further processing. Prior to soil processing the top 0-5cm of soil was placed on an aluminum tray where verdure was removed with a razor blade; subsequently the fairway organic mat (Perennial ryegrass) or the rough thatch layer (Kentucky bluegrass) was also removed with a razor blade, accounting for approximately 1.25 cm and 1.50 cm of the top soil, respectively. The mat and thatch layers were excluded from the soil analysis. Approximately, 12-15g of soil was subsampled and weighed in order to calculate gravimetric soil water content by placing moist soil samples in a 110 °C oven overnight to determine percent moisture. Soil bulk density was calculated based on percent moisture from field samples and specific volume of soil extracted per sample.

Another subsample of 250-500g of soil was taken from each replicated depth, processed through a 2 mm sieve and air dried. Soil fractionation of particulate sand, silt, and clay, as well as soil inorganic nitrogen (N) were determined using the sieving methods, with respective sieve sizes of >53 micrometer (μm), >20 μm , and < 20 μm , respectively. Additionally, 50g of sieved soil was sent to the Colorado State University Soil Laboratory and analyzed for soil carbon, soil texture, and pH.

Soil Inorganic Nitrogen

Soils were collected from each fairway and rough treatment plot at the end of the year (EOY) in the fall of 2011 (DOY 327) using metal soil probes at the same five incremental depths. To estimate soil $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ concentrations, approximately 100 g of sieved soil

collected from baseline soils in the spring (DOY 122) and EOY soil samples from the fall were extracted using 1M KCl and analyzed using a flow injection analyzer (Lachat, Milwaukee, WI).

Measurement of Trace Gas Fluxes

The measurement of turf-atmosphere N₂O and CO₂ exchange for this study began on DOY 166, 2011 and continued through DOY 139, 2012. Nitrous oxide fluxes were measured using the vented chamber method described by Hutchinson and Mosier (1981) and others (Mosier et al., 2006; Parkin and Ventera, 2010). Each chamber consisted of a removable chamber top and a permanently installed collar. Chamber tops were made of poly-vinyl chloride (PVC) pipe that measured 12.5 cm in height and 10.6 cm in diameter. Two PVC trace gas collars, 12.5 cm in height, were permanently installed into the soil in the center of each treatment plot as replicate measurements, totaling 24 collars on the fairway and rough.

In order to not interrupt the golf course play or turf maintenance, the original chamber design was modified. Collars were installed to a depth at which they were level to the ground and the chamber's usual rubber seal was replaced with a fabricated 16 gauge stainless steel band that was bolted to the bottom of the chamber (Figure 1). The steel band over hung the PVC pipe by 2.5 cm and weather filler rod was adhesively applied to the bottom of the PVC pipe to create the necessary airtight seal, allowing the chamber to fit snug on top of the collars during gas sample collection.

On measurement days chambers were placed on collars and gas samples were extracted at 0-, 15-, and 30- minute time intervals using 35 mL polypropylene syringes fitted with nylon stopcocks. A total of six gas measurements were taken for every treatment per sampling interval. Air temperatures were taken at the beginning and end of each 30- minute sampling period for

each section of turfgrass. Temperatures inside the chambers were assumed to be equivalent to ambient air temperatures because chambers were covered with highly reflective foil.

Upon trace gas collection, samples were transported to the USDA-ARS-SPNR laboratories and 25 mL of gas sample was injected into evacuated tube exetainers sealed with butyl rubber septa (Exetainer vial Labco Limited, High Wycombe, Buckinghamshire, UK) for analysis by gas chromatography (GC). The concentrations of N₂O and CO₂ were determined simultaneously for the two trace gases using a fully automated gas chromatograph (Varian Model Inc., Palo Alto, CA). The gas chromatograph was equipped with a Hayesen D packed column and an electron capture detector to quantify N₂O, and a thermal conductivity detector for CO₂. Gas flux rates were calculated according to Hutchinson and Mosier (1981) and flux patterns were evaluated according to increases in concentration inside the chamber head space over time (Livingston and Hutchinson, 1995). Flux calculations included adjustments for prevailing air temperature and for an atmospheric pressure of 640 mm mercury (Hg) using the ideal gas law (Delgado and Mosier, 1996).

Trace gas sampling frequency was at least twice per week throughout the growing season, June through November, and samples were taken between 0900h and 1400h to decrease the diurnal temperature affect. After fertilizer was applied sampling frequency was increased to three times for the following week. During the winter and spring of 2012, with weather permitting, samples were taken once every two weeks, although no additional fertilizers were applied at these times.

Ancillary variables

Each day trace gases were collected the top 10 cm of the soil surface temperature and volumetric water content was also measured using an EC-Tm probe (Decagon Devices In., Pullman, WA). The soil devices were placed directly adjacent to each of the experimental fairway and rough plots and were assumed to represent whole plot temperature and soil water volumetric content. Water filled pore space (WFPS) was calculated as:

$$\text{WFPS} = \frac{VSWC}{1 - \left(\frac{BD}{PD}\right)}$$

Soil bulk density (*BD*) is 1.43 and 1.52 g cm⁻³ for the fairway and rough, respectively, and *PD* is particle density (an assumed valued of 2.65 g cm⁻³).

Statistical and Data Analysis:

The 2011–2012 cumulative trace gas fluxes of N₂O and CO₂ emissions measured from each treatment plot were calculated using linear interpolations between each successive sampling day to provide daily flux estimates for non-sampling days. An analysis of variance (ANOVA) of annual N₂O emissions was used to test the effects of site (fairway and rough) and fertilizer treatment using the statistic analytical program SAS v.9.2 (SAS Institute, 2008, Cary, NC, USA) PROC MIXED linear model. Contrasts of LSD were performed using the Satterthwaite option in the fixed effects portion of the model, with site nested within replications and used as a random variable.

The percentage of applied N lost through annual N₂O emissions was calculated as the difference between the Control and each fertilizer treatment cumulative emission and divided by total kg of N applied, and expressed as emission factors.

Replicate chambers within treatment plots were averaged and treated as individual values for each of three replications. The daily flux averages were calculated for the three fertilization periods F1, F2, and F3 by dividing the cumulative flux for each fertilization period by the days in that sampling period, and log transformed to meet assumptions of normality. Flux averages were subjected to an ANOVA using the PROC MIXED model to test the effects of site, treatment, and fertilization period, along with corresponding interactions (Table 2). Site was nested within replication and treated as a random variable. Individual sampling dates were also statistically evaluated using PROC GLIMMIX to test for significant fluxes per treatment. Significant differences were reported at $P < 0.05$ confidence level.

Pearson's correlations were used to identify significant associations between soil N₂O fluxes and soil WFPS and temperature using the PROC CORR model. Exponential regression analyses were further used to identify the relationship between soil N₂O flux and soil temperature and moisture on the fairway and rough using PROC NLIN. Initially PROC REG was used to estimate the two a and b parameters for the non-linear regression analysis. The PROC NLN output then generated two exact a and b parameters for fairway and rough fertilizer treatments that were used in the exponential equation:

$$N_2O(T) = ae^{bT}$$

where T is temperature and a and b are parameter coefficients (Davidson et al., 1998).

RESULTS AND DISCUSSION

Annual Cumulative Emissions

Results showed a significant interaction between cumulative fairway and rough N₂O emissions and fertilizer treatments ($P < 0.0001$) (Table 2). Cumulative emissions and emission

factors per treatment are presented in Figure 1. Fairway UMaxx and BCMU treated plots had the greatest cumulative emissions of all experimental plots ($P < 0.0001$), totaling 6.5 and 7.6 kg $\text{N}_2\text{O-N ha}^{-1} \text{ yr}^{-1}$, equating to emission factors of 4.0 and 4.7%, respectively (Fig1.a). Annual emissions from fairway UMaxx and BCMU treatments were similar to emissions from an Arizona golf course fairway that emitted 6.4 kg $\text{N}_2\text{O-N ha}^{-1} \text{ yr}^{-1}$ annually from effluent water treatments (Guilbault and Matthias, 1998).

Cumulative emissions from fairway plots treated with UMaxx and BCMU materials were significantly greater ($P < 0.0001$) than those from Polyon treated plots, emitting 34 and 43% more N_2O , respectively. Annual emissions from fairway Polyon treatments totalled 1.9 kg $\text{N}_2\text{O-N ha}^{-1} \text{ yr}^{-1}$, a 1.2% loss of total N applied (Figure1a). UMaxx treated plots applied to the rough section of turf had similar emissions as the fairway Polyon fairway treatments. Emissions from the rough UMaxx treated plots totaled 2.4 kg $\text{N}_2\text{O-N ha}^{-1}$, equivalent to a 1.3% emission factor (Fig.1b). Emission from the fairway Polyon and the rough UMaxx treatments were similar to those measured on a Colorado Front Range home lawn that totaled 2.4 kg $\text{N}_2\text{O-N ha}^{-1} \text{ yr}^{-1}$ (Kaye et al., 2004).

Cumulative emissions from UMaxx and BCMU treatments applied to the rough were reduced by 64 and 80% compared to the respective fairway treatments. In contrast to the fairway site, where UMaxx and BCMU treatments had similar emissions and flux trends, Polyon and BCMU treatments were more comparable on the rough. Polyon and BMCU treatments applied to the rough cumulatively emitted 1.5 kg $\text{N}_2\text{O-N ha}^{-1}$ each, equivalent to a 0.6% loss of total N applied (Figure 1b). In comparison, Bremer (2006) reported annual emissions of 1.65 and 1.60 kg $\text{N}_2\text{O-N ha}^{-1} \text{ yr}^{-1}$ from urea and ammonium sulfate treatments, respectively. The previous study applied a total of 250 kg $\text{N ha}^{-1} \text{ yr}^{-1}$ in multiple applications

over the course of a year to a turfgrass sward in Manhattan, Kansas. Emissions from fairway and rough Control plots were significantly lower than fertilized plots and emissions totaled 0.5 and 0.7 kg N₂O-N ha⁻¹ yr⁻¹, respectively.

N₂O Flux Rates from Fertilizer Treatments

Prior to fertilizer treatment applications to the fairway and rough, fluxes were measured on DOY 157, 162 and 163, 2011, and did not exceed 2.5 g N₂O-N ha⁻¹ day⁻¹. As shown in Table 2, we identified a significant three way interaction between the fairway and rough sites, fertilizer treatments, and fertilization periods (P<0.05). Therefore we compare N₂O flux rates among the three fertilizer treatments during three fertilizations periods (F1, F2, and F3) on the fairway and the rough.

The spring time F1 fertilizer was applied to the fairway and rough plots on DOY 165 of 2011. The F1 fertilizer treatment applications did not immediately increase soil N₂O fluxes, but as the spring season progressed and temperatures rose, fluxes also gradually increased. While there was not a site effect between fertilized treatments, fluxes from treated plots on the rough exceeded those from the fairway, with peak fluxes averaging 25 g N₂O-N ha⁻¹ day⁻¹ several weeks after fertilizer treatments were applied (Fig. 2c). Peak fluxes from rough treatments occurred when soil WFPS was 45%, suggesting that microbial nitrification was the dominant microbial process causing N₂O emissions. Soil WFPS was lower on the rough compared to the fairway, and was likely caused by taller mowing height on the rough. As mowing height is raised, plant water use increases and more water is transpired per unit of ground area (Biran et al., 1981). In turn, greater transpiration rates on the rough caused drier soil conditions, increasing soil aeration and possibly microbial nitrification.

Contrarily, flux trends from fairway fertilized plots were typically below $10 \text{ g N}_2\text{O-N ha}^{-1} \text{ day}^{-1}$ (Fig. 2a), and soil WFPS often exceeded 60% (Fig. 2b), suggesting that denitrification was the dominant process during the F1 fertilization period. In order to explain these low N_2O fluxes, we hypothesize that greater rates of dinitrogen (N_2) or nitric oxide (NO) were being emitted from fairway fertilized plots. Nitrous oxide is just one of the gaseous forms of nitrogen that can be released during denitrification, and under highly anaerobic conditions, redox reactions can alter the amount of nitrate being reduced to dinitrogen (N_2). Davidson (1991) predicted that most N_2O is reduced to N_2 when soil WFPS is 60% or greater. If in fact greater amounts of N_2 or NO were being emitted from fairway plots during the F1 fertilizer period, these gases would be undetected by our methodologies.

The second (F2) round of fertilizer applications were applied to the fairway and rough during July, approximately 55 days after the first fertilization (Figure 2). Rapid and episodic soil N_2O fluxes were triggered on the fairway UMaxx and BCMU treated plots three days following the F2 fertilizer additions. Peak fluxes of 675 and $950 \text{ g N}_2\text{O-N ha}^{-1} \text{ day}^{-1}$ were measured from fairway UMaxx and BCMU treated plots, respectively (Fig. 2a), and contributed substantially to annual emissions, generating approximately 60% of the total for the year. At the time of the F2 application to the fairway soil conditions favored denitrification, with soil temperatures and WFPS reaching 22.5°C and 70%, respectively (Fig. 2b).

Turfgrass systems house a diverse community of soil denitrifying microbes (Yoa and Shi, 2010; Dell et al., 2010), and denitrification rates can be substantial when soil is near saturation (Mancino et al., 1998; Maggiotto et al., 2000). Under wet soil conditions N_2O emissions tend to be the greatest (Dobbie and Smith, 1999; Mathieu et al., 2006), therefore avoiding saturated soil conditions is a recommended N_2O mitigation practice (Grassini and Cassman, 2012). However,

Trenkel (2010) referenced N fertilizer formulated with slow release mechanisms as not typically well controlled. Therefore more information is needed on the soil biochemical processes and management practices that affect N release rates (Venterea et al., 2012).

Less than a week after peak fluxes were measured, fluxes from fairway UMaxx and BCMU treatments declined to $5 \text{ g N}_2\text{O-N ha}^{-1} \text{ day}^{-1}$ for the remainder of the F2 fertilization period. Observed flux patterns in combination with high soil WFPS again suggest that soil microbial denitrification was the dominant process triggering rapid N_2O fluxes from UMaxx and BCMU treatments. Denitrification events tend to produce larger but shorter lived emissions due to the extreme abiotic conditions that must be in place for this process to occur (Skiba and Smith, 1999). Following peak fluxes from fairway UMaxx and BCMU treatments plots, fluxes did not exceed background emission levels, therefore it is possible that emissions were limited by N substrate following rapid fluxes.

Nitrous oxide emissions following the summer fertilization to the fairway were further increased by low plant physiological activity. Nitrous oxide emissions are related to the amount of excess N in the system rather than N inputs (Grassini and Cassman, 2012). Plant N uptake plays a significant role in the production of soil N_2O (Linguist et al., 2012). Warm summer temperatures retard N uptake in cool-season turfgrass species (Hull and Liu, 2005); coupled with wet, warm soil condition that can quickly convert urea to inorganic forms, N losses can be substantial if cool-season grasses physiological activity is low (Petrovic, 1990).

Compared to UMaxx and BCMU treatments, fairway plots treated with Polyon were much more resistant to rapid fluxes following summer (F2) fertilization. Soil N_2O fluxes from fairway Polyon treatments also peaked three days following the second fertilization (Fig. 2a), but

were five and eight times less than fairway UMaxx and BCMU treatments, respectively. Maximum fluxes from fairway Polyon treatments measured $130 \text{ g N}_2\text{O-N ha}^{-1} \text{ day}^{-1}$, however, once initial peaks occurred, N_2O fluxes persisted for several weeks, but rates did not exceed $56 \text{ g N}_2\text{O-N ha}^{-1} \text{ day}^{-1}$. The prolonged and smaller fluxes over the next several weeks aided in significantly lowering cumulative emissions from fairway Polyon treatments. Technology formulated for Polyon coated material is designed to release more N as soil temperatures increase, slowing the release of urea and inhibiting N_2O fluxes by limiting N availability to microbial processes (Halvorson et al., 2013). The temperature controlled release mechanism for Polyon was highly effective in reducing N_2O emissions in the wet fairway soils. Nelson et al., 2008, also found similar results, suggesting that the coated technology formulated for Polyon may greatly reduce N_2O emissions in poorly-drained soils that are subject to denitrification.

Nitrous oxide fluxes from fertilized plots on the rough were significantly lower ($P < 0.0001$) than those measured from the fairway following the second fertilization. Fluxes from rough UMaxx treated plots increased to $24 \text{ g N}_2\text{O-N ha}^{-1} \text{ day}^{-1}$ three days after the F2 application, as shown in Figure 2c. Fluxes from rough Polyon and BCMU treated plots did not significantly increase following application and averaged 9 and $10 \text{ g N}_2\text{O-N ha}^{-1} \text{ day}^{-1}$, respectively, for the second fertilization period. Soil WFPS on the rough turfgrass at the time of F2 fertilization was 55%, aiding in lower N_2O flux rates. Nitrification is often the dominant process in drier soils ($\text{WFPS} > 60\%$) (Bateman and Baggs, 2005; Mathieu et al., 2006; Williams, et al., 1992), and tend to be smaller and generally more common (Skiba and Smith, 1999). However, less than a week after F2 fertilizer application, soil WFPS on the rough increased to 78%, triggering N_2O fluxes of $37 \text{ g N}_2\text{O-N ha}^{-1} \text{ day}^{-1}$ from UMaxx treatments (Fi. 2c and d).

However, UMaxx treated plots were the only treatments on the rough to significantly respond to the increase in soil WFPS.

The third and final F3 fertilization was applied to the fairway and rough in mid-September, about 49 days after the second F2 fertilization (DOY 259 of 2011). Daily fluxes from fairway plots fertilized with UMaxx and BCMU peaked one week following application at 253 and 98 g N₂O-N ha⁻¹ day⁻¹, respectively; a three and tenfold reduction of peak fluxes compared to F2 fertilization, respectively. In contrast to the F2 fertilization, fairway fluxes from UMaxx treatment were greater than BCMU treatments following the F3 fertilization. When peak fluxes occurred following the F3 fertilization fairway soil temperature was 20⁰C and WFPS space was 65%; however soil temperatures began to quickly decline the days following the final fertilization. Similar to flux rates from fairway BCMU treated plots, Bremer (2006) reported peak fluxes of 98 g N₂O-N ha⁻¹ day⁻¹ in a stand of Perennial rye turfgrass after applying urea at 75 kg N ha⁻¹ in a single application on DOY 280, 2003. However, the late season fertilizer applied in the Bremer (2006) study was 21 days later than this current golf course study. However, Poyon treated plots were unaffected by N₂O fluxes following fertilization, and fluxes were not different than background emissions.

