SOIL CHEMICAL PROPERTIES OF SAND-BASED GOLF PUTTING GREEN AT DIFFERENT DEPTHS

A Thesis
Submitted to the Graduate Faculty
of the
North Dakota State University
of Agriculture and Applied Science

By

Yichun Wang

In Partial Fulfillment of the Requirements
for the Degree of
MASTER OF SCIENCE

Major Department:
Plant Sciences

June 2010

Fargo, North Dakota

North Dakota State University
Graduate School

Title

Soil Chemical Properties of Sand-based Golf

Putting Green at Different Depths

By

Yichun Wang

The Supervisory Committee certifies that this ***disquisition*** complies with North Dakota State University's regulations and meets the accepted standards for the degree of

MASTER OF SCIENCE

ABSTRACT

Wang, Yichun, M.S., Department of Plant Sciences, College of Agriculture, Food Systems, and Natural Resources, North Dakota State University, June 2010. Soil Chemical Properties of Sand-based Golf Putting Green at Different Depths. Major Professor: Dr. Deying Li.

USGA-specified golf putting green rootzone is a highly managed, sand dominated turf system. As putting greens age, organic matter accumulation in the form of thatch and mat in the upper rootzone profile causes temporal and spatial changes in soil chemical properties. The objective of the first study was to characterize soil chemical properties in aging putting green rootzones. Four USGA-specified putting greens treated with two rootzone mixtures (sand/peat at 80:20; sand/peat/soil at 80:15:5) and two establishment fertilization regimes (controlled and accelerated) were constructed in sequential years. Samples were collected to a depth of 7.62 cm when the four putting greens were 6, 7, 8, and 9 years old, and were subdivided into 12 layers. The effects of rootzone mixture, establishment fertilization regime, putting green age, and soil depth on total organic C, total N, potentially mineralizable N (PMN), cation exchange capacity (CEC), electrical conductivity (EC), and pH were evaluated. The rootzone mixtures and establishment fertilization regimes had no effect on soil chemical properties investigated saving EC, which was higher in sand/peat/soil rootzones. Total organic C, total N, PMN, CEC, and EC decreased with soil depth whereas soil pH increased with soil depth. The interaction between putting green age and soil depth was significant for total N, CEC, and EC. The initial differences of soil chemical properties disappeared due to topdressing practice over a period of 6 years at the top of the rootzones especially in the 0 to 2 cm layer. The chemical properties of the original rootzone layers are affected by both the age of the putting greens and cultural practices.

Diffuse reflectance Fourier transform infrared (DRIFT) spectroscopy in the near-infrared (NIR) (4000-10000 cm^{-1}) and mid -infrared (MIR) (600-4000 cm^{-1}) region in conjunction with partial least square regression (PLSR) is able to rapidly predict multiple soil properties from a single spectral scanning and is deemed as a promising surrogate for conventional analytical methods. In the second study, by using samples collected in the first study, calibration models were developed for total organic C, total N, CEC, EC, and pH by regressing spectral results of DRIFT-NIR and -MIR with values determined by conventional methods. Results for total organic C, total N, CEC, and EC achieved $R^2 >$ 0.80. Mid infrared and NIR spectroscopy gave similar calibration accuracy for soil properties investigated. Based on rootzone mixture (sand/peat vs sand/peat/soil), putting green age (6-yr-old vs 9-yr-old), and sampling depth (0-3.81 cm vs 3.81-7.62 cm), the whole sample set was further grouped into subsets. Satisfactory accuracy of MIR calibrations and mutual predictions was achieved with subsets of different rootzone mixtures and putting green ages. However, subsets separated by soil depth failed to be predicted with sufficient accuracy within the group. Results of the study verified the potential of using DRIFT-NIR and -MIR to predict soil chemical properties of sand-based turf soil through PLSR modeling; however, model robustness might be affected by sampling depth.

ACKNOWLEDGEMENTS

My three years of education at NDSU was a short journey in my life; however, it helped me greatly. It was great to have worked with my professor Dr. Deying Li because he gave me his guidance and never-ending patience. Because of his sense of humor and positive energy, I have gained a lot of encouragement which has been helpful towards everyday life.

I would like to express my appreciation to Dr. Ron Smith, Dr. Qi Zhang, Dr. Alan Zuk and Kevin Rue. I was fortunate to have worked in such a delightful turf group. Thank you all for your assistance in my research and in life.

I would also like to thank Drs. Tom DeSutter and Rodney Lym for the educative and inspiring instructions and suggestions. Special thanks go to Dr. Roch Gaussoin at University of Nebraska-Lincoln for providing the soil samples.

Finally, I would like to give my special thanks to Sheng Wang, who has been my classmates for 6 years from undergraduate to graduate study. Thanks for everything.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

GENERAL INTRODUCTION

Golf putting greens are highly managed turf systems. A USGA-specified putting green rootzone, which is the most popular construction system, is established using sand as the dominating matrix with low level of organic matter to facilitate the requirements on water infiltration, drainage, and aeration. Besides initial input of organic amendments, the input of turfgrass vegetative materials, mostly as thatch or mat, continually contributes to the soil organic matter (SOM) pool in the rootzone. Soil organic matter undergoes changes in quantity, nature, and spatial distribution; all of which gradually alters the original physical, chemical, and biological properties of the rootzone, and subsequently, affects turfgrass health. As a result, management adjustments are required accordingly. The first part of Chapter 1 in this thesis is a review of literatures on the importance, causes and prevention of SOM as thatch and mat in sand-based turfgrass rootzone.

Conventional analytical methods to determine soil chemical properties can be tedious and costly. Diffuse reflectance Fourier transform infrared (DRIFT) spectroscopy technique provides a useful tool to quantify soil properties rapidly with sufficient accuracy. The second part of Chapter 1 is a review of literatures on the principles, analytical techniques, and applications of infrared spectroscopy.

The study in Chapter 2 was designed to characterize soil chemical properties including total organic C, total N, potentially mineralizable N, cation exchange capacity, electrical conductivity, and soil pH in aging sand-based putting greens. In this study, four experimental putting greens treated with two rootzone mixtures (sand/peat mixture and sand/peat/soil mixture) and two establishment fertilization regimes (accelerated and controlled) were established in sequential years following USGA specifications. Soil samples were collected when the putting greens were 6 to 9 years old and partitioned into 12 layers. Treatment effects, i.e. rootzone mixtures, establishment fertilization regimes, putting green age, and soil depth, were analyzed. The study in Chapter 3 used DRIFT technique in the near-infrared region (NIR) (4000-10000 cm^{-1}) and mid-infrared region (MIR) (600-4000 cm^{-1}) in conjunction with partial least square regression to analyze chemical properties of sand-based turf soil. The adequacy of calibration and accuracy of prediction using DRIFT in MIR and NIR region for analyzing soil chemical properties were evaluated.