Contrary to fairway UMaxx and BCMU treatments, the third fertilization did not increase N₂O fluxes from fairway Poyon treatments and flux rates did not exceed 5 g N₂O-N ha⁻¹ day⁻¹. The coated material formulated in Poyon technology reduces N losses by the altering diffusion rates of urea (Blaylock et al., 2004), with soil temperature being the primary regulator of the physical polymer coating barrier that allows for N to be released into the soil (Shaviv, 2000; Halvorson et al., 2013). Because soil temperature began to steadily decrease over the weeks following F3 fertilization, Poyon capsules were not rapidly degraded and N₂O fluxes did not

increase significantly. During the third fertilization to the fairway there was not a large change in WFPS space (65%), but soil temperatures had dropped to 16⁰C and declined as the fall season progressed.

Soil WFPS and temperature during the F3 fertilization period were similar on the fairway and rough, yet fluxes were low for all fertilizer treatments, especially UMaxx and BCMU. Nitrous oxide fluxes reached maximum rates one week following the third fertilizer application and measured 29, 14, and 17 g N₂O-N ha⁻¹ day⁻¹ from the rough UMaxx, Polyon and BCMU treated plots, respectively (Fig. 2c). Similarly to the fairway, soil temperature on the rough began to steadily decline following F3 fertilization (Fig. 2d). In general cooler temperatures help reduce N₂O emissions from turfgrass systems because physiological activity and N uptake increases in cool-season turfgrass (Kusscow, 1988; Horgan et al., 2002; Baird 2007); therefore N application during cool temperatures enhances environmentally sensitive management (Petrovic, 1990). Our study indicates that late-season fertilization may be a potential mitigation option to minimize N₂O losses, but the degree of effectiveness may greatly depend on the mechanism that controls N fertilizer release as well as turf management practices. More research is needed to definitively quantify plant response and utilization of fall fertilizer applications (Bauer et al., 2012).

Daily flux rates from fairway and rough Control (zero fertilizer) plots averaged 1.8 and 2.8 g N₂O-N ha⁻¹ day⁻¹ for the season, respectively. Low fluxes coupled with low soil mineral N content (Table 3) indicate that N substrate availability restricted biological nitrification and denitrification. Emissions from golf course Control plots from this study are lower than background fluxes of 12.0 g N₂O-N ha⁻¹ day⁻¹ estimated by Townsend-Small and Czimczik (2010) from turfgrass in Irvine, California.

Non-fertilized periods

The winter sampling period had the lowest emissions during the study, with average daily fluxes of $0.8 \text{ g N}_2\text{O-N ha}^{-1} \text{ day}^{-1}$ for all treatments at both fairway and rough sites. As the season progressed into the spring of 2012 soil temperatures rose and soil fluxes also began to gradually increase, although there were no differences between treatments or sites, with fluxes averaging $2.5 \text{ g N}_2\text{O-N ha}^{-1} \text{ day}^{-1}$.

Soil WFPS, Temperature and CO₂ Emissions

Soil WFPS averaged 67 and 58% for the year at the fairway and rough, respectively. However there was more fluctuation in soil WFPS on the rough increasing from 40 to 70% during July to August of 2011. Soil WFPS ($P < 0.05$) and temperature ($P < 0.0001$) were significantly and positively correlated to N_2O fluxes from fairway treatments, explaining 17 and 40% of the variation, respectively. Soil temperature on the rough was also significantly ($P < 0.0001$) correlated to N_2O fluxes, explaining 67% of the variation. However, WFPS was not correlated to N_2O fluxes on the rough, presumably a result of the low soil water content and fluxes throughout the study period. Mosier et al. (1996) also points out that N_2O is evolved through dynamic interactions of soil N, temperature, and moisture, and direct correlations for anyone factor is typically low.

Further, this study also identified a significant ($P < 0.0001$) exponential relationship between N_2O flux and soil temperature for all treatments on the fairway and rough (Fig. 3a-h). Temperature is a major driver of N_2O evolved from soils (Mill et al., 2013). As temperature increases, soil N_2O emissions increase exponentially as long as soil moisture and substrate are not limiting (Meixner and Yang, 2006). Typically rates of nitrification and denitrification

increase as soil temperatures warm, and are less intensive during cooler periods (Skiba and Smith, 2000).

Proper soil N and irrigation management can significantly reduce the risk of N losses in turfgrass systems (Miltner et al., 1995; Horgan et al., 2002; Qian et al., 2003; Groffman et al., 2009). In this research, fertilizer treatments applied to the rough section of turfgrass were much more resistant to episodic and rapid N₂O fluxes than those applied to the fairway, indicating that differences between turf management and perhaps even turf species could have had important effects on N₂O emissions from the fairway and rough turf sites. Mowing heights greatly influence soil water and temperatures (Corre et al., 1996) by increasing plant water use through greater leaf area, transpiring more water per unit of ground area (Biran et al., 1981). Soil temperatures in this study were only measured at the 10cm depth; therefore the taller mowing could have created a much stronger shading effect on the soil surface than these measurements indicate. Also, the Kentucky bluegrass on the rough is a thatch forming sod grass that produces a thick organic layer of dead and living material (Beard, 1973), that generates a cooling effect on the soil surface (Zhang et al., 2013). Furthermore, the thatch organic layer is an important part of the N cycle in thatch forming sod grasses (Hull and Liu, 2005), and microbial activity can rapidly immobilize N in the Kentucky bluegrass thatch layer (Bowman et al., 1989; Miltner et al., 1996; Horgan et al., 2002; Engelsjord et al., 2004; Hull and Liu, 2005; Racitti et al., 2011).

Finally, carbon dioxide measurements were also taken from experimental plots in conjunction with nitrous oxide. Cumulative CO₂ emissions from fertilized treatments on the rough totaled 24 Mg CO₂-C ha⁻¹ yr⁻¹ and significantly exceeded emissions from fertilized treatments on the fairway (P<0.05) that totaled 18 Mg CO₂-C- ha⁻¹yr⁻¹ (data not shown). Greater CO₂ efflux from the rough may indicate a stronger biological sink for N additions compared to

the fairway. Soil CO₂ efflux represents total soil and plant respiration, a measurement of both plant root autotrophic and soil microbial heterotrophic respiration (Ryan and Law, 2005). Soil respiration is indicative of C cycling and soil N demand from plant and microbial activity (Groffman et al., 2009; Lal, 2004).

Soil Inorganic N

Soil ammonium (NH₄-N) and nitrate (NO₃-N) concentrations were taken twice during the study period; prior to fertilizer applications (baseline) and at the end of the year (EOY) in the fall of 2011 approximately 60 days after the final fertilization (soil inorganic N demonstrated in Table 3). Baseline soil inorganic N concentrations were highest in the top 0-5 cm of the soil profile, totaling 15.0 and 23.8 kg NO₃-N ha⁻¹ and 5.2 and 4.6 kg NH₄-N kg ha⁻¹ in the top 0-5 cm of the soil profile on the fairway and rough, respectively. Soil N concentrations were most depleted in the 10-30 cm depth of the soil profile, suggesting good nutrient uptake from a healthy and active turf root zone. Baseline soil NO₃-N concentrations taken at the 30-60 cm on the fairway were 25 kg N ha⁻¹, indicating the downward movement of nitrate. On the rough soil nitrate concentrations at 30-60 cm depth were <10 kg N ha⁻¹. Nitrate concentration measured from the rough are generally consistent with other studies that have suggested low risk of nitrate leaching in turfgrass (Miltner et al., 1995; Horgan et al., 2002). However, Petrovic (1990) points out that the possibility of N leaching from turfgrass systems may differ depending on fertilizer and irrigation rates, as well as age of the turfgrass sward.

Approximately 60 days after the F3 fertilization of 2011, soil samples were taken to measure EOY soil mineral N concentrations. Soil inorganic NH₄-N or NO₃-N concentrations were not significantly different among fertilizer plots, and were therefore averaged across

fertilized plots (Table 3). Soil inorganic N concentrations on fairway and rough Control plots were significantly lower than fertilized plots and did not exceed 5 kg N ha^{-1} for any one depth. Soil $\text{NO}_3\text{-N}$ concentrations from fairway fertilized plots at the 0-5 cm depth were twice as high as the rough in the fall, with concentrations totaling 24.2 and $10.7 \text{ kg NO}_3\text{-N ha}^{-1}$, respectively. Soil $\text{NO}_3\text{-N}$ concentrations at the 30-60 cm depth on the fairway fertilized plots during the EOY were lower than initial baselines samples (EOY concentrations did not exceed $10.3 \text{ kg N ha}^{-1}$ for any depth), and may be from lower fertilization rates applied to experimental plots than what is typically applied to golf course fairways.

CONCLUSION

Annual N_2O emissions from turfgrass at Colorado golf courses can be substantial; however the mechanism controlling N fertilizer release, fertilizer application timing, turf cultural practices, and soil water status significantly impact emissions. This study clearly establishes the effectiveness of Polyon coated material to reduce N_2O emission from cool-season turfgrass fairways during summer when soil conditions are warm and wet and favor denitrification. Applying UMaxx and BCMU materials when soil is cool and dry was effective in mitigating N_2O losses from fairways. Therefore caution to avoid soil conditions that favor denitrification on fairways is advised to reduce N_2O losses, especially from fertilizer types that may solubilize rapidly. The taller mowing height maintained on the rough significantly lowered N_2O emissions from fertilized plots by cooling and drying the soil surface, but these effects were much more significant for UMaxx and BCMU fertilizers that utilized slow release mechanisms than for Polyon that using a temperature controlled released mechanism. Further investigations of soil GHG emissions from golf courses are needed order to: 1) provide better information for local and national GHG emission estimates; 2) improve the choice of fertilizer product to optimize N

use efficiency; and 3) expand input parameters to biogeochemical model that simulate soil carbon and nitrogen dynamics.

TABLES AND FIGURES

Table 3.1. Soil properties on the fairway and rough in the top 10 cm of soil profile.

Site	Sand	Silt	Clay	Bulk density	Soil organic carbon	Soil organic nitrogen
	-----	%	-----	g cm ⁻³	%	%
Fairway	46	12	19	1.43	1.01	0.09
Rough	53	11	13	1.52	1.03	0.1

Table 3.2. Analysis of variance for site (fairway and rough), fertilizer treatments, and fertilization (Fert) period.

Source of variation	DF	P-Value
Site	1	P<0.000
Treatment	3	P<0.000
Fert Period	2	P<0.000
Site *Treatment	3	P<0.000
Site*Fert Period	2	P<0.000
Treatment*Fert Period	6	P<0.000
Site*Treatment* Fert Period	6	P<0.05

Table 3.3. Soil ammonium (NH₄-N) and nitrate (NO₃-N) on the fairway and rough at five incremental depths (cm) for spring 2011 baseline sampling and end of the year (EOY) sampling.

N Treatment	Depth (cm)	Fairway		Rough	
		NH ₄ -N	NO ₃ -N	NH ₄ -N	NO ₃ -N
		-----kg N ha ⁻¹ -----			
2011 Baseline	0-5	5.2a	15.1a	4.6b	23.8a
	5-10	3.6b	3.8b	2.6c	5.4b
	10-30	6.1a	1.1c	4.6b	1.3b
	30-60	6.2a	25.4a	12.2a	7.7b
	60-90	10.3a	4.6b	10.4a	9.1b
2011 EOY Fertilizer	0-5	1.8b	24.2a	6.4a	10.7a
	5-10	1.0b	2.7c	0.8b	3.2a
	10-30	2.9a	5.8bc	1.7b	0.8b
	30-60	3.1a	10.3b	2.7b	0.9b
	60-90	3.1a	7.3b	2.7a	1.7b
2011 EOY Control	0-5	1.7ab	3.4a	2.3a	0.9a
	5-10	0.8b	1.4b	0.8b	1.7a
	10-30	1.7ab	3.5a	3.8a	1.5a
	30-60	3.2a	5.0a	2.4a	0.8a
	60-90	3.2a	3.9a	2.4a	0.6a

Letters indicate significant differences at P<0.05

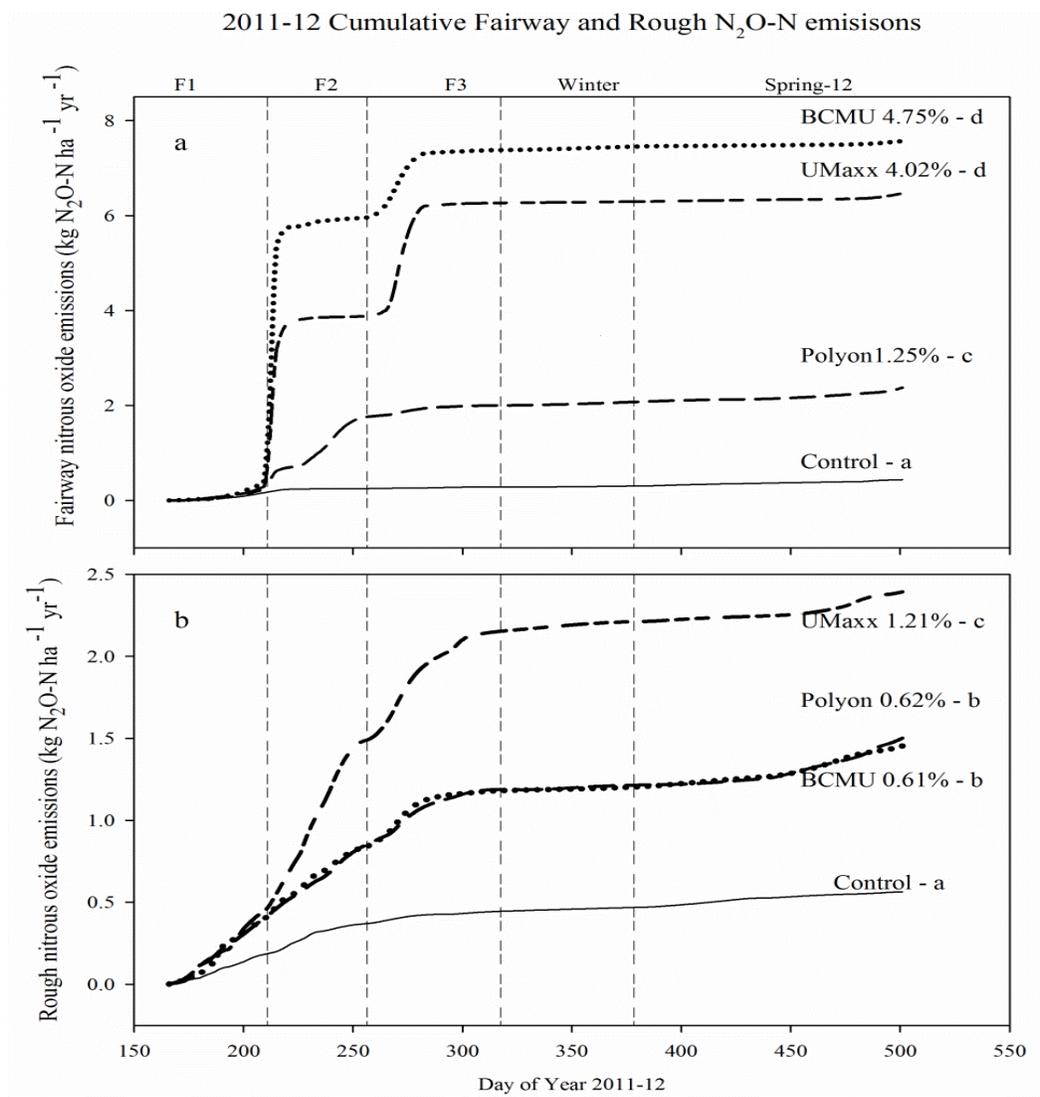


Figure 3.1. Cumulative daily 2011-2012 nitrous oxide (N₂O-N) emissions reported in kilograms (kg) of nitrogen (N) per hectare per year from the fairway (plot a) and rough (plot b) for three fertilizers, UMaxx, BCMU, Polyon, and one Control (zero fertilizer) treatment. The F1, F2, F3 fertilizer applications, and winter and spring 2012 correspond to five measurement times during the year-long study. Letters indicate significant differences (P<0.05) between treatments, and percentages indicate losses of total N applied for the season. Percent loss of total N applied is relative to the difference of emissions from the Control. The X axis is in day of year (DOY).