CHAPTER 1. LITERATURE REVIEW

Soil Organic Matter and its Effects in Sand-based Turfgrass Rootzone

Soil organic matter (SOM) is vital in turf management. Many soil properties and functions, for example, soil structure, aeration, water infiltration/retention, thermal conductivity, nutrient availability, and sorption/desorption of chemicals, are influenced by SOM. In a sand-based turfgrass rootzone, SOM is mainly derived from two sources: 1) initial input of organic amendments (e.g. peat, compost) during rootzone construction; 2) continual input of plant residues from the periodically sloughed roots, stems (stolons /rhizomes) and leaves (Ledeboer and Skogley, 1967; Riem Vis, 1981). The fibrous plant residues produced by turfgrass form visible and definable organic layers in the upper rootzone profile and above the soil surface, and are specifically termed as thatch and mat.

Thatch and Mat

The definition of thatch/mat and how to perceive the definition has been a controversial issue for turf managers and researchers. A widely recognized definition of thatch was proposed by Beard (1973) as "a layer of tightly intermingled living and dead stems and turfgrass roots that developed above the soil surface". However, Turgeon (1991) pointed out that thatch was categorized as part of the soil residual biomass which belonged to the "non-living" part of soil biomass, and therefore, "living tissues" needed to be excluded from the definition or recognition of thatch from a more scientific point of view. Other researchers have also proposed the concept of fibrous thatch and spongy thatch to describe and distinguish thatch under dry or wet soil conditions accordingly (Shildrick, 1985).

Thatch is formed from undecayed or partially decayed roots, shoots, stems and leaves. The major component of thatch is lignin, cellulose, and hemicellulose because other constituents of plant tissues such as sugar, starch, and protein are less abundant and are readily decomposed (Couillard and Turgeon, 1997). Plant tissues with higher lignin content are more resistant to decomposition than tissues with lower lignin content because of the recalcitrant nature of lignin and its ability to physically occlude other constituents from microorganism attacks (Crawford, 1981). As a result, sloughed leaves and clippings are readily decomposed (Ledeboer and Skogley, 1967). Decomposition of leaf and stem tissue normally exceeds root and could be twice as fast as that of root tissue (Duble and Weaver, 1974; Soper et al., 1988); and within an organ, vascular strands are more resistant to decomposition than other tissues (Ledeboer and Skogley, 1967).

Mat was defined by Beard (1973) as the "organic layer buried and/or intermixed with soil and become part of the soil profile from partially decayed thatch". There can be minor mineral components in the thatch layer. But thatch is otherwise called mat when a significant amount of soil is incorporated into it. Mat is commonly found on golf putting greens with topdressing; however, deposition of soil in thatch also may be caused by other mechanisms such as earthworm activities (Turgeon, 1991).

Causes of Excessive Accumulation of Organic Matter

When the input of plant residues exceeds the rate of decomposition, thatch/mat accumulation occurs above or in the upper profile of turfgrass rootzone (Beard, 1973). Rate of production of plant materials is essentially determined by grass species and cultivars (Shearman et al., 1980; Stier and Hollman, 2003). Vigorous species/cultivars with extensive lateral stem/root systems are prone to produce a thick thatch layer. Golf putting greens established with creeping bentgrass or bermudagrass therefore tend to have thatch problems. Thatching tendency is also positively correlated to the total cell-wall content, especially lignin content of grass species (Duble and Weaver, 1974; Shearman et al., 1986). In addition, environmental factors, such as sunlight condition, and management practices such as irrigation regime, mowing height, nitrogen rate, and nitrogen sources also contribute to excessive production of plant residues.

Decomposition of plant residues is mediated by soil microorganisms. Rate of decomposition is essentially determined by the quality of organic substrate and abundance of soil microbes. Plant residues with C:N ratio in the range of 25:1 to 30:1 are favorable for microbial decomposition (Beard, 1973). Abundance of soil microbes, especially soil bacteria, is the key factor in controlling the decomposition of thatch/mat. Sand-based rootzone itself is an unfavorable environment for colonization of microbes due to lack of organic substrate. Incorporation of soil into thatch can improve the accessibility of microbes and thus, improve thatch decomposition (Sartain and Volk, 1984).

Soil and environmental conditions, such as good aeration, optimal temperature, moisture, and slightly acidic to neutral pH (6.5-8.5) that favor microbial activity decrease thatch accumulation (Beard, 1973; Turgeon, 1991). On the contrary, extreme acidic/alkaline conditions and poor aeration that suppress microbial activity increase thatch accumulation. Generally, cool and humid geographical regions are unfavorable for microbial activities and therefore are more prone to have excessive thatch/mat accumulation (Carrow, 2004a). Moreover, pesticide application could also affect thatch/mat accumulation by diminishing populations of soil microbes (Meinhold et al., 1973). Once excessive organic matter accumulation occurs in turfgrass rootzone, the resulting low level of oxygen could cause reduced microbial activity, more surface-rooting, and subsequently even more accumulation (Carrow, 2004b).

Overall Changes of Soil Organic Matter in Time and Space

For most sand-based putting green rootzones, SOM content might 1) reach equilibrium between production and decomposition and remain in the range of 2-4% by weight; 2) reach equilibrium and weigh less than 2% due to higher rate of decomposition; or 3) accumulate to a higher level (larger than 4%) due to insufficient decomposition rates (Carrow et al., 2001). In most cases, especially in cool and humid regions where net production exceeds microbial decomposition, SOM accumulation near the rootzone surface of sand-based turf seems to be unavoidable even under regular management practices (Carrow et al., 2001). A survey of SOM dynamics on 16 golf course putting greens showed that SOM concentration increased under regular aeration and topdressing treatments, and that the equilibrium between decomposition and production was reached in 45 years with SOM concentration increasing from 0.6% to 3.9% (Qian and Follett, 2002).

There could be a rapid influx of diverse microbial communities and populations within the first year of a newly constructed sand-based putting green; it tends to stabilize in the following 2 to 3 years (Bigelow et al., 2002). Over time, microbial populations in the rootzone increase along with increasing amount of organic substrates. Kerek et al. (2002) investigated 47 putting greens from 3 to 25 years old and found that microbial biomass (MB) increased linearly with age of putting greens. The portion of total soil MB associated with particulate organic matter (POM) increased significantly from 25.6% for an 8-yr-old green to 77.8% for a 28-yr-old green while MB in the mineral fraction remained constant with age. The author thus speculated that humus accumulation within POM rendered both POM and associated MB more resistant to degradation. Shi et al. (2006) observed that soil enzyme activities increased along with increasing microbial biomass C and soil organic C as putting green aged.