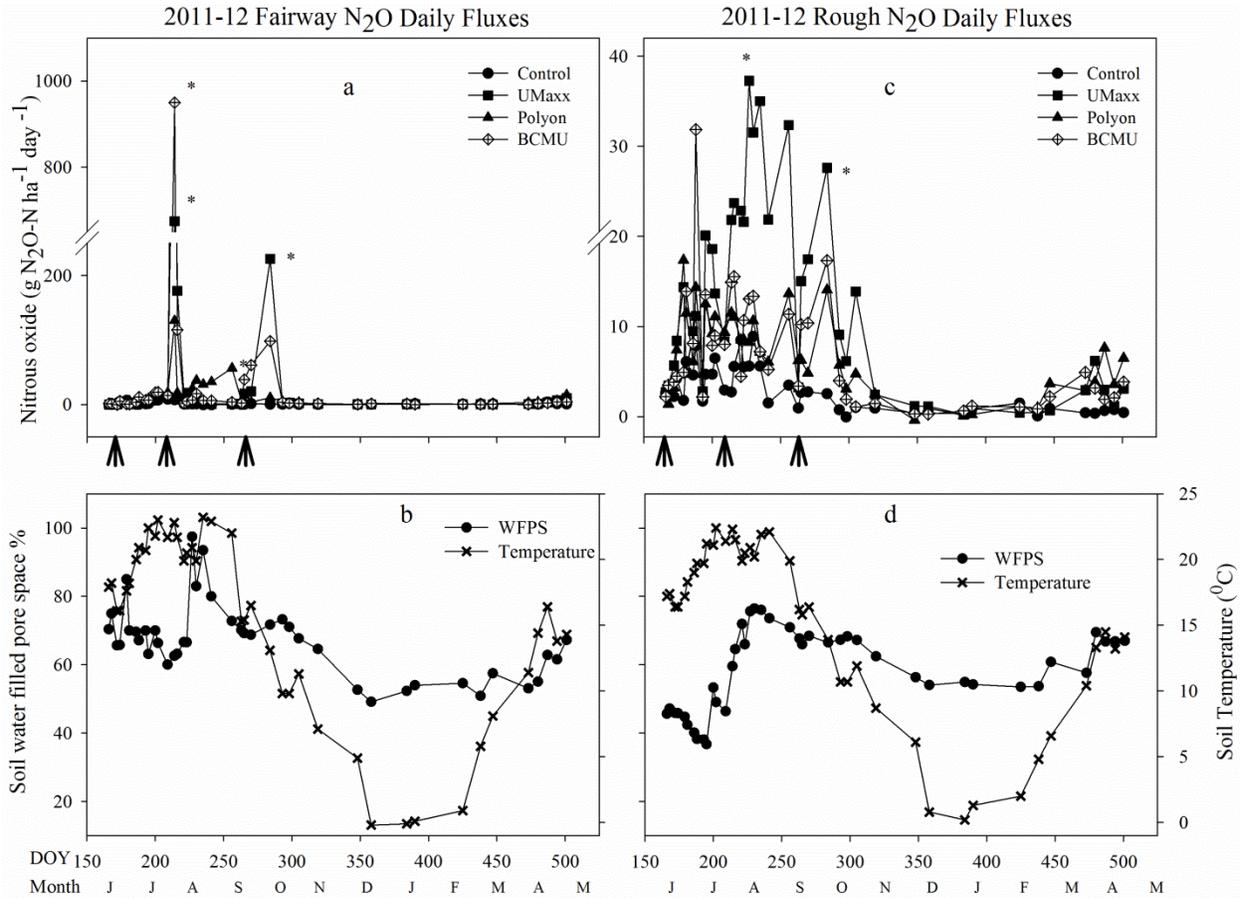


Figure 3.2. Daily 2011-2012 N₂O-N fluxes reported in grams (g) of nitrogen (N) per hectare per year from the fairway (plot a) and rough (plot c) on each sampling day from three fertilizer treatments UMaxx, Polyon and BCMU and one Control (zero fertilizer). Flux rates presented for treatments are the mean of three replications. Arrows indicate the three fertilizer applications. Asterisks indicate significantly high flux rates from fertilizer treatments. Notice the break in scale for fairway N₂O flux. Fairway (plot b) and rough (plot d) soil water filled pore space and temperatures for each sampling day are presented in the bottom graphs and are on equal scales. The X axis is in day of year (DOY) and each corresponding month is abbreviated below.

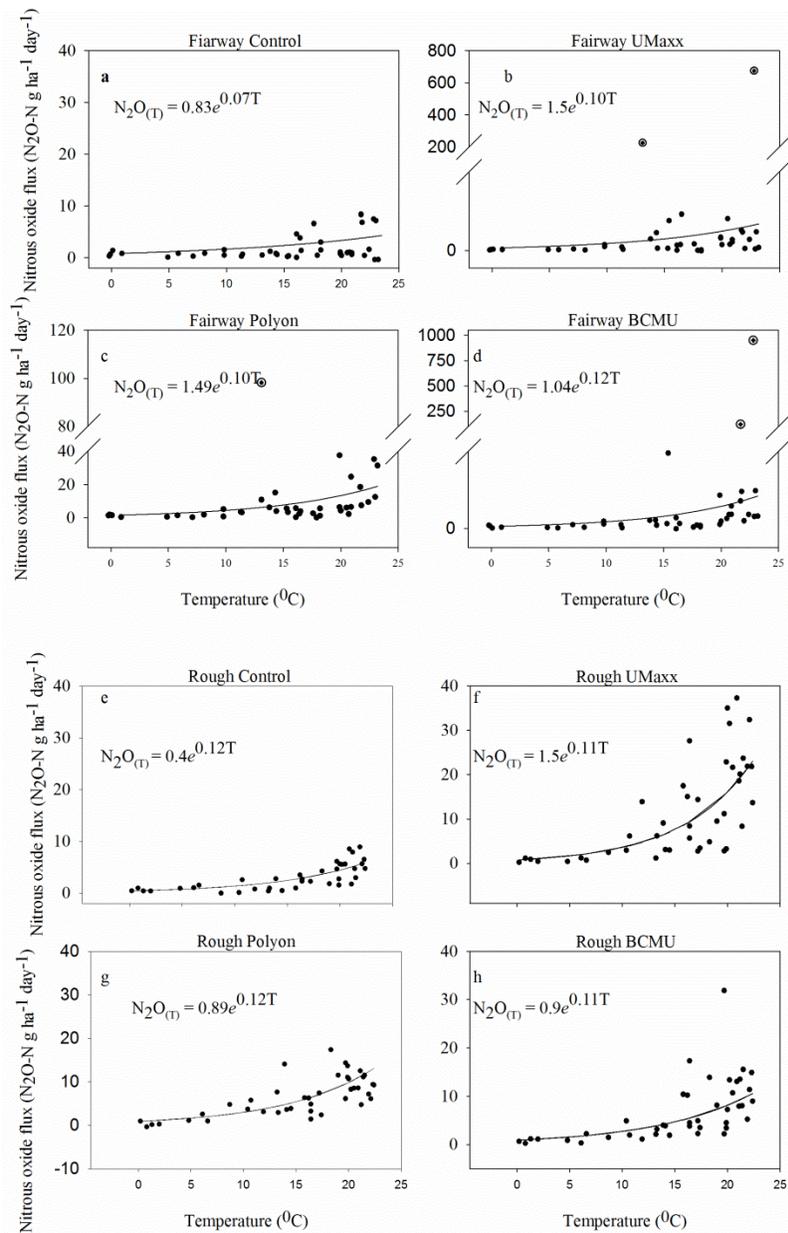


Figure 3.3. Fairway (plots a-d) and rough (plots e-h) regression analyses for nitrous oxide and soil temperature from UMaxx, Polyon, and BCMU treatments and one Control (zero fertilizer). Notice the break in scale for fairway fertilizer treatments N₂O flux rates. Large N₂O fluxes on the fairway represented by partially filled circles were not used in the regression analysis due to a lack of fit in the non-linear regression curve.

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CHAPTER 4:
METHANE EMISSIONS FROM A COLORADO GOLF COURSE: EFFECTS OF SOIL
DRAINAGE

SYNOPSIS

Methane is an important greenhouse gas, and soils act as both a source and a sink, thus influencing atmospheric concentrations. Further, anthropogenic land use change has caused significant interruptions to the global methane atmospheric budget by increasing emission (e.g. from flooded rice systems) and altering soil methane oxidation potentials (urban encroachment). Due to intensive management and expanding areas and intensive management, these urban ecosystems are increasingly important to regional studies of greenhouse gas budgets. In 2011, a field study established on a golf course included fairway, rough and restored native area. Measurements of soil bulk density and annual water filled pore space (WFPS) indicated that the first site selected had poor drainage. Methane emissions in 2011 totaled 0.55, 0.36 and 0.31 kg CH₄-C ha⁻¹ yr⁻¹ from fairway, rough, and native sites, respectively. In 2012, a second field site was selected on a well-drained soil at the golf course. In 2012, emissions from the poorly-drained fairway, rough and native grass areas totaled 0.58, 0.76, and 0.40 kg CH₄-C ha⁻¹ yr⁻¹, and emissions from well-drained fairway and rough totaled 0.38 and 0.01 kg CH₄-C ha⁻¹ yr⁻¹, respectively, with 0.14 kg CH₄-C ha⁻¹ yr⁻¹ net methane consumption at the native site. Soil was observed to be largely saturated at poorly drained sites, and soil compaction was correlated to reduced methane oxidation. Increased soil aeration reduced soil emissions and increased oxidative capacity at the well-drained field sites. There was a “turfgrass effect” on methane

emissions from golf course turfgrass sites, indicating that highly managed turfgrass may have a greater effect on atmospheric methane concentrations by reducing soil oxidation and increasing methanogenesis than previously considered.

INTRODUCTION

Methane is a potent greenhouse gas (GHG) with 25 times greater global warming potential (GWP) than that of carbon dioxide (Forster et al., 2007). Because of the strong radiative forcings, a small change in CH₄ atmospheric concentration can have a potentially large impact on future climate (Bridham et al., 2013). Soil methane production can originate from both natural and anthropogenic sources, but globally human induced emissions make up 60% of the total (US EPA, 2010). The increase in atmospheric methane is from an increase in sources combined with a decrease in methane sinks (Rigby et al 2008). Aerobic soils that foster soil microbes that use methane as an energy and carbon source are the largest biological sink for methane (Dutaur et al., 1997). Mosier et al. (1996) demonstrated that temperate grasslands an important global CH₄ sink and that land use changes that alter the methane oxidation potential have significant effects on the global CH₄ atmospheric budget.

Atmospheric CH₄ is derived primarily from biological activity under anoxic conditions by methanogenic bacterial that anaerobically digest organic matter (Le Mer and Rogers, 2001). Methane production from soils indicates that field locations possess methanogenic microbial populations (Chan and Parkin, 2001), which are probably ubiquitous but have mostly been studied in rice field soils (Le Mer and Rogers, 2001). Water logged upland soils, including forested and cultivated sites, were found to promote methanogenesis and increase methanogenic populations (Mayer and Conrad, 1990). Depending on management practices, such as (N)

fertilization and soil practices that effect soil aeration (i.e. irrigation, tillage, or compaction), grassland soils may act as simultaneous sinks (CH_4 oxidation) and sources (methanogenesis) of CH_4 (Kahlil and Baggs, 2004; Chan and Parkin, 2001). It is generally accepted that anthropogenic disturbance to native soils through tillage, fertilization, and irrigation tends to decrease soil CH_4 oxidation capacity by up to two-thirds (Smith and Conen, 2004; Ojima et al. 1993; Mosier et al. 1991).

Approximately two-thirds of anthropogenic CH_4 sources are from agriculture production systems (Mosier et al., 1997) leading to a large amount of research compared to other managed systems, such as urban lawns or golf courses. Rapid urban growth and the associated use of turfgrass (Bandaranayake et al., 2003) converts previously native and arable land to suburban homes and cities (Scheyer and Hipple, 2005) and those living in urban areas will comprise up to 70% of the population by 2050 (World Health Organization, 2013). Much of urban spaces are made up of lawns that are often intensively managed with N fertilizer and irrigation water inputs (Nowak et al., 1996; Nowak et al., 2001; Groffman and Pouyat, 2009). Milesi et al. (2005) estimated an increase to 16 million hectares (Mha) of turfgrass in the U.S., placing greater urgency to quantifying GHG fluxes from urban lands. Previous work to quantify gas exchange in turfgrass systems has shown that make substantial contributions to mitigating atmospheric CO_2 while also improving soil quality (Qian and Follett, 2002; Qian et al., 2010; Pouyat et al., 2006). However, fertilization and irrigation however greatly alters trace gas fluxes in managed urban turfgrass ecosystems (Kaye et al., 2004; Horgan et al., 2002), thereby impacting regional methane budgets (Groffman and Pouyat, 2009). However, to date there is limited information regarding the extent of soil-atmospheric exchange of GHGs involving urban turfgrass (Zirkle et al., 2011).

Golf courses are common managed ecosystems in urban areas, with an approximately 32,000 courses globally (Tanner and Gange, 2005), totaling an estimated 1.95 Mha (Bartlett and James, 2011). Estimating emissions from golf courses is complex due to the various management regimes for each section of maintained turf (i.e. greens, fairway, rough and restored native grassland) (Bartlett and James, 2011). To sustain functional and aesthetic quality, fertilizer, mowing and irrigation are routinely applied but at different rates per section. The degree of management is typically fairway > rough > restored native grassland. Golf courses serve millions of golfers around the world and generate billions (USD) to the global economy (KPMG, 2008). Golf courses also serve as important urban green spaces; have higher economic returns per hectare than agriculture; and support ecological biodiversity (Watson et al.; KPMG, 2008; Tanner and Grange, 2005). The extent to which these benefits are diminished by GHG emissions and their associated environmental consequences is uncertain. Differences in soil N status (Chan and Parkin, 2011), soil cultural aeration practices (Mosier et al., 1991), as well as irrigation and mowing frequencies affect soil moisture and temperature (Thurlow et al., 1995) and impact soil CH₄ production and consumption capacity.

Initially the objective of this research was to quantify the soil-atmospheric exchange of methane from a golf course fairway, rough and restored native area, but the study expanded in the second year to evaluate soil drainage effects on turfgrass methane emissions. The hypothesis of this study is that methane fluxes from golf course turfgrass will be affected by differences in management intensity on the fairway, rough and restored native sections, and that soil drainage characteristics will influence soil methane oxidation potentials.

MATERIAL AND METHODS

Study Site and Experimental Design

This study was conducted at golf course near Fort Collins, on the Front Range of Colorado, where population growth is rapid (US Census, 2010) and land use has dramatically changed from rural to suburban areas. Historically, the golf course land was used as a 100-year-old sheep/alfalfa farm. In 2005 golf course construction began, and it was opened for use to golfers in 2007. Perennial ryegrass (*Lolium perenne*) was seeded on the fairway in 2006 and Kentucky bluegrass (*Poa pratensis* L.) was sodded on the rough in 2006. Restored native section consisted of a mixed grass community of smooth brome grass (*Bromus inermis*); blue grama (*Bouteloua gracilis*); and buffalograss (*Buchloe dactyloides*). Fairways are mowed three times per week at 1.9 cm height. Roughs are mowed one or two times per week at 6.35 cm height. In 2011, irrigation water was applied daily to fairways and rough starting in March and ending in October, to meet a 100% evapotranspiration (ET) rates. In 2012, the same irrigation rates were applied to fairways, but irrigation rates were increased to meet 150% ET demand for golf course roughs.

The golf course was established on a soil classified as 67.4% Larim gravelly sandy clay loam, and 32.6% Ascalon sandy clay loam. Mean air temperature during the first study period, June 2011 to May 2012 was 10.1 °C, 1.2 °C above the 20 year average, and precipitation totaled 124 mm. The second year of the study, May 2012 to June 2013, precipitation totaled 119 mm, and mean annual temperature was 10.2 °C, approximately 1.6 °C above the 20 year average. Soil bulk density, soil organic carbon and nitrate concentration are presented in Table 1, and soil mineral fractions of sand, silt and clay for each site are presented in Table 2.

To test for effects of soil drainage on methane emissions, two sites at the golf course were with poorly and well-drained soil characteristics that were determined by bulk density, annual soil water filled space (WFPS), and nitrate concentrations at each fairway, rough and native section. The first set of experimental field plots were selected at the poorly-drained site on day of year (DOY) 122 of 2011 to an adjacent fairway (32.066°N, 57.65°W), rough (32.064°N, 57.69°W), and native (32.075°N, 57.636°W) where there was minimal soil disturbance during golf course construction (from here, these plots will be referred to as PD16 fairway, rough and native). The well-drained field site was selected on DOY 95, 2012 to an adjacent fairway (32.107°N, 56.934°W), rough (32.105°N, 56.945°W), and native (32.113°N, 56.976°W) (from here, WD5 fairway, rough and native). The well-drained field site is located on the front nine of the golf course where there is a strongly sloping man-made hill that was built during golf course construction.

Two similar randomized complete block designs were established on fairways and roughs to accommodate three treatments including UMaxx[®], Polyon[®], and a control (zero fertilizer) in replications of three. Briefly, two different enhanced efficiency fertilizers (EENFs) sources were applied to evaluate treatment effects on soil trace gas emissions. These were UMaxx[®] (47% N) (Koch Agronomic Services, LLC, Wichita, KS) is formulated with nitrification dicyandiamide (DCD) and urease thiophosphoric triamide (TPT) inhibitors that restrict microbial and enzyme activity; and Polyon[®] (42% N) (Agrium Advanced Technologies, Loveland, CO) is a polymer coated controlled released urea fertilizer that is regulated by soil temperature.

Each fertilized plot received a total of 150 kg N ha⁻¹ applied in three seasonal applications at a rate of 50 kg N ha⁻¹ each. The PD16 plots were fertilized during June, July and September (DOY 165, 210, and 259) of 2011 and again the following year in May, July and

October (DOY 139, 205 and 303) of 2012. The WD5 plots were fertilized during the same months of 2012 but the first two fertilizations were slightly delayed (DOY 153, 216, and 303). Preceding each fertilizer application, 8-10 mm of irrigation water was applied to the soil to increase fertilizer solubility.

On DOY 174 of 2012, approximately 21 days after the first fertilization to the well-drained rough, golf course management reportedly applied $1.2 \text{ m}^{-3} \text{ ha}^{-1}$ of composted cattle manure to the WD5 rough (no other experimental sites received compost additions). Organic dairy cattle manure and had a density of 958.7 kg m^{-3} , pH of 9.2, EC of 32.8 dS m^{-1} (saturated paste), 0.65% N with $272 \text{ mg NH}_4\text{-N kg}^{-1}$ and $12 \text{ mg NO}_3\text{-N kg}^{-1}$, 0.27% P, and 1.44% K.

One year prior to the PD16 fairway and rough plots selection as study sites, golf course turf manager fertilized the fairway and rough with a total of 250 and 175 kg N ha^{-1} of Polyon®, respectively during May and July of 2010. In May and July of 2011, golf course maintenance fertilized the WD5 fairway and rough using 250 and 175 kg N ha^{-1} of Polyon®, on the respective sites, approximately one year prior to selection of experimental WD5 plots w.