As sand-based putting greens mature, greater amounts of humic substances and higher degrees of humification of SOM in the rootzone profile can be observed. Kerek et al. (2002) reported that C in fulvic acid and humic acid increased with increasing putting green age. Kerek et al. (2003) also found that C and N bonded in humic acid increased significantly as green aged and C/N ratios decreased from 21.0 to 9.3 in the study of 11 golf putting greens aged from 4 to 28 years old. In the study by Shi et al. (2006), results of infrared spectroscopy suggested that relative to polysaccharides, aliphatic and carboxylic compounds increased with putting green age, which indicated a greater degree of humification and oxidation of SOM.

Limited studies have investigated the spatial distribution of SOM in sand-based turfgrass rootzone. Baker et al. (1999) observed an increase in SOM content in the rootzone of 18 putting greens four years after establishment. The main concentration of SOM was located in the upper 20 mm of the rootzone area and SOM content decreased with soil depth. Qian et al. (2009) noted that deep-rooted grasses sequestered greater amount of soil organic C in the 10 to 20 cm depth of turf soil profile than shallow-rooted grasses. Glasgow et al. (2005) in a survey investigating SOM levels from a range of sand-based putting greens in New Zealand reported that the buildup of SOM in the surface 20 mm was faster than in the lower depth, and a threshold level of SOM could be reached there in a year or two. Similar results was reported by Goodman (2009) indicating that SOM accumulated faster in the top 2.54 cm and a threshold of 4% could be reached in five years. It should also be noted that in sand-based rootzones, leaching of dissolved SOM might cause the redistribution of SOM in the profile (Skjemstad et al., 1998).

Effects of Soil Organic Matter on Turf Quality and its Management

Soil organic matter plays an important role in modifying soil physical, chemical, and biological properties, which in turn, modify the aeration, water and nutrient status in the rizhosphere. The effect of thatch/mat on soil properties depends on the quantity and quality of thatch/mat; whether it is fibrous or amorphous humic substances; whether it is in recalcitrant or labile; and whether it is in sand-based or soil-based rootzones (Carrow, 2004a; Shildrick, 1985; Turgeon, 1991).

Aeration. In soil-based turfgrass rootzone, extracellular polysaccharide produced by soil microbes during the decomposition of plant residues improves soil structure by serving as adhesive agent in soil aggregation (Turgeon, 1991). Formation of soil aggregation contributes to more macro-pores and better aeration. In sand-based turfgrass rootzone, structured and fibrous thatch layer on the soil surface is characterized with more macro-pores than the underlying soil (Hurto et al., 1980). However, spongy thatch under wet conditions or a mat layer with abundant colloidal humus tends to block macro-pores in the rootzone surface causing reduced oxygen diffusion rate (Carrow, 2004a). Low aeration combined with heat stress is detrimental to turfgrass root and shoot growth and causes declination in turf quality during summer months (Huang et al., 1998; Carrow, 2004a). Anaerobic microbial activity induced by low oxygen is also the cause of the "black layer" problem in sand-based turfgrass rootzone (Hodges, 1992). Formation of black layers will in turn bring more water and aeration stress.

Water status. In the intermingled mat layer, blocked macro-pores causes reduced water infiltration, saturated hydraulic conductivity, and excessive water retention (Baker et al., 1999; Carrow, 2004a; Glasgow et al., 2005). McCoy (1992) found that SOM content alone cannot explain pore volume distribution of sandy rootzone, and that fiber content of organic amendments modified plant available water status by affecting pore size distribution. Moreover, formation of organic acid (fulvic acid) during decomposition of SOM by fungi could cause hydrophobic conditions by coating sand particles near the rootzone surface (Karnok et al., 1993).

Nutrient status. Thatch/mat plays an important role in soil C and N sequestration (Qian et al., 2009). Relative to the recalcitrant part, other part of SOM that is readily decomposable could supply nutrients (N, P, K and S) through mineralization. Kerek et al. (2003) investigated the C and N content among fractions of soil humus and found that mobile humic acid, which was younger in age, represented a larger proportion of SOM and was richer in N than calcium-bound humic acid. The author thus concluded that labile SOM was an important N source that could supply N to turfgrass through mineralization in established putting greens.

Formation of humic substances contributes to greater cation exchange capacity (CEC) and nutrient retention (Turgeon, 1991). McClelan et al. (2007) reported that CEC and nutrient levels increased with putting green age, which was likely attributed to the formation of the mat layer. Soil organic matter also indirectly affects nutrient status of turfgrass rootzone by influencing fertilization efficiency (Nelson et al., 1980). For instance, thatch/mat was found to reduce N leaching in turf and greater volatilization of urea-N was observed in the thatch layer (Nelson et al., 1980; Engelsjord et al., 2004).

Other effects. A limited layer of thatch/mat in sand-based turfgrass rootzone is normally beneficial because it provides resiliency and wear tolerance, and insulates the soil against temperature extremes (Beard, 1973). Soil organic matter also can bind and deactivate chemicals and reduces chemical effectiveness (Branham and Wehner 1985; Hixson et al., 2009). Older turf with higher SOM was found to bind more pesticide than the younger ones (Hixson et al., 2009). A series of secondary problems such as increased disease susceptibility and insect problems may also occur to thatch soils (Carrow, 2004b).

Management of excessive thatch/mat. Researchers have extensively investigated mechanical, cultural and biological practices alone or in combination to prevent or mitigate excessive surface SOM accumulation in golf putting greens (Berndt et al., 1990; Callahan et al., 1998; McCarty et al., 2007). Mechanical practices such as vertical mowing, core cultivation, grooming, and topdressing are commonly used for alleviating thatch/mat development in sand-based turfgrass rootzone (Dunn et al., 1981; Carrow et al., 1987; Murphy 1993; Callahan et al., 1998). Topdressing dilutes surface SOM and has become the most important routine management practices for thatch control for sand-based putting green (White and Dickens, 1984).

Analysis of Soil Properties Using Vibrational Infrared Spectroscopy

Conventional soil analyses are often time and labor consuming, costly, and destructive. Spectroscopic techniques provide alternative tools to characterize soil constituents and determine soil properties in a more efficient way (Swift, 1996). Among various spectroscopic techniques, vibrational infrared (IR) spectroscopy, in particular, has the advantages of being information-rich to both organic and inorganic materials, and sensitive to both solid and liquid components in a soil matrix (Janik et al., 1998; Johnston and Aochi, 1996). The advent of Fourier transform infrared (FTIR) spectrometer further expanded the application of vibrational IR spectroscopy in soil analysis. As a promising surrogate to conventional soil analysis, vibrational IR spectroscopy is an analytical tool featured with rapid analysis, low cost, and versatility (Janik et al., 1998).

Analytical Principles

The basis of vibrational IR spectroscopy analysis is the transition of energy levels of bonded atoms within molecules (Coleman, 1993). When the frequency of IR radiation matches the transition energy of a particular vibrational mode of bonded atoms that is IR-active, the radiation is then absorbed and an absorption spectrum is yielded (Coleman, 1993). The peak position of a spectrum is signature of the molecular structure and absorption intensity is proportional to the concentration of the molecule according to Beer' Law (Griffiths and de Haseth, 1986). Complex polymers may exhibit several featured peaks associated with submolecular groups of atoms (functional groups) and vibrational modes.

Infrared spectra from 10 to 10000 cm^{-1} is subdivided into near-infrared (NIR) region (4000-10000 cm^{-1}), mid-infrared (MIR) region (400-4000 cm^{-1}) and far-infrared (FIR) region (10-400 cm^{-1}) (Johnston and Aochi, 1996). Soil analysis uses both the NIR and MIR region, and the FIR region is complementary to the MIR region (Johnston and Aochi, 1996). The MIR region is dominated by fundamental vibrational modes, and most soil minerals and functional groups of SOM have characteristic absorption bands in this region (Coleman, 1993; Reeves et al., 2001). The NIR region is dominated by overtones and combinations of fundamental vibrational modes with only bands due to C–H, N–H and O–H groups (Malley et al., 2004).

Assignment of diagnostic absorption bands of soil minerals and functional groups of SOM has been extensively studied and documented. For instance, quartz has strong characteristic absorption bands near 1100-1000 cm^{-1} due to O–Si–O stretching; carboxylic acid has characteristic absorption bands near 1750-1630 cm^{-1} due to C=O stretching, and near 3500-3200 cm^{-1} due to O–H stretching (Johnston and Aochi, 1996). Components can be identified by examining the vibrational spectra of a soil material for the presence of those diagnostic absorption bands.

Vibrational IR spectroscopy has been applied in many areas of soil analysis such as identification of soil components, characterization of humus substances, determination of soil properties, and remote sensing (Swift, 1996; Janik et al., 1998; Malley et al., 2004). In general, soil constituents have less distinct peaks and are low in absorption in the NIR region; while on the contrary, stronger absorption and more intensified peaks exist in the MIR region (Reeves et al., 2001; Malley et al., 2004). Therefore, the NIR spectroscopy

(NIRS) is mostly applied in quantitative studies while the MIR spectroscopy (MIRS) is more of a qualitative tool over the past three decades. But in recent years, there has been arising interest in quantitative analysis of soils using MIRS with the development of instrumentations and sampling techniques.

Analytical Tools

Early NIRS and MIRS analysis of soil was conducted using dispersive IR spectrometer, which was later replaced by FTIR spectrometer (Griffiths and de Haseth, 1986). Innovation of the key optical component of interferometer makes FTIR spectrometer superior to dispersive IR spectrometer in sensitivity, resolution, spectral precision, and frequency reproducibility (Johnston and Aochi, 1996). Along with the development of FTIR, broader sampling techniques such as attenuated reflection, diffuse reflection (DR), reflection absorption, and photoacoustic become available for soil studies in addition to the traditional transmission spectroscopy (Griffiths and de Haseth, 1986; Johnston and Aochi, 1996). Choice of sampling techniques generally depends on the type and nature of a soil sample (Culler, 1993).

Of those sampling techniques, transmission IR spectroscopy using a potassium bromide (KBr) disc and FTIR adapted with DR (DRIFT) are powerful tools for analysis of particulate solids and therefore have been the dominant IR techniques for analysis of soil matrix (Culler et al., 1993; Janik et al., 1998). A study by Niemeyer et al. (1992) comparing the two techniques reported that the DRIFT technique showed several advantages over transmission IR spectroscopy in soil analysis including: 1) simple sample preparation; 2) reduced water interference; 3) higher resolution; 4) higher sensitivity to species of low concentration; and 5) enhancement of some weak peaks.

The basic principle of DR sampling technique is that incident radiation on a powder sample being scattered is collected and directed to the detector (Culler, 1993). The DRIFT technique suffers from two major drawbacks: absence of bands caused by samples with high absorptions and distortions, and inversions of bands caused by specular components (Culler, 1993). Thus, for DRIFT to overcome the distortions, samples have to be diluted with non-absorbing salts such as KBr. In addition, Beer's Law for DRIFT is replaced by Kubelka-Munk (KM) theory to correct for the nonlinearity in quantitative studies (Culler, 1993). However, recent studies have demonstrated that KBr dilution and conversion of KM function is unnecessary when multivariate regression techniques are used in quantitative studies (Janik et al., 1998; Reeves et al., 2001).

Qualification of Soil Organic Matter

Compared to soil minerals, SOM is more complex with various proportions of functional groups such as –COOH (carboxyl) and –C=C– (aromatic), each with its characteristic absorption peaks. It is feasible to discriminate SOM by examining the characteristic absorption peaks of different functional groups (Swift, 1996). For instance, ratios between aliphatic and aromatic peaks as well as ratios between O-containing peaks and C, H and N- containing peaks have been investigated as indicators of the reactivity of humic substances (Niemeyer et al., 1992; Wander and Traina, 1996).

Mid infrared spectroscopy performs better in detecting subtle differences in composition of SOM than NIRS (Reeves et al., 2001). The DRIFT-MIR technique was shown to be a sensitive tool to fingerprint SOM from difference sources (Arz et al., 2008) and to characterize peat, compost, and physically/chemically extracted SOM fractions in terms of their degrees of humification (Niemeyer et al., 1992; Wander and Traina, 1996). Other studies characterized SOM through spectra of the whole soil matrix (Ellerbrock et al., 1999). However, peaks due to unknown components make it difficult to extract information of SOM from the whole soil spectra (Janik et al., 1998). In addition, peaks indicating functional groups of SOM could be masked or interfered by soil minerals, especially when the soil is low in SOM content (Skjemstad et al., 1998). Subtraction of mineral spectra is one of the methods to overcome this interference only when isolated bands can be found (Griffiths and de Haseth, 1986; Janik and Skjemstad, 1995; Ellerbrock et al., 1999).

Quantitative Analysis of Soil Properties

Principles. Soil components or functional groups that are responsible for the property of interest have characteristic absorption bands in the MIR and NIR region. Through multivariance regression analysis, empirical calibration models that relate IR spectral intensities at different wavelengths with the analyte concentrations determined by laboratory-based methods (reference values) are built. Then, properties of unknown samples can be predicted using those established calibration models (Westerhaus et al., 2004).