Soil Analysis

Whole soil baseline samples were extracted on DOY 122 of 2011 for PD16 fairway, rough, and native sections at incremental depths of 0-5, 5-10, 10-30, 30-60 and 60-90 cm in four replications. Baseline soil samples were collected for the WD5 fairway, rough, and native section on Julian DOY 95 of 2012 using the same procedures. The first soil sample was extracted using a flat bladed shovel by under-cutting a 25 cm^3 section from 0-5, 5-10 and 10-30 cm as described by Follett (2009), and the remaining depths were taken with a metal soil core of a known volume. Each collected intact soil sample was immediately and carefully placed into plastic

bags to minimize soil disturbance and moisture loss. Soil samples were transported back to the USDA-ARS-SPNR laboratory facilities, weighed, and stored at 10°C until further processing.

Prior to processing on the 0-5cm depth, each square of soil was carefully placed on a tin tray and verdure was cut away using scissors; then the fairway Perennial ryegrass mat and rough Kentucky bluegrass thatch was removed, accounting for approximately 1.25 and 1.5cm top portion of the sample, respectively. There was no organic layer on the native soil samples, but biomass was removed from the top depth. A 10-15g subsample of moist field soil was taken from each depth, and placed in a 110 °C drying oven overnight to determine gravimetric soil water content. Gravimetric water content values were then used to calculate soil bulk density. Approximately 250- 500g per depth were then further processed through a 2 mm sieve, air dried, and sent to Colorado State University Soil Laboratory and analyzed for pH, soil texture, soil organic matter, and soil mineral nitrate (NO₃⁻). Soil organic matter was converted to soil carbon based on the conversion coefficient of 0.58 (soilquality.org.au).

Trace Gas Collection and Analysis

The measurement of turf- atmosphere CH₄ exchange for this study began on DOY 166 of 2011 and continued through DOY 172, 2013 using the vented chamber method described by Hutchinson and Mosier (1981) and others (Mosier et al., 2006; Parkin and Ventera, 2010). Each chamber consisted of a removable chamber top and an anchor installed into the soil. Chamber tops were constructed with poly-vinyl chloride (PVC) pipe measuring 12.5 cm in height and 21.2 cm in diameter. The PD16 fairway and rough study plots measured 1.5 m² in size, and replications were separated by 60 cm borders. Experimental plots on the WD5 fairway and rough measured 2.25 m² and 1.64 m², respectively, and the three replications were separated by

60 cm borders. Experimental plots at each native site measured 3 m², and three anchors were evenly spaced and installed in the center. Two PVC trace gas anchors were installed into the soil in the center of each plot as duplicate measurements, totaling 18 anchors on fairway and rough.

The original chamber design was modified to avoid interrupting golf course play and turf maintenance would not be interrupted. To do this, anchors were installed level to the ground and the chamber's usual rubber seal was replaced and a 16 gauge stainless steel band was fabricated and bolted to the bottom of the chamber. The steel band over hung the PVC pipe by 2.5 cm and weather filler rod was adhesively applied to the bottom of the PVC pipe to create the necessary airtight seal, allowing the chamber to fit tight on top of the anchor during trace gas sample collection.

On measurement days chambers were placed on anchors and gas samples from inside the chamber were extracted at time intervals of 0-, 15-, and 30- minutes, and gas samples were extracted using 35 mL polypropylene syringes fitted with nylon stopcocks. A total of six gas measurements were taken for every treatment per time interval on fairways and roughs, and three gas samples were taken for each time interval on the native section. Air temperatures were taken at the beginning and at the end of each 30- minute sampling period on all measured sections. Temperatures inside the chambers were assumed equivalent to ambient air temperatures because chambers were covered with highly reflective foil. Along with trace gas samples, soil temperature and volumetric water content was measured at the top 10 cm of the soil profile at each experimental plot using an EC-Tm probe (Decagon Devices In., Pullman, WA).

Upon trace gas collection, samples were transported back to the USDA- ARS-SPNR laboratories and 25 mL of gas sample was injected into evacuated tube exetainers sealed with

butyl rubber septa (Exetainer vial Labco Limited, High Wycombe, Buckinghamshire, UK) for analysis by gas chromatography (GC). The concentration of CH₄ in the injected exetainer sample was determined using a fully automated gas chromatograph (Varian Model Inc., Palo Alto, CA), equipped with a Poropak and Hayesen N packed column and flame ionization detector for CH₄ (Mosier et al., 1991). Gas flux rates were calculated according to Hutchinson and Mosier (1981) and flux patterns were evaluated according to increases in concentration inside the chamber head space over time (Livingston and Hutchinson, 1995). Flux calculation included adjustments for prevailing air temperature and for an atmospheric pressure of 640 mm mercury (Hg) using the ideal gas law (Delgado and Mosier, 1996).

Trace gas sampling frequency was twice per week throughout the 2011 and 2012 growing seasons were taken between the times of 0900h and 1400h to represent the average temperature of the day. Sampling frequency was three times the week following N fertilizations. During the 2011 and 2012 winter and spring sampling frequency was one to four times per month, although no additional fertilizers were applied at these times.

Soil Water Filled Pore Space

Water filled pore space (WFPS) was calculated as

$$\text{WFPS} = \frac{V_{\text{SWC}}}{1 - \left(\frac{BD}{PD}\right)}$$

where BD is the soil bulk density at each randomized complete block site (fairway, rough and native), and particle density (*PD*) is 2.65 g cm⁻³.

Statistical Analysis

Annual cumulative CH₄ emissions for each treatment plot were calculated for the 2011 and 2012 growing seasons at the poorly-drained sites, and the 2012 growing season at the well-drained sites. Linear interpolations were used to calculate annual emissions between successive sampling days to provide daily flux estimates for non-sampling days. Daily flux rates were calculated by dividing cumulative emissions by the total number of days for each sampling period over the two seasons. Due to an insignificant EENF treatment effect on the fairways and roughs, the mean methane emissions for the three treatments was taken for each replication, totaling eighteen calculated fluxes per sample for the fairway and rough. Adjacent native plots were sampled in conjunction with fairway and rough plots. The three plots (no subplots) on the native sections were each treated as replications and cumulative methane emissions were also calculated using linear interpolation for non-sampling days.

Cumulative emissions for each fairway and rough treatment was treated as a replication (totaling three replications), and cumulative emission from each of the three native plots were treated as a replication. Analysis of variance (ANOVA) was performed to test for effects of site (fairway, rough, native), year, and drainage (PD16 and WD5) using the statistical analysis program SAS ® v.9.2 (SAS Institute, 2008, Cary, N.C., USA) PROC MIXED linear model. Contrasts of means were performed using the Satterthwaite option in the fixed effects portion of the model. Site and year were nested within replication in the random variable portion of the model.

Average fluxes for each treatment were used as three replications for daily fluxes on the fairway and rough. Methane flux per sites was correlated with soil WFPS (WFPS is calculated above) and temperature using Pearson's correlation in the SAS ® PROC CORR.

RESULTS

Soil Methane Emissions

Results indicated a weak site effect ($P=0.06$) between fairway, roughs and native sites, and CH_4 fluxes from turfgrass field sites were dominantly positive for the duration of the study, indicating that soil methanogenesis exceeded oxidation. In 2011, the first year of the study period in 2011, emissions from the poorly-drained (PD16) fairway and rough totaled 0.55 ± 0.04 and $0.36 \pm 0.04 \text{ kg CH}_4\text{-C ha}^{-1} \text{ yr}^{-1}$ (Fig. 1a, d), and daily fluxes averaged 1.5 ± 0.11 and $1.1 \pm 0.12 \text{ g CH}_4\text{-C ha}^{-1} \text{ day}^{-1}$, respectively. Cumulative emissions from the PD16 native site were similar to the fairway and rough, totaling $0.31 \pm 0.05 \text{ kg CH}_4\text{-C ha}^{-1}$, and daily fluxes averaged $0.8 \pm 0.15 \text{ g CH}_4\text{-C ha}^{-1} \text{ day}^{-1}$.

There was a significant year effect ($P<0.05$) at the poorly-drained golf course experimental sites between 2011 and 2012, with emissions increasing during for 2012. However, emission increased only slightly from the PD16 fairway and restored native sites measuring 0.58 ± 0.09 and $0.40 \pm 0.1 \text{ kg CH}_4\text{-C ha}^{-1} \text{ yr}^{-1}$ (Fig. 1a and 1g); daily fluxes averaged 1.6 ± 0.09 and $1.2 \pm 0.4 \text{ g CH}_4\text{-C ha}^{-1} \text{ day}^{-1}$, respectively. Methane emission increases were most significant from PD16 rough soil during the 2012 measurement period, totaling $0.76 \pm 0.08 \text{ kg CH}_4\text{-C ha}^{-1} \text{ yr}^{-1}$ (Fig. 1d), with average annual daily fluxes nearly doubling from the previous year to $2.1 \pm 0.2 \text{ g CH}_4\text{-C ha}^{-1} \text{ day}^{-1}$. However during the growing season of 2012 emission increases from the poorly-drained rough were only slightly greater than the previous year, and it was not until the early spring of 2013 that emissions significantly spiked from the poorly-drained

rough. In fact as demonstrated in Figures 1 a, d and g, all field sites during the early spring of 2013 had a spike in methane emissions due to an increase in WFPS and temperature, but were the most significant at the PD16 rough site.

Measurements of soil methane started at the well-drained (WD5) field sites during the spring of 2012. Emissions at the well-drained (WD5) fairway totaled $0.28 \pm 0.02 \text{ kg CH}_4\text{-C ha}^{-1} \text{ yr}^{-1}$, and daily fluxes averaged $0.71 \pm 0.07 \text{ g CH}_4\text{-C ha}^{-1} \text{ day}^{-1}$ for the year. The WD5 rough site had the lowest methane emissions ($P < 0.05$) of regularly fertilized and irrigated treatment plots in the study, with cumulative emissions totaling $0.02 \pm 0.05 \text{ kg CH}_4\text{-C ha}^{-1} \text{ yr}^{-1}$ (Fig. 1d), and daily flux averages of $0.04 \pm 0.05 \text{ g CH}_4\text{-C ha}^{-1} \text{ day}^{-1}$, nearly ten times less than poorly-drained field sites. The WD5 rough soil had a weak methane oxidative capacity for several weeks during the onset of the 2012 study, but methane consumption potentials were lost when golf course turf managers reportedly applied $1.2 \text{ m}^{-3} \text{ ha}^{-1}$ of composted cattle manure (derived from alfalfa) on DOY 174 of 2012 (no other treatment sites received compost additions). Upon compost additions, soil immediately changed to a net source, inducing a strong inhibitory effect on soil CH_4 oxidation. Prior to compost additions, WD5 rough soil maintained weak CH_4 oxidation capacity (consuming on average $1.0 \text{ g CH}_4\text{-C ha}^{-1} \text{ day}^{-1}$), but the soil quickly changed from a sink to a source, emitting up to $1.0 \text{ g CH}_4\text{-C ha}^{-1} \text{ day}^{-1}$. The inhibitory effect began to decline throughout the summer, and soil began to regain oxidation capacity, which gradually increased as the season progressed (Fig. 1d). The restored native section at the well-drained site was the only field plot to have net CH_4 consumption, totaling $0.14 \text{ kg CH}_4\text{-C ha}^{-1} \text{ yr}^{-1}$ in 2012 (Fig. 1g), with soil oxidation rates averaging $0.39 \pm 0.3 \text{ g CH}_4\text{-C ha}^{-1} \text{ day}^{-1}$ for the year.

Soil Water Filled Pore Space and Temperature

Correlations between methane flux and soil temperature and WFPS are presented in Figures 2 and Figures 3, respectively. There was a significant and positive correlation between methane flux and soil temperature (Fig. 2a) and WFPS (Fig. 3a) on the poorly-drained fairway in 2011, with 20% of the variation explained for each variable. There were similar correlations at the poorly-drained rough in 2011 between soil temperature (Fig. 2b) and WFPS (Fig. 3b), with 18% of the variation explained for soil temperature and WFPS. In 2011, irrigation water applications were applied to meet 100% ET demand to the fairway and rough. Due to heavy rainfall in the early spring, coupled with irrigation water applications, soil at the poorly-drained (PD16) fairway was near saturation (>70% WFPS) (Fig. 1b). Soil WFPS was typically below 50% on the poorly-drained rough at the beginning of the 2011 season, but increased to 70% in the middle of the summer of 2011(DOY 210) (Fig. 1e)..

In 2012, daily irrigation water was applied to meet 100% of ET demand on golf course fairways, but annual soil WFPS was reduced to 58% at the PD16 fairway (Table 1). However no significant correlations were found between methane flux and temperature or WFPS at the PD16 fairway in 2012. Soil WFPS averaged 33% at the PD16 native in 2012, but only soil temperature ($P < 0.01$) was negatively correlated to methane flux at the PD16 native site in 2012 (Fig. 2f), explaining 25% of the variation in methane flux.

Irrigation was increased to 150% ET demand to golf course roughs during the 2012 growing season. Greater irrigation water applications increased average WFPS at the PD16 rough to an average of 65% during 2012. However, as demonstrated in Figure 1d, emission increases during the 2012 growing season were small when irrigation was applied, and it was not until early spring of 2013 that emissions increased. In fact emissions from all experimental plots

increased during the spring of 2013, and greater methane effluxes correlated with an increase in both soil temperatures and WFPS starting on DOY 400 (see WFPS in Fig. 1b, e, and h; soil temperatures in Fig. 1 c, f, and i).

Soil bulk density was 20% lower (Table 1) and sand content was 10% greater (Table 2) at the well-drained field sites compared to the poorly-drained location. Differences in soil structure and mineral fraction significantly decreased ($P < 0.0001$) WFPS at the WD5 fairway (50%) compared to poorly drained sites during the 2012 growing season. Irrigation water was also applied at 150% ET to the WD5 rough, but increased drainage and greater rates of plant transpiration further depleted soil WFPS ($P < 0.0001$) to 40% for the year (Table 1). Soil nitrate concentrations are shown in Table 1 for the poorly and well-drained field plots. Soil $\text{NO}_3\text{-N}$ concentrations at the well-drained plots are less than half of those measured at the poorly-drained plots, indicating that reduced soil water content also slowed N turnover rates at the well-drained field plots.

DISCUSSION

Emissions from the golf course turfgrass plots are in accordance with Groffman and Pouyat (2009) who indicated that turfgrass systems to restricted soil methane oxidation capacity. While there was a degree of variability ($P = 0.06$) at the golf course field sites, turfgrass plots were typically a steady weak source ($1.0 \text{ g CH}_4\text{-C ha}^{-1} \text{ day}^{-1}$) of methane over the course of the two year study, with the strength of the source occasionally increasing or decreasing due to changes in WFPS. Correlations between WFPS and soil temperature to CH_4 flux at each site were only significant for three of the measurement periods (Figures 2a-i and 3a-i). Mosier et al. (1996) helps by clarifying that there are complex interactions and dynamics of soil abiotic factors that

affect GHG emissions throughout space and time, typically making correlations weak for any one variable weak.

As Delgado et al. (1996) and Aronson et al. (2012) found, this study also observed that CH₄ consumption was severely inhibited by high soil water content. Soil water content is often the dominant factor controlling soil methane emissions (Mosier et al., 1997), with soil temperature strongly influencing microbial activity (Shütz et al., 1990). While there are dynamic interactions of soil oxygen levels, soil water and temperature, and nutrient availability control methane flux from soil (Silver, 1999), soil water status is generally regarded as the greatest predictor of methane flux (Aronson et al., 2012). Soil water controls gas diffusivity in the soil profile (Dunfield et al., 1993; Gullledge and Schimel, 1998; Hütsch, 2001). Therefore, soil WFPS is often used as a proxy to gas diffusion rates (van der Weeden, et al., 2012), and is a common and widely used metric to investigate soil GHG emissions (Baggs and Bateman, 2005; del Prado et al., 2006). As gas diffusivity declines methane consumption is restricted, and is often negatively correlated with increasing soil water (Delgado and Mosier, 1997; Keller and Reiners, 1994).

According to these observations, poorly-drained soils at the field sites located on the back nine of the course restricted soil aeration, and thereby inhibited soil CH₄ oxidation. Soil bulk density was 20% lower at the well-drained sites, and while irrigation was applied at equal rates, greater soil drainage potentials significantly decreased ($P < 0.0001$) soil WFPS at the well-drained field plots. Soil structure has a major influence on soil WFPS (Ball, 2013), and WFPS will differ in soils with different bulk densities. Soil properties that effect aeration highly impact soil emissions (Kaye et al., 2005), with well drained soils generally having greater oxidative potentials (Janssen et al., 2009; Phillips et al., 2009). The potential for soil to emit GHG is

greatly affected by soil physical conditions such as bulk density that influence gas diffusivity, porosity, air permeability, and water retention (Ball, 2013), with soil compaction restricting aeration and severely reducing methane oxidation potentials (Ball et al., 1997). Soil water acts as a diffusive barrier to methane consumption (Koschorreck and Conrad, 1993) slowing diffusion rates by 10^4 fold compared to soil air (Kammann et al., 2001).

Furthermore, soil water content plays a significant role in N status of soils (Zhang et al., 2013). As shown in Table 1, soil $\text{NO}_3\text{-N}$ concentration was two fold greater at the poorly-drained field plots than the well-drained sites, indicating that lower WFPS at the WD5 field sites also affected soil mineral N levels by restricting nitrification rates. As soil water content is decreased, diffusion of ammonium slows, thereby limiting N turnover (mineralization and nitrification) and directly influences soil CH_4 flux potentials (Mosier et al., 1991).

Nitrogen is an important nutrient to sustain turfgrass quality (Hull and Liu, 2005), but soil N additions have been found to inhibit CH_4 oxidation capacity (Mosier et al., 1991; Hütsch et al., 1994; Hütsch, 1998; Baggs and Blum, 2004; Acton and Baggs, 2011) through complex interactions and competitions of nitrifying and oxidizing soil microbes (Hütsch, 1998; Baggs and Blum, 2004). Methane oxidation potentials are negatively correlated to soil mineral N concentrations (Chan and Parkin, 2001) with CH_4 consumption decreasing by up to 90% in cultivated and fertilized cropped soils compared to native grasslands (Mosier et al., 1997).