Multivariance regression methods including stepwise multiple linear regressions (SMLR), principle components regression (PCR), partial least squares regression (PLSR), regression trees, and neutral networks have been used to establish calibration models in IR analysis (Westerhaus et al., 2004). The most frequently used statistical method has been PLSR which calculate scores to indicate each factor's contribution to a spectrum and regress on the scores against the reference values (Westerhaus et al., 2004). Partial least squares regression was found to produce better prediction accuracies over PCR and SMLR in NIRS and MIRS analysis (Bolster et al., 1996; Vasques et al., 2008).

Comparison of NIRS and MIRS. Near infrared spectroscopy and MIRS combined with multivariance regression analysis have been widely investigated for their ability in quantifying soil physical, chemical and biological properties such as SOM, total C, organic C, carbonate, total N, mineralizable N, biomass N, moisture content, pH, electrical conductivity (EC), particle size fractions, cation exchange capacity (CEC), exchangeable cations, and plant available nutrients (Ben-Dor and Banin, 1995; Chang et al., 2001; Reeves et al., 2001; Janik et al., 2009; Minasny et al., 2009). Both MIRS and NIRS are confirmed capable to predict fundamental soil properties such as clay, total C and total N, as well as those secondary soil properties that correlate well with the fundamental soil constituents such as CEC.

Mid infrared spectroscopy was found to be at least equal or even superior to NIRS in predicting soil properties (Reeves et al., 2001; McCarty et al., 2002; Madari et al., 2006; Minasny and McBratney, 2008). For instance, MIRS was reported to have greater accuracy over NIRS in predicting soil pH (Reeves et al., 2001). Both McCarty et al. (2002) and Madari et al. (2006) reported that MIRS outperformed NIRS in soil C prediction and it was speculated that MIR region contained more information related to soil C. Dilution of sample is normally deemed as necessary in MIRS analysis because of the nonlinearities due to strong absorptions; however, successful predictions by MIRS-PLSR or -PCR analysis using samples without dilution were reported in recent studies (Reeves et al., 2001).

Quantification of SOM and total organic C. Soil organic matter and total organic C content have been predicted successfully from spectra of the whole soil matrix using NIRS and MIRS. Couillard et al. (1997) achieved $R^2 = 0.90$ on predicting SOM content of undisturbed turf soils collected from golf putting greens using NIRS-PLSR analysis. Vasques et al. (2008) estimated total organic C and four organic C fractions (recalcitrant C, hydrolyzable C, hot-water-soluble, and mineralizable C) using DR- visible-NIRS and multivariate regression analysis. Total organic C was estimated with the highest accuracy ($R^2 = 0.86$) followed by the recalcitrant C ($R^2 = 0.82$), while the less stable hydrolyzable C was found to be difficult to model in their study ($R^2 = 0.40$). In another study of soil C by McCarty et al. (2002), organic C (without acid pretreatment to remove carbonate) was predicted with $R^2 = 0.94$ using MIRS and with $R^2 = 0.82$ using NIRS. In this study, a significantly better prediction for total organic C was obtained by removing soil carbonate.

Although accurate predictions of SOM and total organic C by MIRS and NIRS have been reported, there are cases where poor predictions were produced. For instance, Working on soils collected from Israel, Ben-Dor and Banin (1995) used DR-NIRS analysis to gain $R^2 = 0.69$ for modeling and $R^2 = 0.55$ for prediction. The author speculated that the poor calibration and prediction performance was possibly attributed to the fact that organic matter in the calibration and validation sets differed greatly in decomposition stage and functional groups. Many other studies have demonstrated that in quantitative analysis by

MIRS and NIRS, type-specific or homogenous soil sample sets could result in less biased prediction, and less influence of mineral component (Morra et al., 1991; Janik et al., 2009; Minasny et al., 2009).

Quantification of total N. Overall, total N has been accurately predicted from spectra of the whole soil matrix by NIRS and MIRS. Madari et al. (2006) predicted total N in bulk soil samples and eight aggregate fractions in Ferralsols using both DRIFT-NIRS and -MIRS in combination with PLSR analysis. Total N was predicted with $R^2 > 0.96$ using either method. Similar precision for total N was obtained by Reeves et al. (2001) with $R^2 > 0.95$ using MIRS in predicting soils collected from two locations in Maryland. Chang et al. (2001) achieved $R^2 = 0.85$ in predicting total N of soils collected from 448 sites in major land resource areas using NIRS-PCR. As noted earlier, calibration models for total N using one soil type might not perform well on other soil types. For instance, Minasny et al. (2009) reported that the model for total N ($R^2 = 0.74$) generated using soil samples from one location resulted in poor prediction ($R^2 = 0.59$) of soil samples from a different location.

Quantification of CEC, pH and EC. Cation exchange capacity, pH and EC are considered secondary soil properties. Only if these properties correlate well with solid constituents or soil solution concentrations that are in equilibrium with the solid constituents, are they then predictable (Minasny et al., 2009).

In general, CEC can be predicted by NIRS and MIRS with moderate to good accuracy (Janik et al., 1998; Malley et al., 2004). The accuracy of CEC predictions depends on the sensitivity of MIRS and NIRS for the type and content of clay and organic matter because of the high correlation between CEC and those components (Janik et al., 1998). Ellerbrock et al. (1999) reported a high correlation between soil CEC and the intensity of carboxyl band of SOM measured by MIRS. In the study by Ben-Dor and Banin (1995), CEC was calibrated with $R^2 = 0.82$ and predicted with $R^2 = 0.64$ using NIRS. Chang et al. (2001) predicted CEC using NIRS-PCR resulted in $R^2 = 0.81$.

The accuracy of pH predictions by NIRS is only judged to be acceptable because hydrogen ions are not primary absorbers in the NIR region (Malley et al., 2004). For instance, Chang et al. (2001) predicted pH with $R^2 = 0.55$ using NIRS-PCR analysis. Couillard et al. (1997) predicted pH with R^2 in the range of 0.80-0.90 using NIRS-PLS on undisturbed turf soil. Results of Reeves et al. (2001) showed that MIRS provided a significantly better prediction of pH ($R^2 = 0.94$) than NIRS ($R^2 = 0.87$) and the author therefore speculated that minerals responsible for pH did not absorb in the NIR region but did in the MIR region.