Additionally, soil methane oxidation was also inhibited at turf control plots (zero fertilizer), where control plots had similar methane effluxes as fertilized plots that received $150 \text{ kg N ha}^{-1} \text{ yr}^{-1}$. Nitrifying bacteria that are responsible for the majority of CH_4 uptake may suffer from nitrite toxicity (Schnell and King, 1994), and inhibition may prevail long after the soil NH_4^+ concentrations have declined to levels of unfertilized soils (Mosier, et al., 1991). In general

human alterations to soils are thought to significantly reduce soil methane sink capacity (Ojima, 1993), with fertilization and irrigation water applications causing possible permanent shifts in soil microbial populations (Bedard and Knowles, 1989).

The greatest methane emissions from turf plots occurred during the spring of 2013 following a large precipitation event immediately followed by warm soil temperatures. Soil emissions can be greatly impacted by climate conditions (Kaye et al., 2005; Le Mer and Rogers, 2001). However, poorly-drained sites were much more affected by methane effluxes than well-drained sites. High organic matter in the top portion of the turf-soil profile may have contributed further to methane effluxes from increased anaerobic digestion of soil organic matter (SOM). High soil organic carbon inputs from plant growth directly increase methane production, and thereby indirectly stimulate the methanogen microbial populations that rely upon C as a substrate (Neue, 1993; Denmend et al., 2010).

The WD5 rough site was unique to other fertilized sites in that soil methane oxidation potentials were not completely retarded by either fertilizer or irrigation applications, but instead WD5 rough soil was a weak CH₄ sink for several periods of the year-long study (Fig. 1d). Methane emission from the WD5 rough were comparable to a study by Kammann et al. (2001) which also found that fertilization of up to 400 kg N ha⁻¹ did not inhibit CH₄ oxidation capacities on a German grassland soil with sandy loam over clay, and as soil dried methane oxidation increased.

The well-drained native site was the only study plot at the golf course to maintain stable soil oxidation capacity. However, total CH₄ consumption from the well-drained native soil however was ten times less than oxidation rates of urban turf measured by Kaye et al. (2004), who estimated urban soil to consume up to 1.5 kg CH₄-C ha⁻¹ yr⁻¹ on the Front Range of

Colorado, with daily averages of $4.8 \text{ g CH}_4\text{-C ha}^{-1} \text{ day}^{-1}$. The Kaye et al. (2004) study was kept under home lawn conditions, which typically has less intensive fertilizer and irrigation management inputs than highly managed golf courses. However the WD5 native was a minimally disturbed soil with no fertilizer or irrigation inputs. Typically undisturbed soils tend to absorb more CH_4 than what is produced (Wang and Bettany, 1995). Soil becomes a stronger sink for methane consumption as soils dry (Braun et al., 2013); yet microbial methane consumption also becomes restricted when soil water is a limiting factor (Schnell and King, 1996). Therefore, due to dry condition during the 2012 growing season, soil moisture may have been the limiting factor for methane consumption at the WD5 restored native site since WFPS was typically around 20%.

As several authors (Chan and Parkin, 2001; Le Mar and Rogers, 2001; Halvorson et al., 2011) have reported, agricultural soils may act simultaneously as methane sinks and sources, depending on aeration, environmental variables, and N availability. Theoretically, since soil methane dynamics are closely related to human management inputs, there should also be a certain degree of control over GHG flux from human managed soils (LeMer and Roger, 2001). This too may well be the case for turfgrass systems, since turf-soil management practices can greatly effect soil aeration, N availability, and temperature. Therefore management practices that increase of soil aeration and reduce N fertilizer inputs could contribute substantially to lowering CH_4 emissions from golf course turfgrass.

CONCLUSION

Contrary to the initial hypothesis there was little difference in methane emissions between golf course turfgrass sections managed as fairways, roughs and restored native sections, and turfgrass was typically a steady weak source of methane year around, regardless of management.

Study data suggest that nitrogen fertilization and irrigation applications significantly affect methane production and oxidation potentials on soils managed at golf courses. However, by increasing soil aeration, soil oxidation potentials can be increased, as was observed at well-drained field sites. Regardless, the findings of this study indicate that intensely managed urban grasslands, such as golf courses, may have significantly greater effects on atmospheric methane concentrations than previously considered. The harmful effects of inhibited methane consumption could potentially be mitigated by increasing soil aeration through better irrigation management, especially at poorly-drained locations, and by not exceeding recommended fertilizer rates of cool-season turfgrass.

TABLES AND FIGURES

Table 4.1. Soil properties of the poorly drained and well drained fairway, rough and native experimental sites in the top 10 cm of the soil profile. Average soil water filled pore space (WFPS) is presented for 2011 and 2012. Bulk density, soil organic matter (SOM), nitrate (NO₃-N) were measured from baseline soil samples only, therefor in 2012 these values are presented as NA for poorly drained sites because they were not re-measured

Site	Drainage	Year	Bulk density	Soil WFPS	Soil organic matter	NO ₃ -N
			g cm ⁻³	%	g kg ⁻¹ soil	mg kg ⁻¹ soil
Fairway	Poorly-drained	2011	1.43	67	16.3	25.6
Rough	Poorly-drained	2011	1.52	58	14.5	37.4
Native	Poorly-drained	2011	1.42	33	1.0	1.0
Fairway	Poorly-drained	2012	NA	60	NA	NA
Rough	Poorly-drained	2012	NA	65	NA	NA
Native	Poorly-drained	2012	NA	40	NA	NA
Fairway	Well-drained	2012	1.10	50	19.5	10.5
Rough	Well-drained	2012	1.09	40	17.2	7.5
Native	Well-drained	2012	1.14	20	0.6	1.1

Table 4.2. Percent sand, silt and clay in the 0-10 cm of the soil profile for the poorly-drained (PD16) and well-drained (WD5) fairway, rough and native field plots

Site	Sand	Silt	Clay
	-----	%	-----
PD16 Fairway	46	12	19
PD16 Rough	53	11	13
WD5 Native	45	12	19
WD5 Fairway	61	15	24
WD5 Rough	62	15	23

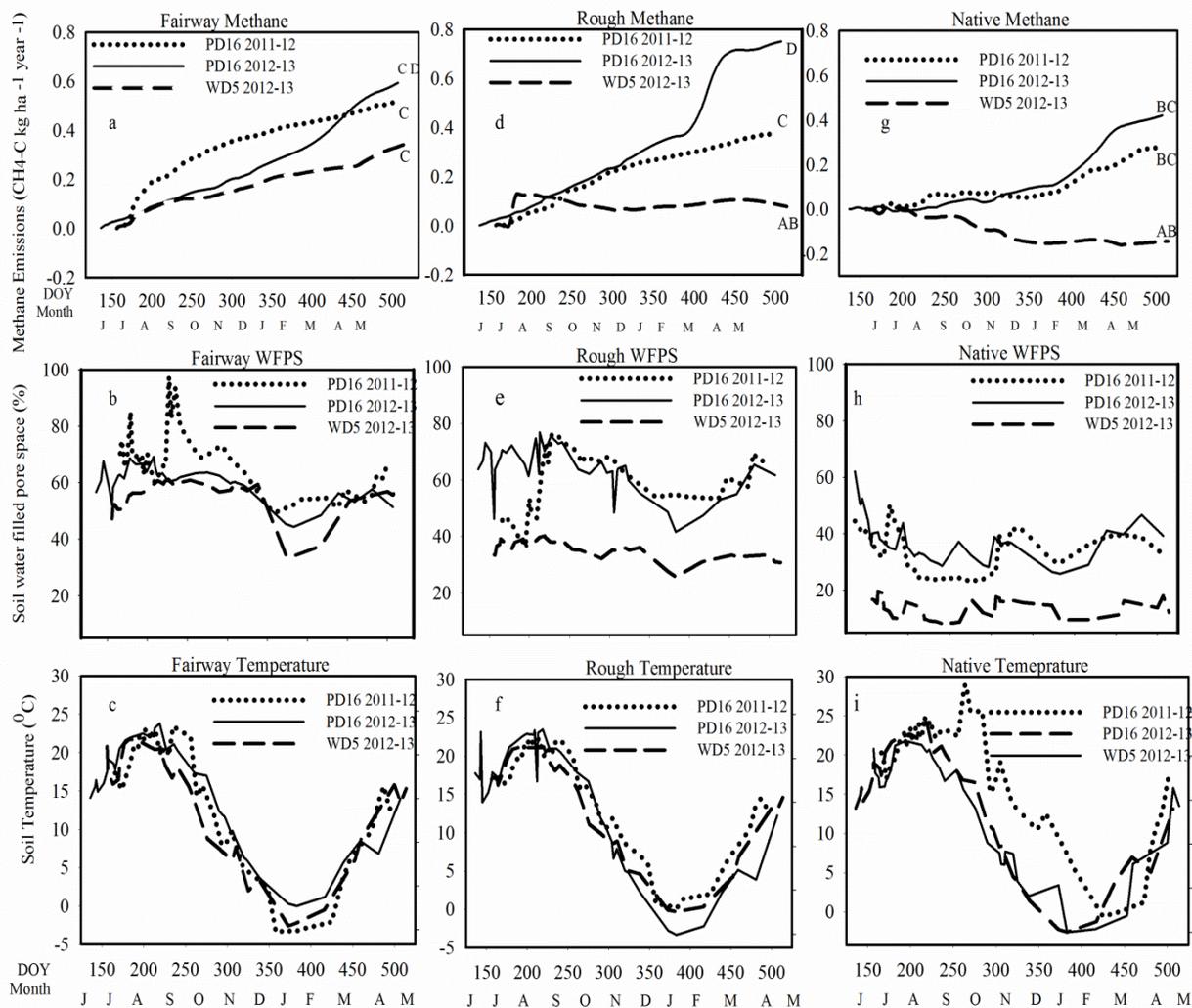


Figure 4.1. a-i. Daily cumulative methane soil emissions (g per hectare per year) are presented in figures a, d and g from poorly drained (PD16) and well-drained (WD5) fairways, roughs, and native sites, respectively. Presented methane emissions are the mean of three treatments in replication of three. Cumulative methane emission followed by letters are significantly different at $P < 0.05$. Soil water filled pore space (percent %) (b, e and h) and soil temperature (Celsius) (figures c, f, and i) are presented for at the PD16 and WD5 experimental plots during 2011 through 2013. X axis's are in day of year (DOY) and the corresponding month is abbreviated below the Julian day.

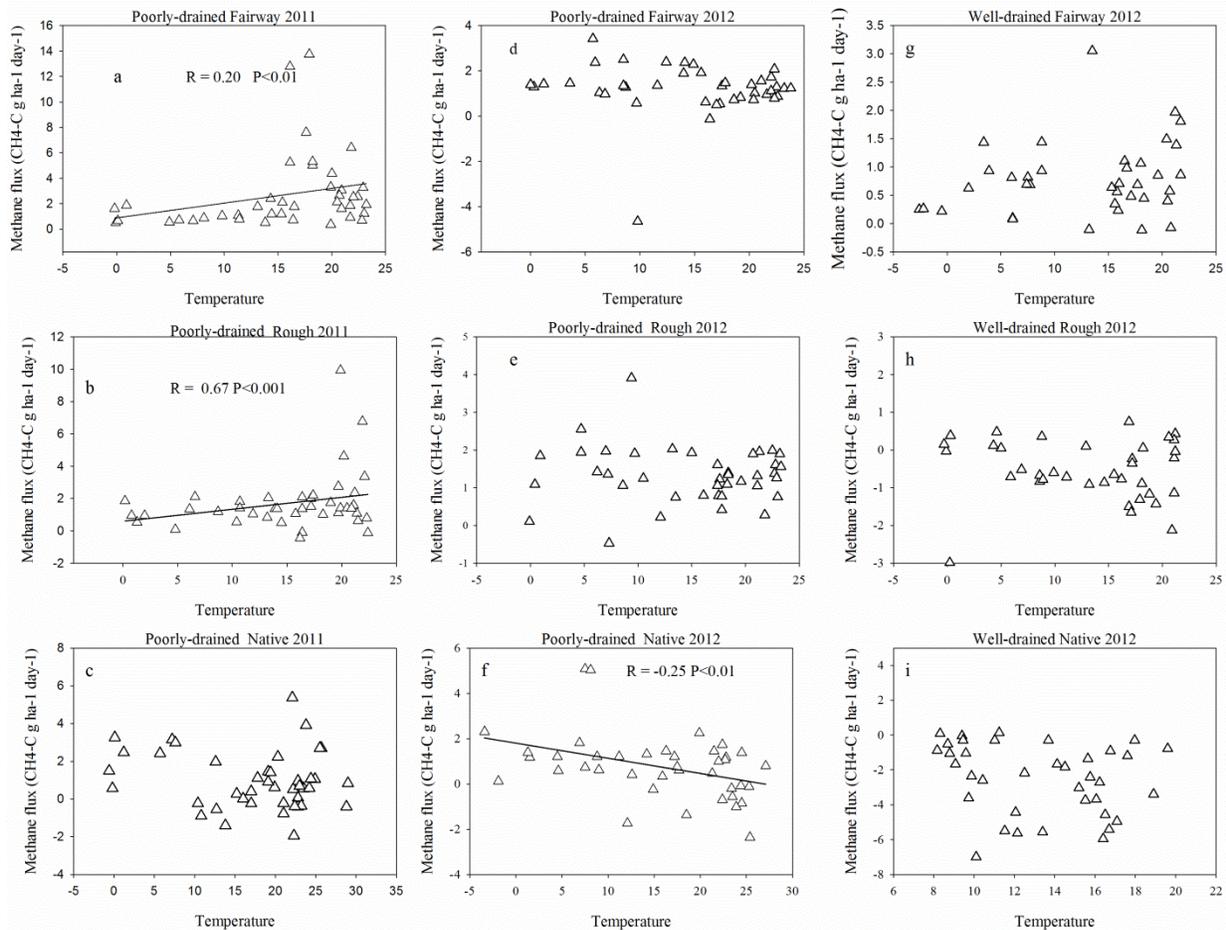


Figure 4.2. a-i. Correlations for soil methane flux and soil temperature from the poorly-drained and well-drained fairway, rough and native soils. Soil methane emissions were measured from poorly-drained sites for two consecutive years (2011-2012 and 2012-2013) and one year from well-drained sites (2012-2013). P-values, r-square (r^2), and linear regression are presented at each test site where significance exceeds ($P < 0.05$).

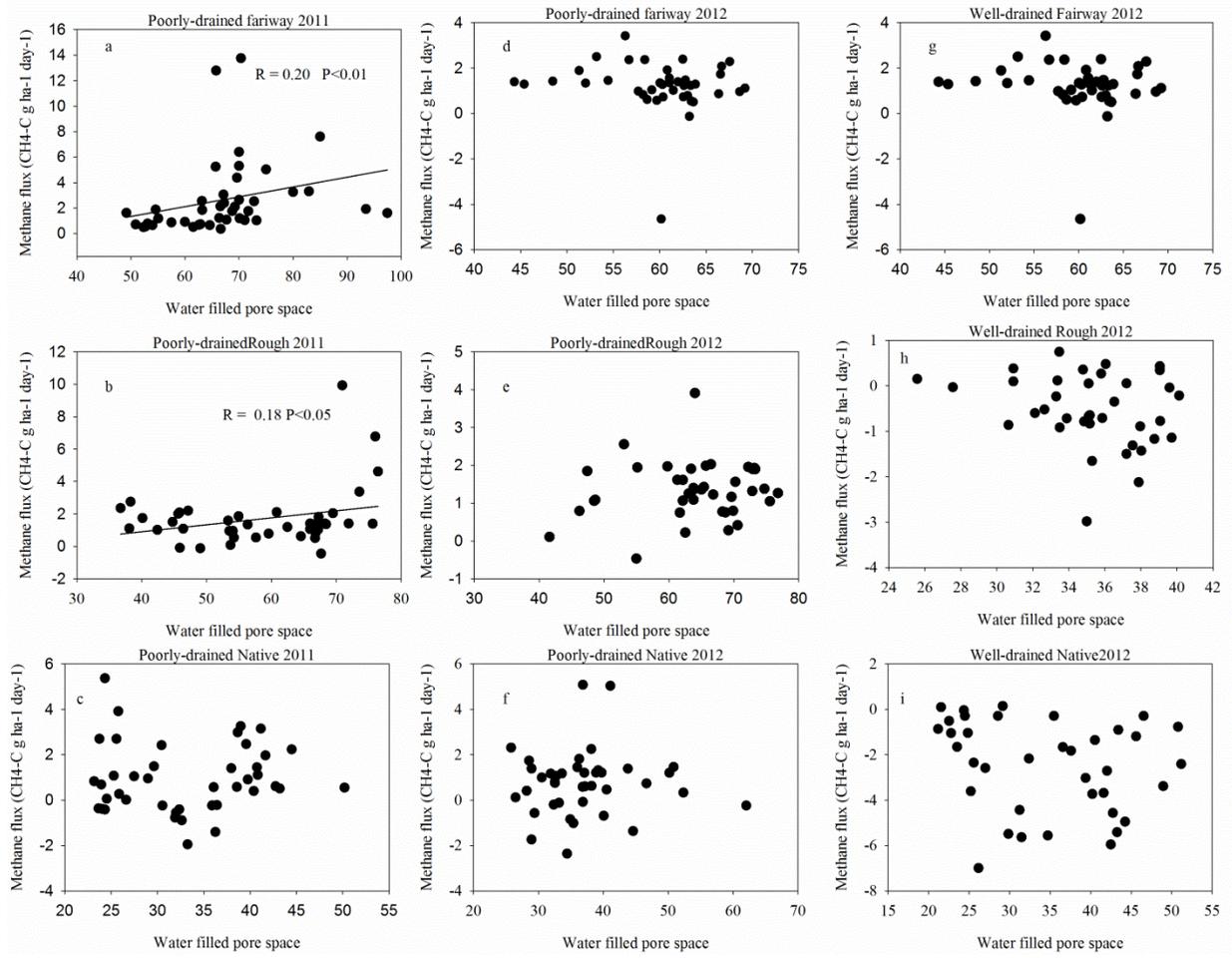


Figure 4.3. a-i. Correlations for soil methane flux and water filled pore space (WFPS) from the poorly-drained and well-drained fairway, rough and native soils. Soil methane emissions were measured from poorly-drained sites for two consecutive years (2011-2012 and 2012-2013) and one year from well-drained sites (2012-2013). P-values, r-square (r^2), and linear regression are presented each test site where significance exceeds ($P < 0.05$).

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CHAPTER 5:
SOIL DRAINAGE EFFECTS ON N₂O EMISSIONS FROM A
COLORADO GOLF COURSE USING CONTROLLED RELEASED FERTILIZERS

SYNOPSIS

The high potency, recent rapid accumulation in atmospheric concentrations and lack of significant surface sinks, N₂O is one of the most important GHGs of the 21st Century. Turfgrass systems have been quantified as a source of N₂O however fertilizer technologies that use different mechanisms to control the release of N substrate may reduce N₂O emissions. Yet further investigations are needed to test the effectiveness of these products under a variation of conditions. Two fertilizers that use two different mechanisms to control the release of N, UMaxx® and Polyon®, were applied at a rate of 150 kg ha⁻¹ yr⁻¹ to a golf course fairway and rough in three seasonal applications (50 kg ha⁻¹ each) at a poorly-drained (PD16) and well-drained (WD5) field site. Soil drainage characteristics were based on soil bulk density and water filled pore space (WFPS). Soil WFPS at PD16 fairway and rough often exceeded 60% during the summer producing peak fluxes from UMaxx treatments of 2025 and 995 g N₂O–N g ha⁻¹ day⁻¹, with emissions totaling 20.0 and 14.9 kg N₂O–N ha⁻¹ yr⁻¹, respectively. Annual emissions from WD5 fairway and rough UMaxx treatments totaled 8.9 and 2.3 kg N₂O–N ha⁻¹ yr⁻¹, respectively. Polyon treatments were more resistant to N₂O fluxes across drainage sites and emissions did not exceed 2.8 kg N₂O–N ha⁻¹ yr⁻¹. Polyon uses a temperature controlled barrier to diffusion that was more resistant to N₂O losses during conditions that favored denitrification, whereas the nitrification and urease inhibitors formulated for UMaxx were less effective.

INTRODUCTION

Nitrous oxide is a potent greenhouse gas (GHG) that has nearly 300 times the global warming potential as carbon dioxide (CO₂) (Solomon, 2007). Unlike CO₂, and CH₄, there are no significant surface sinks for N₂O; coupled with long atmospheric residence time from slow photo-dissociation, and its associated ozone depletion potential, N₂O is an important GHG of the 21st Century (Ravishankara et al. 2009). While there are significant natural sources of N₂O emissions from soils and oceans, anthropogenic interruption of natural N cycle in soils has caused N₂O emissions to increase (Syakila and Kroeze, 2013). Agricultural expansion has been identified as a primary source of increased atmospheric N₂O concentrations (Syakila and Kroeze, 2011).

Soil microbial nitrification and denitrification processes occur with favorable environmental conditions that include temperature, N substrate availability, and moisture. Nitrification requires aerobic soil conditions, whereas soil anaerobic conditions and a labile source of C are required for denitrification, but both processes can occur simultaneously within soil microsites (Stevens et al., 1997; Mathieu et al., 2006). Soil water filled pore space (WFPS) plays an important role in nitrification and denitrification because it regulates soil aeration (Menéndez et al., 2009), with nitrification being favored in drier soils (Skiba et al., 1992; Bateman and Baggs, 2005), and denitrification in the dominant process under wet soil conditions (WFPS exceeds 60%) (Linn and Doran, 1984; Bateman and Baggs, 2005; Bessou et al., 2010).

Soil structure and porosity influence soil air filled pore space (McTaggart et al., 2002), and soil physical conditions at the surface regulate emissions by influencing gas diffusion rates (Ball et al., 1997). Soil N₂O emissions significantly increase when soil aeration is impaired by compaction, leading to greater rates of denitrification from reduced soil oxygen (Sitaula et al.,

2000; Bessou et al., 2010) making it necessary to assess the effects of soil physical properties on N₂O emissions (McTaggart et al., 2002). Soil physical properties such as drainage indirectly mediate soil emissions (Skiba and Ball, 2002) and while GHG production in soils is primarily from biological sources, the soil physical environment influences biological activity through soil water status and temperature (Gregorich et al., 2006; Ball, 2013).

While agriculture is an important source of nitrous oxide, recently it has become more critical to consider the impacts of urban land use on soil emissions. Research suggests that regional GHG budgets that do not include urbanized areas may be underestimating emissions (Townsend-Small and Czimczik, 2010; Kaye et al., 2004). Turfgrass is a common landscape in and around urban areas (Zirkle et al., 2011; Milesi et al., 2005), covering approximately 16 million hectares (Mha) in the United States (Milesi et al., 2005) and along with urbanization will continue to expand (Racitti et al., 2008; Bandaranayake et al., 2003). Improved understanding of the implications of turfgrass management on soil C and N dynamics is needed to better quantify the environmental effects of urbanization (Racitti et al., 2008; Pouyat et al., 2009).

Studies have found that emissions from fertilized turfgrass systems can be substantial (Guilbault and Matthias, 1998; Magiotto et al., 2000). While turfgrass systems have been quantified as making contributions to atmospheric carbon dioxide (CO₂) concentration through SOC sequestration (Qian and Follett, 2002) the high global warming potential (GWP) of N₂O, emissions can greatly reduce the benefits of CO₂ sequestration in turf systems (Townsend-Small and Czimick, 2010). Nitrogen is the most limiting nutrient in turfgrass systems, and improving N use efficiency in turfgrass systems is current goal of research (Hull and Liu, 2005).

Advancements in nitrogen fertilizer technologies that modify the reaction of N substrate in the soil environment may lower N₂O emissions by increasing plant nutrient availability (Blaylock, 2008; Olson-Rutz et al., 2009) and decreasing biological nitrification and denitrification. Limiting the amount of reactive components for microbial process could lead to lower N₂O emissions (Granli and Bøckman, 1994). Such mechanisms that control the release of N substrate include nitrification and urease inhibitors, uncoated slow release, and coated N fertilizers (Blaylock, 2008). However, due to the large spatial and temporal variability of N₂O emissions more research is needed to assess the performance of the different N release mechanisms in a variety of ecosystems (Halvorson et al., 2013).

Fertilizer technologies formulated with different mechanisms to regulate the release rate of N are marketed for turfgrass systems. Given the common intensity in which golf course turf is culturally managed and the size and abundance of golf courses, an estimated 2.0 million hectares (Mha) globally (Bartlett and James, 2011). Due to the often high N fertilizer and irrigation management practices, these recreational areas may contribute a substantial portion of local N₂O emissions and could therefore greatly benefit from increased N efficiencies offered by advancements in fertilizer technology. The objective of this research was to evaluate N₂O emissions from two urea fertilizers that use different mechanisms to control the release of N substrate within the soil environment. Fertilizer sources were applied to turfgrass managed as golf course fairways and roughs at two locations that have poorly-drained and well-drained soil characteristics. Our hypotheses include differences in turfgrass management intensity, soil drainage, and N release mechanisms will have significant effects on N₂O emissions. Observing patterns and fluxes over such spatial and seasonal periods should give insight to key abiotic

factors driving N₂O emissions for the controlled N releases mechanisms employed for each fertilizer type.

MATERIAL AND METHODS

Site Description and Experimental Design

Historical land use for the field location was a 100 year old alfalfa sheep farm. Golf course construction began in 2005 and the course was opened to golfers in 2007. In 2006 the fairway was seeded with Perennial ryegrass (*Lolium perenne*), and the rough was sodded with Kentucky bluegrass (*Poa pratensis*). Fairways are mowed three times per week to a 1.9 cm height, and roughs are mowed one or two times per week to a height of 6.35 cm height during the growing season. In 2012, irrigation was applied daily from March to October at approximately 100 and 150 % evapotranspiration (ET) demand on the fairway and rough, respectively.

Particle size distribution of sand, silt, and clay are presented for each fairway and rough at the poorly and well-drained sites in Table 1. During the study period, May 2012 through May 2013, there was a total of 146 mm of precipitation, approximately 100 mm below the 20 year average. Mean annual temperature was 10.2 °C, approximately 1.6 °C above the 20 year average. The year 2012 was the hottest and driest year in region 4 of Colorado State (NOAA, 2013) of a 118 year record.

In order to compare the effects of drainage on nitrous oxide emissions, two sites at the golf course were chosen with poorly and well-drained soil characteristics. Determination of soil drainage potentials were made by soil bulk density, annual soil water filled pore space, and soil nitrate (NO₃-N) concentrations in the top 10 cm of the soil profile and are presented in Table 2.

The poorly-drained (PD16) sites were chosen due to its low position on the back nine of the golf course where there was minimal soil disturbance during golf course construction. An adjacent fairway (32.066°N, 57.65°W) and rough (32.064°N, 57.69°W) were selected at the poorly-drained site on day of year (DOY) 122 of 2011. The well-drained site (WD5) was selected on DOY 95 of 2012 on the front nine of the golf course at an adjacent fairway (32.107°N, 56.934°W) and rough (32.105°N, 56.945°W). The well-drained site was selected due to its location on the front-nine of the course where there is a strongly sloping hill that was created during golf course construction.

A randomized complete block was established on each of the poorly and well-drained sites to adjacent fairways and roughs to accommodate three treatments consisting of two fertilizers (UMaxx[®] and Polyon[®]) and one Control (zero fertilizer) in replications of three. UMaxx[®] (47% N) (Koch Agronomic Services, LLC, Wichita, KS) uses two soil enzyme inhibitors for enhanced efficiency that restricts nitrification and urease activity with dicyandiamide (DCD) and thiophosphoric triamide (TPT), respectively. Polyon[®] (Agrium Advanced Technologies, Loveland, CO) (42% N) is a polymer coated EENF technology to control the release of urea fertilizer that regulated through soil temperature.

Three fertilizer treatments were applied to poorly-drained fairway and rough during May, July and October on DOY 139, 205 and 303 of 2012. The well-drained fairway and rough were fertilized at similar times during June, August and October on DOY 153, 216, and 303 of 2012. Each fertilization event was applied at a rate of 50 kg N ha⁻¹, totaling 150 kg N ha⁻¹ of fertilizer applied during the 2012 growing season. Fertilizer was applied by hand in a sand mixture to attain an even distribution of fertilizer. After fertilization 8-10 mm of irrigation water was applied to the soil of each plot.

On DOY 174 of 2012, approximately twenty-one days after the first fertilization to the well-drained rough, golf course management reportedly applied $1.2 \text{ m}^{-3} \text{ ha}^{-1}$ of composted cattle manure to the WD5 rough (no other experimental sites received compost additions). Organic dairy cattle manure had a density of 958.7 kg m^{-3} , pH of 9.2, EC of 32.8 dS m^{-1} (saturated paste), 0.65% N with $272 \text{ mg NH}_4\text{-N kg}^{-1}$ and $12 \text{ mg NO}_3\text{-N kg}^{-1}$, 0.27% P, and 1.44% K.

Approximately one year prior to project initiation on the poorly-drained fairway and rough, the golf course maintenance personnel fertilized the fairway and rough in May and July of 2010 with a total of 250 and 175 kg N ha^{-1} of Polyon ®, respectively. In 2011, experimental plots at poorly-drained sites were fertilized with a total of 150 kg N ha^{-1} of UMaxx and Polyon materials and were applied in three applications of 50 kg N ha^{-1} during June, July and September. Golf course personnel fertilized the well-drained fairway and rough, one year prior to project initiation in May and July of 2011 using a total of 250 and 175 kg N ha^{-1} of Polyon ®, on the respective sites.

Soil Analysis

In order to quantify soils characteristics, four replications of intact whole soil samples were extracted from the corner of each randomized complete block at the poorly-drained sites on DOY 122, 2011 at incremental depths of 0-5, 5-10, 10-30, 30-60 and 60-90 cm. Baseline soil samples were collected using the same procedures from well-drained sites on DOY 95, 2012. As described by Follett et al. (2009), the first replication of soil sampled at each field plot was taken using a flat bladed shovel by under-cutting a 25 cm^3 section from each 0-5, 5-10 and 10-30 cm depth. The 30-60cm and 60-90cm depths were extracted with an oakfield soil core of a known volume. Only the top 0-5 and 5-10 cm of the three remaining replications were extracted by

undercutting with the flat bladed shovel, and the three lower depths were extracted using soil cores. Upon extraction each intact soil sample was carefully placed in plastic bags to preserve field moisture and soil structure. Soil samples were transported back to the USDA-ARS laboratory facilities where the total weight of each sample was recorded and stored at 10°C.

Soil bulk density was determined on unprocessed soils by determining gravimetric soil water content and calculated based on specific soil core volumes. Two replicates of approximately 12-15g of soil was subsampled from each replicated depth; moist samples were weighed and placed in a 110 °C oven overnight to determine total soil moisture content.

Just prior to soil processing, the top 0-5 cm depth of soil was carefully placed on an aluminum tray and the verdure from each sample was removed using a razor blade; separately the fairway mat and rough thatch layers was also removed accounting for the top 1.25cm and 1.5cm of the top portion of sample, respectively. Once the top layer of organic matter was removed, sub-samples of approximately 250-500g of soil per depth were processed through a 2 mm sieve and rock and plant roots were removed. Sieved soils were used to physically separate soil fractions of sand, silt, and clay using sieve sizes of >53 micrometer (μm), >20 μm and <20 μm , respectively. Additionally, another 50g of sieved soil was sent to Colorado State University Soils Laboratory to determine nitrate (NO_3^-), soil organic matter, pH, and texture. Soil organic matter was converted to soil carbon based on the conversion coefficient of 0.58 (soilquality.org.au).

Trace Gas Collection and Analysis

The measurement of turf-atmosphere N_2O exchange for this study began on DOY 136, 2012 and continued through DOY 172, 2013. The vented chamber method described by

Hutchinson and Mosier (1981) and others (Mosier et al., 2006; Parkin and Ventera, 2010) was employed for trace gas collection. Each chamber consisted of a removable chamber top and a collar that was permanently installed into the soil. Chambers tops were constructed with polyvinyl chloride (PVC) pipe that measured 12.5 cm in height and 21.2 cm in diameter. Fairway and rough 16 study plots measured 1.5 m² in size, and replications were separated by 60 cm borders. Experimental plots at fairway and rough 5 measured 2.25 m² and 1.64 m², respectively, and the three replications were separated by 60 cm borders. Experimental plots at the restored native sites measured 3 m², and three collars were evenly spaced and installed in the center. Two PVC trace gas collars were installed into the soil in the center of each plot as duplicate measurements, totaling 18 collars on the PD16 and WD5 fairways and roughs.

To decrease the interruption of golf course play and turf maintenance, the chamber design was modified so trace gas collars were completely level to the ground. In order for chamber to fit on top of submerged collars, the customary rubber seal of the trace gas chamber was replaced and with a 16 gauge stainless steel band. The band was bolted to the bottom of the chamber and over hung the PVC pipe by 2.5 cm. Weather filler rod was adhesively applied to the bottom of the PVC pipe to create the necessary airtight seal allowing the chamber to fit onto the top of the collar during trace gas sample collection.

Trace gas samples were taken between the times of 0900h and 1400h to represent the average temperature of the day. On measurement days chambers were placed on collars and gas samples from inside the chamber were extracted using 35 mL polypropylene syringes fitted with nylon stopcocks at time intervals of 0, 15, and 30 minutes upon installing the chambers. A total of six gas measurements were taken for every treatment per sampling interval on each fairway and rough. Three trace gas samples were taken per time interval on the restored native sections.

Air temperatures were taken at the beginning and at the end of each 30 minute sampling period on all measured sections. Temperatures inside the chambers were assumed to be equivalent to ambient air temperatures because chambers were covered with highly reflective foil.

Once trace gas samples were collected, samples were transported back to the Fort Collins, CO. USDA-ARS-SPNR laboratories and 25 ml of gas sample was injected into evacuated exetainer vials that were sealed with butyl rubber septa (Exetainer vial Labco Limited, High Wycombe, Buckinghamshire, UK) for analysis by gas chromatography (GC). The concentration of N₂O in the sample was determined using a fully automated gas chromatograph instrument (Varian Model Inc., Palo Alto, CA), equipped with a Hayesen D packed column and an electron capture detector for N₂O. Gas flux rates were calculated according to Hutchinson and Mosier (1981), and flux patterns were evaluated according to increases in concentration inside the chamber head space over time (Livingston and Hutchinson, 1995). Flux calculations also include adjustments for prevailing air temperature and for an atmospheric pressure of 640 mm mercury (Hg) using the ideal gas law (Delgado and Mosier, 1996).

Sample frequency was at least once per week for each location throughout the study period, and was intensified to three times per week the week following N fertilizations.

Ancillary Variables

Each day that trace gases were collected the top 10 cm of the soil surface temperature and soil volumetric water content were measured (VSWC) using an EC-Tm probe (Decagon Devices Inc., Pullman, WA). The soil devices were placed directly adjacent to each of the experimental fairway and rough plots and were assumed to represent whole plot soil water content and temperature.

Soil water filled pore space (WFPS) was calculated as:

$$\text{WFPS} = \frac{VSWC}{1 - \left(\frac{BD}{PD}\right)}$$

soil bulk density (BD) is based on measured values on the PD16 fairway and rough (1.52 and 1.42 g cm⁻³, respectively), or the WD5 fairway and rough (1.10 and 1.09 g/cm⁻³ respectively), and particle density (PD) was assumed to be 2.65 g cm⁻³.