Electrical conductivity is a measurement of total soluble salts in the soil. A review of EC prediction by NIRS noted that most studies gave $R^2 < 0.7$ (Malley et al., 2004). Few studies by far predicted EC by MIRS. Minasny et al. (2009) found that it was possible to develop accurate calibration models for EC using MIRS; however, the model failed to be validated using soils from a different location ($R^2 = 0.08$). According to a review of MIRS by Janik et al. (1998), EC was among those soil properties whose predictions were less reliable because they related to chemistry of soil solution and depended more on transient criteria.

Application in the Analysis of Sand-based Turf Soil.

To date, limited research utilizes vibrational IR spectroscopy in characterizing sand-based turf soil. Early attempt of using NIRS technique for analyzing sand-based turf soil was given by Couillard et al. (1997). The author predicted soil properties of a 10-yr-old creeping bentgrass putting green using NIRS-PLSR analysis. Among the selected soil properties, SOM content, particle size fractions, K, and pH were predicted with sufficient accuracy. However, PLSR and "leave-one-out" cross validation was used as evaluation of prediction in the study by Couillard et al. (1997) and a separate validation process was missing. More recently, Shi et al. (2006) utilized FTIR-MIR to characterize chemically separated SOM fractions from sand-based turf soil and detected the correlations between featured functional groups of SOM and the age of turf. Using DRIFT-MIR or -NIR technique for determination of chemical properties of sand-based turf soils has not been investigated.

References

Arz, R.R.E., S.J. Chapman, A.H. Jean Robertson, J.M. Potts, F. Laggoun-Defarge, S. Gogo, L. Comont, J.R. Disnar, and A.J. Francez. 2008. FTIR spectroscopy can be used as a screening tool for organic matter quality in regenerating cutover peatlands. Soil Biol. Biochem. 40:515-527.

Baker, S.W., S.J. Mooney, and A. Cook. 1999. The effects of sand type and rootzone amendments on golf green performance. I. Soil properties. J. Turfgrass Sci. 75:2-17.

Beard, J.B. 1973. Turfgrass science and culture. Prentice Hall, Englewood Cliff, NJ.

Ben-Dor, E., and A. Banin. 1995. Near infrared analysis as a method to simultaneously evaluate several soil properties. Soil Sci. Soc. Am. J. 59:364-372.

Berndt, W.L., P.E. Rieke, and J.M.Jr. Vargas. 1990. Kentucky bluegrass thatch characteristics following application of bio-organic materials. HortScience 25:412-414.

Bigelow, C.A., D.C. Bowman, and A.G. Wollum, II. 2002. Characterization of soil microbial population dynamics in newly constructed sand-based rootzones. Crop Sci. 42:1611-1614.

Bolster, K.L., M.E. Martin, and J.D. Aber. 1996. Determination of carbon fraction and nitrogen concentration in tree foliage by near infrared reflectance: a comparison of statistical methods. Can. J. For. Res. 26:590-600.

Branham, B.E., and D.J. Wehner. 1985. The fate of diazinon applied to thatched turf. Agron. J. 77:101-104.

Callahan, L.M., W.L. Sanders, J.M. Parham, C.A. Harper, L.D. Lester, and E.R. Mcdonald. 1998. Cultural and chemical controls of thatch and their influence on rootzone nutrients in a bentgrass green. Crop Sci. 38:181-187.

Carrow, R.N. 2004a. Surface organic matter in bentgrass greens. USGA Green Sect. Rec. 42:11-15.

Carrow, R.N. 2004b. Surface organic matter in bermudagrass greens: A primary stress ? Golf Course Manage. 72:102-105.

Carrow, R.N., B.J. Johnson, and R.E. Burns. 1987. Thatch and quality of Tifway bermudagrass turf in relation to fertility and cultivation. Agron. J. 79:524-530.

Carrow, R.N., D.V. Waddington, and P.E. Rieke. 2001. Turfgrass soil fertility and chemical problems: Assessment and management. Ann Arbor Press, Chelsea, MI.

Chang, C.W., D.A. Laird, M.J. Mausbach, and C.J. Hurburgh. 2001. Near infrared reflectance spectroscopy-principal component regression analyses of soil properties. Soil Sci. Soc. Am. J. 65:480-490.

Coleman, P.B. 1993. Theoretical considerations. p. 1-10. *In* P.B. Coleman (ed.) Practical sampling techniques for infrared analysis. CRC Press, Boca Raton, FL.

Couillard, A., and A.J. Turgeon. 1997. Composition of turfgrass thatch. Commun. Soil Sci. Plant Anal. 28:1199-1207.

Couillard, A., A.J. Turgeon., J.S. Shenk, and M.O. Westerhaus. 1997. Near infrared reflectance spectroscopy for analysis of turf soil profiles. Crop Sci. 37:1554-1559.

Crawford, R.L. 1981. Lignin biodegradation and transformation. John Wiley & Sons, NY.

Culler, S.R. 1993. Diffuse reflectance infrared spectroscopy: Sampling techniques for qualitative/quantitative analysis of solids. p. 93-105. *In* P.B. Coleman (ed.) Practical sampling techniques for infrared analysis. CRC Press, Boca Raton, FL.

Duble, R.L., and R.W. Weaver. 1974. Thatch decomposition in bermudagrass turf. Int. Turfgrass Soc. Res. J. p. 445-451.

Dunn, J.H., K.M. Sheffer, and P.M. Halisky. 1981. Thatch and quality of Meyer zoysia in relation to management. Agron. J. 73:949-952.

Ellerbrock, R.H., A. Hohn, and H.H. Gerke. 1999. Characterization of soil organic matter from a sandy soil in relation to management practice using FT-IR spectroscopy. Plant Soil 213:55-61.

Engelsjord, M.E., B.E. Branham, and B.P. Horgan. 2004. The fate of nitrogen-15 ammonium sulfate applied to Kentucky bluegrass and perennial ryegrass turfs. Crop Sci. 44:1341-1347.

Glasgow, A., R. Gibbs, K.W. McAuliffe, and C. Liu. 2005. An investigation of organic matter levels in New Zealand golf greens. Int. Turfgrass Soc. Res. J. 10:1078-1084.

Goodman, H.D. 2009. Organic matter accumulation beneath maintained turfgrass systems. MS Thesis. North Carolina State Univ.

Griffiths, P.R., and J.A. de Haseth. 1986. Fourier transform infrared spectroscopy. Wiley and Sons, NY.

Hixson, A.C., W. Shi, J.B. Weber, F.H. Yelverton, and T.W. Rufty. 2009. Soil organic matter changes in turfgrass systems affect binding and biodegradation of simazine. Crop Sci. 49:1481-1488.

Hodges, C.F. 1992. Interaction of cyanobacteria and sulfate-reducing bacteria in subsurface black layer formation in high-sand content golf greens. Soil Biol. Biochem. 24:15-20.