Statistical Data Analysis:

Daily average N₂O fluxes for each of the three fertilization periods during the 2012 growing season were calculated by dividing cumulative emissions by the number of days for each study period. Daily flux averages of the three fertilization periods were subject to an analysis of variance (ANOVA) using SAS v.9.2 program (SAS Institute, 2008, Cary, NC, USA) PROC MIXED model, where the effects of drainage (poorly and well-drained) and site (fairway and rough) were nested in the random variable portion of the model statement. A test of LSD was performed to evaluate the effects of site, treatment, fertilization period, drainage, and their corresponding interactions. Significant differences were reported at $P < 0.05$ confidence level. All data were log transformed to meet assumptions of normality.

Cumulative emissions for each treatment were calculated by integrating the measured emission data with linear interpolations between the consecutive sampling times. Linear interpolations for 2012–2013 cumulative N₂O emissions for each treatment plot were used to estimate flux values between successive sampling day, providing daily flux estimates for non-sampling days. An analysis of variance (ANOVA) was performed to test effects of treatment, site (fairway and rough), drainage (poorly and well-drained), and corresponding interactions using

the PROC MIXED linear model from statistic analytical program SAS v.9.2 (SAS Institute, 2008, Cary, NC, USA). Contrasts of LSD were performed using the Satterthwaite option in the fixed effects portion of the model. Location and site were nested within replication and used as random variables.

In order to calculate emission factors for each treatment, the percent of applied N lost through annual N₂O emissions was calculated as the difference of cumulative emission between the Control and each EENF treatments and divided by total kg N applied per hectare. The net value is expressed as a percentage of the N applied to calculate the appropriate fertilizer emission factors.

PROC GLM multiple regression analysis was used to test the relationship between N₂O flux and WFPS and temperature and corresponding interactions. The exponential relationship between N₂O flux and soil temperature was further tested by initially using PROC REG to estimate *a* and *b* parameters for the PROC NLN model. Exponential regression analyses were then used to fit the exact *a* and *b* parameter coefficients used in the regression equation between N₂O fluxes and soil temperature for each fertilizer and Control treatments:

$$Flux_{N_2O} = ae^{bT}$$

where *T* is temperature (Davidson et al., 1998).

RESULTS

N₂O Fluxes from Fertilizer Treatments

Statistical analysis identified a three way interaction between site (fairway and rough), fertilization period, and EENF treatment ($P < 0.05$); and a second three way interaction was identified between site, fertilization period, and soil drainage (PD16 and WD5) ($P < 0.05$).

Upon the first fertilizer additions in the spring peak fluxes of $49 \text{ g N}_2\text{O-N ha}^{-1} \text{ day}^{-1}$ were measured from poorly-drained (PD16) fairway UMaxx treated plots approximately one week following application. Unlike the previous treatment, the application of Polyon EENF to the PD16 fairway did not trigger significant N_2O fluxes (Fig. 1a). Fertilizer additions to the PD16 rough did not significantly increase N_2O fluxes for any one treatment, and fluxes remained low for this period ($< 10 \text{ g N}_2\text{O-N ha}^{-1} \text{ day}^{-1}$) (Fig. 2a). The WD5 fairway had the greatest fluxes following the first fertilization with fluxes from UMaxx treatments peaking at $200 \text{ g N}_2\text{O-N ha}^{-1} \text{ day}^{-1}$ one week following the first fertilization, and Polyon treated plots spiked to $46 \text{ g N}_2\text{O-N ha}^{-1} \text{ day}^{-1}$ approximately one month after the fertilization (Fig. 1c). Plots treated with UMaxx at the WD5 rough peaked at $38 \text{ g N}_2\text{O-N ha}^{-1} \text{ day}^{-1}$ two weeks following application, but fluxes from WD5 rough plots treated with Polyon remained below $10 \text{ g N}_2\text{O-N ha}^{-1} \text{ day}^{-1}$ (Fig. 2c).

Approximately three weeks after the first fertilizer applications were applied; compost derived from cattle manure was applied to the WD5 rough by golf course personnel (no other sites received compost additions). However due to the low concentrations of compost, soil effluxes remained low. Peak fluxes from compost additions were 25, 24, and $13 \text{ g N}_2\text{O-N ha}^{-1} \text{ day}^{-1}$ from WD5 rough UMaxx, Polyon, and Control plots, respectively, less than a week later. After this, fluxes typically remained below $10 \text{ g N}_2\text{O-N ha}^{-1} \text{ day}^{-1}$ for most treatments; that is

except for UMaxx treated plots where fluxes increased a second time to $30 \text{ g N}_2\text{O-N ha}^{-1} \text{ day}^{-1}$ approximately two weeks after compost was applied.

The second fertilization occurred during the summer, approximately sixty days following the first treatment application. Three days following the second fertilization to the PD16 fairway and rough, fluxes from UMaxx treated plots increased to 230 and $135 \text{ g N}_2\text{O-N ha}^{-1} \text{ day}^{-1}$, but peak fluxes were not reached for another week when maximum flux rates of 2025 and $995 \text{ g N}_2\text{O-N ha}^{-1} \text{ day}^{-1}$, respectively (Fig. 1a and 2a). Following peak fluxes from PD16 UMaxx treatments, soil efflux returned to background levels. WD5 fairway UMaxx treated plots were also significantly affected by summer fertilizer additions and peaked at $489 \text{ g N}_2\text{O-N ha}^{-1} \text{ day}^{-1}$ three days following the second application (Fig. 1c). Plots treated with Polyon at the PD16 fairway and rough plots however remained fairly low, peaking at 50 and $58 \text{ g N}_2\text{O-N ha}^{-1} \text{ day}^{-1}$ three and thirty days after application, respectively (see Fig. 1a and Fig. 2a). The WD5 fairway and rough Polyon treated plots were the least affected by second fertilization during the summer and peak fluxes only measured 36 and $10 \text{ g N}_2\text{O-N ha}^{-1} \text{ day}^{-1}$, respectively (Fig. 1c, and Fig. 2c).

The final fertilization occurred late in October of 2012 (DOY 303), and soil N_2O fluxes never exceeded $3.6 \text{ g N}_2\text{O-N ha}^{-1} \text{ day}^{-1}$ for any EENF treatment, and emissions from late fall fertilization were significantly lower ($P < 0.05$) than the first two fertilizations. In fact, fluxes were so low following the third fertilization that there was no difference in flux rates from those observed during the subsequent winter. As the fall season progressed into winter PD16 fairway plots treated with Polyon began to exhibit winter injury, but no other plots were affected by the late fertilization.

Daily average fluxes were also calculated for the 2012-13 winter and spring periods on the PD16 and WD5 fairways and roughs, although no fertilizers were applied at these times. There were no significant differences among treatments at the fairway and rough sites during the winter and fluxes averaged $2.5 \text{ g N}_2\text{O-N ha}^{-1} \text{ day}^{-1}$. As winter progressed into spring all ENNF daily fluxes increased to an average of $5.0 \text{ g N}_2\text{O-N ha}^{-1} \text{ day}^{-1}$. The study ceased trace gas sampling at the end of May 2013.

Regression Analysis of Soil N₂O Flux and WFPS and Temperature

Soil water filled pore space averaged 60 and 65% at the PD16 fairway and rough, and was significantly greater ($P < 0.0001$) than soil WFPS at the WD5 fairway and rough, that averaged 50 and 40%, respectively. We used regression coefficients (R^2) to test the relationship between N₂O flux, WFPS and soil temperature and interactions for each treatment. Soil WFPS and temperature was significantly ($P < 0.0001$) related to N₂O flux at PD16 fairway and UMaxx treated plots, with respective R^2 values of 0.15 and 0.38. A significant interaction was identified for soil WFPS and temperature PD16 fairway ($P < 0.0001$) and rough ($P < 0.01$) Polyon treatments (R^2 values = 0.44 and 0.37, respectively); however WFPS was not a significant variable alone, indicating that WFPS was only significant when temperature was not a limiting factor. A significant interaction between soil WFPS and temperature was also related to N₂O flux at PD16 rough UMaxx treatments ($R^2 = 0.35$). A significant interaction between soil WFPS and temperature was related to N₂O fluxes at the WD5 fairway and rough UMaxx treated plots ($R^2 = 0.2$ and 0.44), respectively. Only temperature was significantly ($P < 0.0001$) related to N₂O flux for WD5 fairway and rough Polyon treatments ($R^2 = 0.39$ and 0.28 , respectively).

Additionally, there was a significant ($P < 0.0001$) exponential relationship between soil temperature and N_2O emissions for all treatment plots. Golf course N_2O fluxes were log transformed, and values were fitted to an exponential regression against soil temperature for each treatment (Figures 3a-m). In order to increase the goodness of fit to exponential regressions, high N_2O flux measured from poorly drained and well-drained fairways treated with UMaxx materials were excluded in regression analysis (omitted values are presented with different symbols). By omitting such values for UMaxx treatments, values for intercepts and slopes were decreased for regression equations because following rapid losses soil N_2O fluxes returned to background level. Also by omitting high flux values for UMaxx treatments this created a comparable difference in slope and intercept values compared to those of the corresponding Polyon treatments

Cumulative N_2O Emissions

Due to the significant site (fairway and rough) by treatment interaction ($P < 0.01$) and the significant treatment by drainage (poorly and well-drained) interaction ($P < 0.01$), cumulative N_2O emissions are also compared. The greatest annual cumulative emissions were from UMaxx treated plots at the poorly-drained fairway and rough, totaling 20.0 and 14.9 kg N_2O -N $ha^{-1} yr^{-1}$, equating to annual emission factors of 12.7 and 9.1%, respectively (Fig. 4a-b), respectively. The majority of the N_2O emitted from UMaxx treated plots were induced by the summer fertilization event. Cumulative emissions from the UMaxx treated plots at the well-drained fairway were similar to those treatments applied the PD16 rough, emitting a total of 8.9 kg N_2O -N $ha^{-1} yr^{-1}$, a loss of 5.2% of total N applied (Fig. 4c).

Cumulative emissions from Polyon treated plots were significantly lower than the previous UMaxx treatments, and were statistically similar across all treatment sites; nor did they differ significantly from Control (zero fertilizer) plots (see Fig. 4a-d). Polyon treatments applied to the PD16 fairway and rough plots and WD5 fairway plots emitted a total of 2.8, 2.8 and 2.1 kg N₂O-N ha⁻¹ yr⁻¹, respectively; a 1.2, 1.1, and 0.6, % loss of total annual N applied at the three respective sites (Fig. 4a-c). The difference in emission factors between the PD16 and WD5 Polyon treated plots was from greater emissions (not significant) from PD16 plots, and greater emissions from the WD5 fairway Control plots (zero fertilizer). The Control WD5 plots emitted 1.2 kg N₂O-N ha⁻¹ yr⁻¹ (last fertilized in 2011), whereas Control PD16 fairway plots had not been fertilized since 2010 and only emitted 0.9 kg N₂O-N ha⁻¹ yr⁻¹. Cumulative emissions from the WD5 rough UMaxx and Polyon treated plots totaled 2.3 and 1.5 kg N₂O-N ha⁻¹ yr⁻¹, a 0.9 and 0.3% loss of total fertilizer applied (Fig. 4d), respectively, and were also statistically similar to other Polyon and Control treatment plots.

DISCUSSION

Soil N₂O Flux, Drainage, and WFPS

Nitrous oxide fluxes from this study responded similarly to other studies, with fluxes increasing upon fertilizer additions (Mosier et al., 1998), typically within days following applications (Goodroad and Keeney 1984; Veldkamp et al 1998; Dobbie et al., 1999; Akiyama et al., 2000; McTaggart et al., 2002), and were especially significant after summer fertilizer applications (Dobbie and Smith, 2002). Furthermore, soil structure and porosity created considerable differences in WFPS and soil nitrate concentrations between the poorly and well-drained sites (See Table 2). Soil drainage potentials as influenced by structure have a great deal

of influence on the soil moisture and soil nitrogen (Skiba and Ball, 2002). Therefore our data suggests that differences in soil drainage at the poorly and well-drained field sites also influenced N₂O emissions. Soil water content plays a significant role in soil N dynamics (Zhang et al., 2013). Lower soil nitrate concentrations at the WD5 sites indicate that low soil WFPS reduced nitrification rates (NH₄⁺ to NO₃⁻). Decreased soil water content slows N turn over in the soil by lowering ammonium diffusion rates (Mosier et al., 1991), and have important effects on microbial denitrification by limiting N substrate, a critical factor effecting soil N₂O emissions in the upper portion of the soil profile (Conen et al., 2000).

Soil structure has a major influence on soil WFPS and WFPS will differ in soils with different bulk density (Ball, 2013), with differences within soils typically caused by compaction (Bessou et al., 2010). There is a tightly coupled relationship between WFPS and N₂O emissions, and WFPS is one of the most important factors affecting soil N₂O efflux (Smith et al., 1998; Dobbie et al., 1999; Akiyama et al., 2000). Soil WFPS is often used as a proxy to gas diffusion rates (van der Weeden, et al., 2012), and is a common and widely used metric to investigate soil N₂O emissions (Baggs and Bateman, 2005; del Prado et al., 2006). Differences in soil bulk density that affects soil water status may also cause variation in the relationship between WFPS and N₂O emissions (Castellano, et al., 2010). Regression analysis showed there was a significant relationship between WFPS and N₂O flux for several of the golf course fertilizer treatments, but this relationship was typically more significant for UMaxx treatments than for Polyon treatments; this may be due to Polyon materials having a greater response to temperature than to soil water content.

The effects of soil WFPS between poorly and well-drained field sites was much more significant for UMaxx materials than for Polyon treatments, especially following the second

application fertilizer during the summer. During the summer, poorly-drained sites had high soil WFPS (>65%) that contributed to the rapid and episodic N₂O fluxes from UMaxx treatments after fertilizer additions. Nitrous oxide flux trends observed from UMaxx treatments during the summer fertilization period are indicative of denitrification, where large peak fluxes were followed by low background emissions. When soil WFPS reaches 60% soil microbial activity becomes anaerobic due to reduced soil oxygen levels (Linn and Dorn, 1984). Denitrification tends to produce greater but shorter lived N₂O fluxes because N substrate is depleted after large soil emissions (Skiba and Smith, 1999); these emissions typically return to background levels because environmental conditions aiding the denitrification process are not typically sustained for long periods of time (Akiyama et al., 2000; Skiba and Smith, 1999).

Polyon treatments were more resistant to rapid N₂O fluxes following summer fertilization soil WFPS was high and peak fluxes from PD16 Polyon treatments were 25 to 50 times lower compared to UMaxx treatments. Instead of rapid episodic peak fluxes followed by low background emissions, plots treated with Polyon were affected by smaller N₂O fluxes for longer period of time (several weeks), demonstrating a greater resistance to microbial denitrification through a more controlled release of urea. In general Polyon treatments were not significantly affected by soil drainage potentials at the two drainage sites and demonstrated a consistent release rates that reduced N₂O emissions. Our results are contrary to Akiyama et al. (2013), who observed high flux rates from polymer coated urea in an imperfectly drained rice field in Japan that was periodically saturated.

Soil WFPS at the WD5 fairway did not typically exceed 55% during the summer, helping to lower N₂O fluxes from UMaxx treatments by four and two fold compared to PD16 treated sites. Microbial denitrification was most likely negligible at the WD5 rough where soil WFPS

never exceeded 42%. In sufficiently aerated soils microbial nitrification is the dominant process (Robertson 1989; Mathieu et al., 2006). The WD5 rough was the one site where UMaxx and Polyon materials had comparable flux rates throughout the season. Low soil water content at the WD5 rough diminished peak fluxes from UMaxx treatments by 95% during summer fertilization compared to the poorly-drained rough. Our emission reduction calculations are double of those reported by Akiyama et al. (2000) who calculated a 54% reduction when soil WFPS at field plots was maintained at 35-50%. Compost applications to the WD5 rough increased emission from WD5 rough plots, but emissions were relatively low. As found by Oenema et al. (1997) manure additions create a non-limiting factor of soil mineral N once excreta is transformed to NH_4^+ , generating soil N_2O emissions.

Nitrous oxide emissions were very low for all treatments sites following the third fertilization in the fall of 2012, and as indicated by the low soil temperatures (below 10°C) turf was going into dormancy. Late fall application of Polyon materials to the PD16 fairway caused winter injury from this materials slow rate of diffusion, causing damage to tender green turf during winter conditions. UMaxx treated plots at this site were not damaged following the late fertilization timing and greater solubility likely prevented winter injury. The biggest concern regarding late fall fertilization to turfgrass is the increased risk of winter injury (Wilkinson and Diff, 1972). Miltner et al. (2004) and others (Koski and Street, 2010) recommend using a more soluble or quickly available form of fertilizer in the fall. Therefore it may be best to apply Polyon materials during early fall conditions. Furthermore, Baer et al. (2012) notes an importance difference between late fall and dormant fertilization, where late fall applications are intended for autumn turfgrass utilization, while dormant fertilization is meant for winter hardiness and spring green up. Therefore the final fall fertilization in this study may have been more effective in

increasing winter hardiness, making UMaxx EENF a far better product for this application timing.

Cumulative N₂O emissions

Cumulative emissions from Polyon treated plots and fertilizer treatments applied to the WD5 rough are similar to N₂O emissions of 1.6 to 2.5 kg ha⁻¹ yr⁻¹ from other turfgrass studies (Kaye et al., 2004; Bremer, 2006; Groffman et al., 2009; Townsend-Small and Czimczik, 2010). Cumulative emissions from WD5 fairway UMaxx treatments are also similar to emissions reported by Guilbault and Matthias (1998) who measured 6.4 kg N₂O-N ha⁻¹ yr⁻¹ from a golf course fairway in Arizona after applying effluent water treatments. Cumulative emissions from poorly-drained UMaxx treatments far exceed those from other turfgrass N₂O emission studies. However the nearly 80% of total emissions from PD16 UMaxx treatments occurred following summer fertilization, otherwise emissions following the spring and fall fertilizations were not markedly different from other treatments. Unlike, Dobbie and Smith (2002) who reported significant decreases in N₂O emissions from urea treatments that used nitrification and ureases inhibitors from grasslands that had high soil WFPS, golf course UMaxx treatments applied to nearly saturated soils were subject to rapid losses.