Huang, B., X. Liu, and J.D. Fry. 1998. Effects of high temperature and poor soil aeration on root growth and viability of creeping bentgrass. Crop Sci. 38:1618-1622.

Hurto, K.A., A.J. Turgeon, and L.A. Spomer. 1980. Physical characteristics of thatch as a turfgrass growing medium. Agron. J. 72:165-7.

Janik, L.J., S.T. Forrester, and A. Rawson. 2009. The prediction of soil chemical and physical properties from mid-infrared spectroscopy and combined partial least-squares regression and neural networks analysis. Chem. and Intell. Labor. Syst. 97:179-188.

Janik, L.J., R.G. Merry, and J.O. Skjemstand. 1998. Can mid infrared diffuse reflectance analysis replace soil extractions ? Austr. J. Exp. Agric. 38:681-696.

Janik, L.J., and J.O. Skjemstad. 1995. Characterization and analysis of soils using mid-infrared partial least-squares: II.Correlations with some laboratory data. Aust. J. Soil Res. 33:637-650.

Johnston, C.T., and Y.O. Aochi. 1996. Fourier transform infrared and Raman spectroscopy. p. 269-321. *In* D.L. Sparks (ed.) Methods of soil analysis. Part 3. SSSA Book Ser. No. 5. SSSA, Madison, WI.

Karnok, K.A. [J.], E.J. Rowland, and K.H. Tan. 1993. High pH treatments and the alleviation of soil hydrophobicity on golf greens. Agron. J. 85:983-986.

Kerek, M., R.A. Drijber, and R.E. Gaussoin. 2003. Labile soil organic matter as a potential nitrogen source in golf greens. Soil Biol. Biochem. 35:1643-1649.

Kerek, M., R.A. Drijber, W.L. Powers, R.C. Shearman, and R.E. Gaussoin. 2002. Accumulation of microbial biomass within particulate organic matter of aging golf greens. Agron. J. 94:455-461.

Ledeboer, F.B., and C.R. Skogley. 1967. Investigations into the nature of thatch and methods for its decomposition. Agron. J. 59:320-324.

Madari, B.E., J.B., Reeves III., P. Machado, E. Torres, C.M. Guimaraes, and G.M. McCarty. 2006. Mid- and near-infrared spectroscopic determination of soil compositional parameters and structural indices in tow Ferralsols. Geoderma 136:245-259.

Malley, D.F., P.D. Martin, and E. Ben-Dor. 2004. Application in analysis of soils. p. 729-784. *In* C.A. Roberts et al. (ed.) Near-infrared spectroscopy in agriculture. Agron. 44. ASA, CSSA, and SSSA, Madison, WI.

McCarty, G.W., J.B. Reeves, V.B. Reeves, R.F. Follett, and J.M. Kimble. 2002. Mid-infrared and near-infrared diffuse reflectance spectroscopy for soil carbon measurement. Soil Sci. Soc. Am. J. 66:640-646.

McCarty, L.B., M.F. Gregg, and J.E. Toler. 2007. Thatch and mat management in an established creeping bentgrass golf green. Agron. J. 99:1530-1537.

McClellan, Ty.A., R.C. Shearman, R.E. Gaussoin, M. Mamo, C.S. Wortmann, G.L. Horst, and D.B. Marx. 2007. Nutrient and chemical characterization of aging golf course putting greens: establishment and rootzone mixture treatment effects. Crop Sci. 47:193-199.

McCoy, E.L. 1992. Quantitative physical assessment of organic materials used in sports turf rootzone mixes. Agron. J. 84:375-381.

Meinhold, V.H., R.L. Duble, R.W. Weaver, and E.C. Holt. 1973. Thatch accumulation in bermudagrass turf in relation to management. Agron. J. 65:833-835.

Minasny, B., and A.B. McBratney. 2008. Regression rules as a tool for predicting soil properties from infrared reflectance spectroscopy. Chemom. Intell. Lab. Syst. 94:72-79.

Minasny, B., G. Tranter, A.B. McBratney, D.M. Brough, and B.W. Murphy. 2009. Regional transferability of mid-infrared diffuse reflectance spectroscopic prediction for soil chemical properties. Geoderma 153:155-162.

Morra, M.J., M.H. Hall, and L.L. Freeborn. 1991. Carbon and nitrogen analysis of soil fractions using near infrared reflectance spectroscopy. Soil Sci. Soc. Am. J. 55:288-291.

Murphy, J.A., P.E. Rieke, and A.E. Erickson. 1993. Core cultivation of a putting green with hollow and solid times. Agron. J. 85:1-9.

Nelson, K.E., A.J. Turgeon, and J.R. Street. 1980. Thatch influence on mobility and transformation of nitrogen carriers applied to turf. Agron. J. 72:487-492.

Niemeyer, J., J. Chen, and J.M. Bollag. 1992. Characterization of humic acids, composts, and peat by diffuse reflectance Fourier-transform infrared spectroscopy. Soil Sci. Soc. Am. J. 56:135-140.

Qian, Y., and R.F. Follett. 2002. Assessing soil carbon sequestration in turfgrass systems using long-term soil testing data. Agron. J. 94:930-935.

Qian, Y., R.F. Follett., and J.M. Kimble. 2009. Soil organic carbon input from urban Turfgrasses. Soil Sci. Soc. Am. J. 74:366-371.

Reeves, III. J.B., G.W. McCarty, and V.B. Reeves. 2001. Mid infrared diffuse reflectance spectroscopy for the quantitative analysis of agricultural soils. J. Agric. Food Chem. 49:766-772.

Riem Vis, F. 1981. Accumulation and decomposition of organic matter under sports turf. Int. Turfgrass Soc. Res. J. 4:201.

Sartain, J.B., and B.G. Volk. 1984. Influence of selected white-rot fungi and topdressings on the composition of thatch components of four turfgrasses. Agron. J. 76:359-362.

Shearman, R.C., B.E. Anderson, D.M. Kopec, and T.P. Riordan. 1986. Thatch accumulation in tall fescue turfs. HortScience 21:1164.

Shearman, R.C., E.J. Kinbacher, and D.H. Steinegger. 1980. Thatch accumulation in Kentucky bluegrass as influenced by cultivar, mowing, and nitrogen. HortScience 15:312-313.

Shi, W., D.B. Dell, and K. Iyyemperumal. 2006. Soil enzyme activities and organic matter composition in a turfgrass chronosequence. Plant Soil 288:285-296.

Shildrick, J.P. 1985. Thatch: A review with special reference to UK golf courses. J. Sports Turf Res. Inst. 61:8-25.