CONCLUSION

Our study demonstrates turfgrass systems managed at golf courses contribute to global N₂O emissions; however by applying fertilizer during cool periods or by increasing soil aeration during warm periods, N₂O emissions can be greatly decreased. We also found that soil drainage affected WFPS, soil nitrate concentration and therefore annual N₂O emissions. The greatest difference in emissions between poorly and well-drained sites was observed following summer

fertilization using UMaxx materials. Our research suggests that Polyon is a superior turfgrass product that restricts N₂O emissions during warm periods particularly when conditions favor microbial denitrification. Oppositely, UMaxx treatments were highly susceptible to losses during periods when soil was warm and wet, and may be a more appropriate fertilizer to apply during the late fall season when turf is going into dormancy, helping to promote spring green up and reduced risk of winter injury. In conclusion we emphasize the importance of selecting the most appropriate type of fertilizer to inhibit losses and maintain turf quality. Cultural management of turf that increases soil aeration, particularly irrigation management, is an important strategy to mitigate N₂O emissions, especially in poorly-drained areas of golf courses.

TABLES AND FIGURES

Table 5.1. Percent sand, silt and clay in the 0-10 cm of the soil profile for the poorly-drained (PD16) and well-drained (WD5) fairway, rough and native field plots.

Site	Sand	Silt	Clay
	-----%-----		
PD16	46	12	19
Fairway			
PD16 Rough	53	11	13
WD5	61	15	24
Fairway			
WD5 Rough	62	15	23

Table 5.2. Soil bulk density, pH, organic matter (OM), annual water filled pore space (WFPS), and soil nitrate (NO₃-N) concentrations for the poorly-drained (PD16) and well-drained (WD5) fairway, rough and native field plots in the top 0-10cm of the soil profile.

Site	Bulk density g cm ⁻³	pH paste	SOC g kg ⁻¹ soil	WFPS %	NO ₃ -N mg kg ⁻¹
PD16 Fairway	1.43	7.7	16.3	60	25.6
PD16 Rough	1.52	7.8	14.5	65	37.4
WD5 Fairway	1.10	7.1	19.5	50	10.5
WD5 Rough	1.09	7.2	17.2	40	7.5

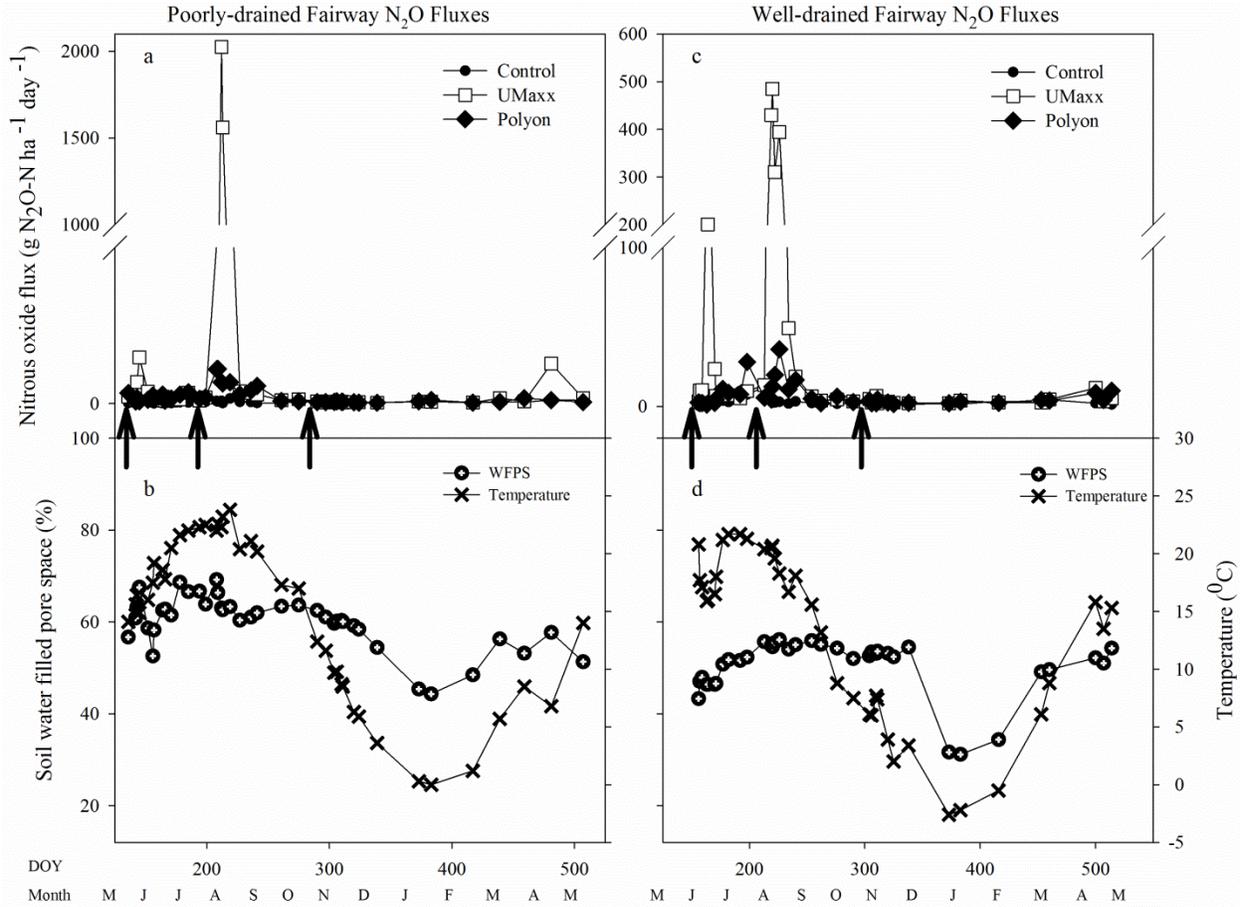


Figure 5.1.a-d. Measured nitrous oxide fluxes from poorly drained (PD16) and well-drained (WD5) fairways from three treatments, UMaxx, Polyon, and the Control (zero fertilizer). Notice the scale difference and the breaks in scale on the vertical axis for N_2O flux in figures a and c. Soil nitrous oxide flux presented for each treatment is the average of three replications. Three fertilization dates (PD1, PD2, and PD3 and WD1, WD2 and WD3) are presented according to the day of year (DOY) in which they were applied. Soil water filled pore (WFPS) (left axis) and soil temperature (right axis) are presented for each day that soil N_2O flux was sampled.

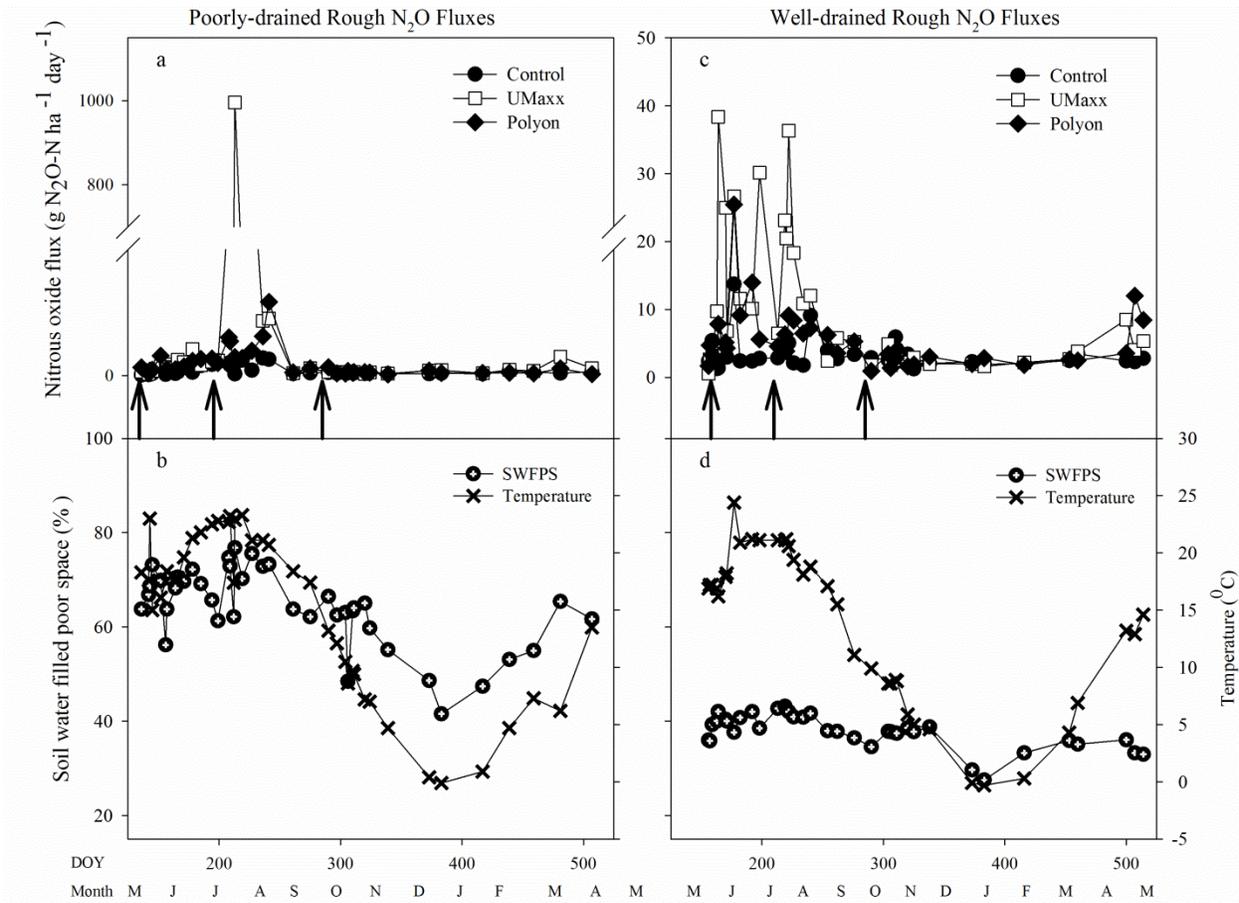


Figure 5.2.a-d. Seasonal nitrous oxide fluxes from three treatments, UMaxx, Polyon, and the Control (zero fertilizer) from the PD16 and WD5 roughs. Notice the difference in scale and the break in scale on the vertical axis for N_2O in figure a. Soil nitrous oxide flux presented for each treatment is the average of three replications. Three fertilization dates (PD1, PD2, and PD3 and WD1, WD2 and WD3) are presented according to the day of year (DOY) in which they were applied. Soil water filled pore (WFPS) (left axis) and soil temperature (right axis) are presented for each day that N_2O fluxes were sampled.

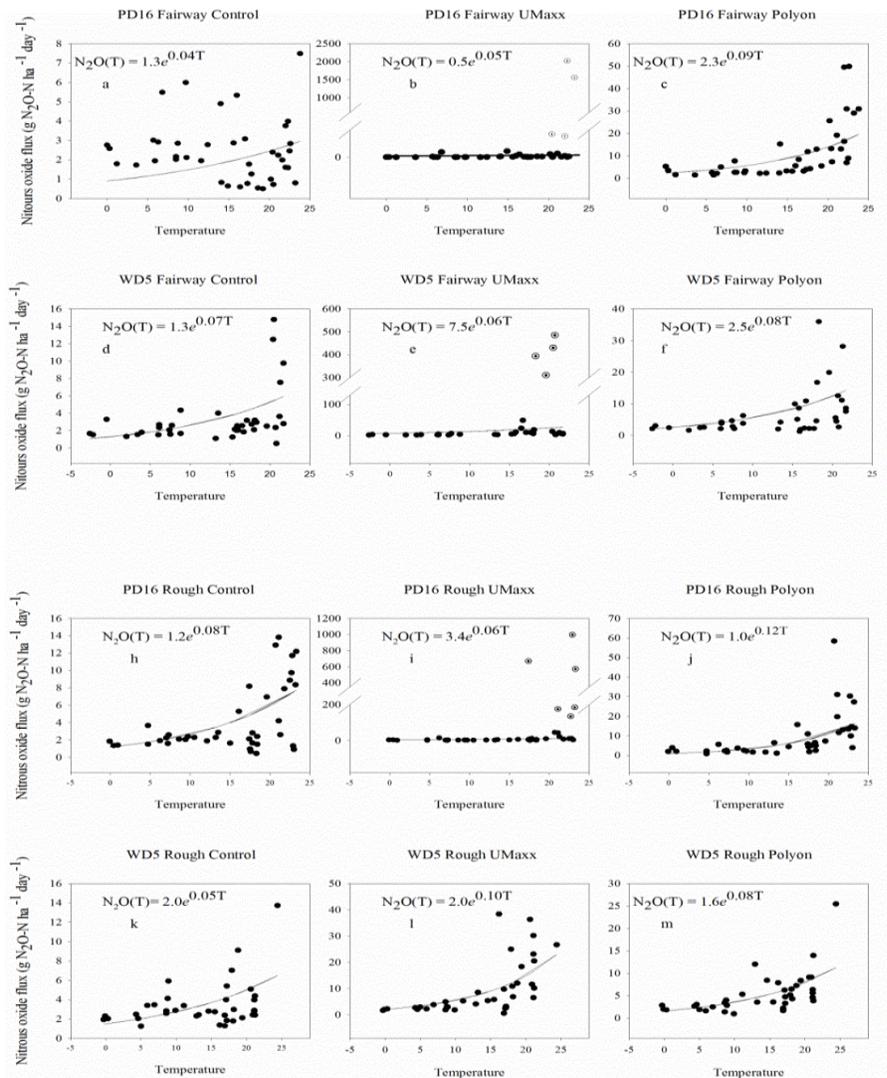


Figure 5.3.a-m. Exponential regressions for nitrous oxide and soil temperature for UMaxx, Polyon and Control treatments from poorly- drained (PD16) and well-drained (WD5) fairways and roughs. Exponential equations for each treatment are presented for each treatment and temperature (T) is the independent variable. P-values are <0.0001 for all treatments presented. Notice the break in scale on fairway and PD16 UMaxx treatments. Values represented by open crosshairs circles were not used in the regression analysis but presented with data.

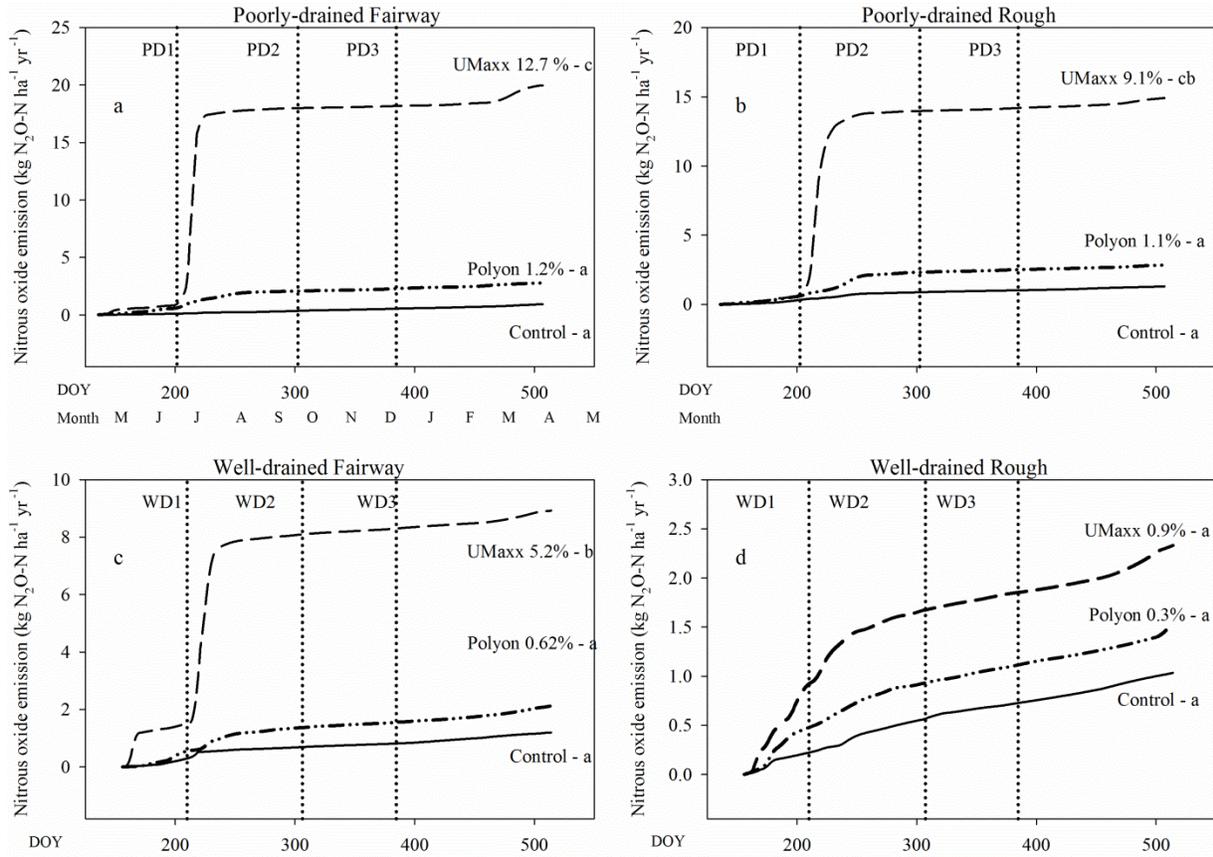


Figure 5.4. a-d. Annual cumulative nitrous oxide emissions in 2012-2013 from a poorly drained (PD16) and a well-drained (WD5) fairway and rough with two EENFs, UMaxx and Polyon, and one Control treatments. The three fertilizer applications (PD1, PD2, and PD3 or WD1, WD2, and WD3) to fairways and roughs are indicated by vertical dash lines. Percent of total fertilizer applied is presented for each treatment and letters indicate significant differences at $P < 0.05$.

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