Skjemstad, J.O., L.J. Janic, J.A. Taylor. 1998. Non-living soil organic matter: What we know about it? Aust J. Exp. Agric. 38:667-680.

Soper, D.Z., J.H. Dunn, D.D. Minner, and D.A. Sleper. 1988. Effects of clipping disposal, nitrogen, and growth retardants on thatch and tiller density in Zoysiagrass. Crop Sci. 28:325-328.

Stier, J.C., and A.B. Hollman. 2003. Cultivation and topdressing requirements for thatch management in A and G bentgrasses and creeping bluegrass. HortScience 38:1227-1231.

Swift, R.S. 1996. Organic matter characterization. p. 1011-1069. *In* D.L. Sparks et al. (ed.) Methods of soil analysis. Part 3. SSSA. Book Ser. 5. SSSA, Madison, WI.

Turgeon, A.J. 1991. Turfgrass management, 3rd ed. Prentice Hall, Regents, NJ.

Vasques, G.M., S. Grunwald, and J.O. Sickman. 2008. Modeling of soil organic carbon fractions using visible-near-infrared spectroscopy. Soil Sci. Soc. Am. J. 73:176-184.

Wander, M.M., and S.J. Traina. 1996. Organic matter fractions from organically and conventionally managed soils: II. Characterization of composition. Soil Sci. Soc. Am. J. 60:1087-1094.

Westerhaus, M., J. Workman, Jr., J.B. Reeves III, and H. Mark. 2004. Application in analysis of soils. p. 133-174. *In* C.A. Roberts et al. (ed.) Near-infrared spectroscopy in agriculture. Agron. 44. ASA, CSSA, and SSSA, Madison, WI.

White, R.H., and R. Dickens. 1984. Thatch accumulation in bermudagrass as influenced by cultural practices. Agron. J. 76:19-22.

CHAPTER 2. SOIL CHEMICAL PROPERTIES OF GOLF GREENS OF DIFFERENT ROOTZONE MIXTURES AND FERTILIZATIONS DURING ESTABLISHMENT

Abstract

The temporal and spatial changes of soil chemical properties of sand-based rootzones of putting greens are not well understood. This study was conducted to investigate total organic C and selected chemical properties as influenced by soil depth, putting green age, rootzone mixture and establishment fertilization regime. Four USGA-specified putting greens were constructed in sequential years from 1997 to 2000. Main plot was treated with two types of rootzone mixtures (sand/peat at 80:20 by volume, sand/peat/soil at 80:15:5 by volume) and establishment fertilization regimes (accelerated and controlled). Soil samples were collected when the greens were 6, 7, 8, and 9 years old, and were partitioned to 12 equal layers before analysis. The rootzone mixtures and establishment fertilization regimes had no effect on soil properties saving electrical conductivity (EC), which was higher in sand/peat/soil rootzones. Total organic C, total N, cation exchange capacity (CEC), EC, and potentially mineralizable N (PMN) decreased whereas soil pH increased with soil depth. The initial differences of soil chemical properties disappeared due to topdressing practice over a period of 6 years at the top of the rootzones especially in the 0 to 2 cm layer. The chemical properties of the original rootzone layers are affected by both the age of the putting greens and cultural practices.

Introduction

Soil properties determine turfgrass health and turf quality. Sand or sand/amendment mixtures have been specified for rootzone constructions to alleviate soil compaction and provide sufficient water and nutrient retention, and adequate air and water movement. Various cultural practices also are adopted by turfgrass managers to maintain the optimal physical and chemical conditions in the rootzone over time (White and Dickens, 1984; Rowland et al., 2009). Physical properties of various rootzone mixtures have been extensively studied (Li et al., 2000; Ok et al., 2003; Bigelow et al., 2004) at the time of construction. Ok et al. (2003) investigated the physical and chemical properties of California (100 % sand), USGA (sand/peat at 90:10, v:v), and California-Z (sand/zeolite at 85:15, v:v) rootzones over two years after the construction and concluded that both the order and absolute values of capillary porosity changed over time although the total porosity remained relatively stable.

However, as turf matures, accumulations of a definable layer of organic material on the top of soil profile result in thatch and mat. Thatch is defined as "a layer of tightly intermingled living and dead stems and turfgrass roots that developed above the soil surface" (Beard, 1973). Under thatch, a distinguishable layer of soil with high organic matter content usually exits as a result of soil deposition in the thatch, and this particular layer is called mat. Excessive thatch/mat reduces water infiltration, aeration and renders the grass more vulnerable to diseases and other stresses (Turgeon, 1991; Carrow, 2004).

Little information is available on the long-term effects of construction methods and management practices on the soil properties. McClellan et al. (2007) examined the changes of nutrient levels and chemical properties of USGA-specified putting greens over 7 years from establishment. The results of this study showed that CEC and essential nutrient (except for available K) levels in the depth of 0 to 7.6 cm decreased after the establishment year, but then increased several years later, probably due to mat development with no effects of rootzone mixtures (sand/peat vs sand/peat/soil) observed (McClellan et al., 2007). A follow-up study by McClellan et al. (2009) sampled to different depths from soil surface in three manners: 1) 0 to 7.6 cm and 7.6 to 10 cm; 2) 0 to 2.5 cm, 2.5 to 10 cm, and 10 to 20 cm; 3) mat and original rootzone. Organic matter (OM), CEC, total soluble salts (TSS) and soil nutrients decreased with soil depth whereas pH increased with soil depth (McClellan et al., 2009). It was also observed that by separating the soil into mat layer and original rootzone, soil properties followed the same trend in different depths crossing different green ages (McClellan et al., 2009).

From the work by McClellan et al. (2007) and McCllelan et al. (2009), it seems that soil properties in different layers of the soil profile is affected by the age of putting greens, and different schemes of dividing soil layers results in different interpretations. Therefore, a more detailed investigation on the effects of soil depth on soil properties is needed to understand the aging process of golf putting greens. Furthermore, to better understand organic matter status in the rootzone profile, soil properties such as organic C and total N need to be further investigated.

The objective of this study was to study soil organic C and selected chemical properties as affected by rootzone mixture, fertilizations during the establishment year, putting green age, and soil depth.

Materials and Methods

Soil samples used in this study were collected in June 2006 from four experimental putting greens aged 6, 7, 8, and 9 years old from the University of Nebraska-Lincoln John Seaton Anderson Turfgrass Research Facility located near Mead, NE (41°11' N, lat. 96° 28' W). Within each green, twelve soil cores were collected with one core per plot. The soil cores (0- 7.62 cm) were taken using a 10.2-cm diameter cup cutter, kept cool with ice packs, and transported to North Dakota State University, where each soil core was subdivided into 12 equal cross sections with each section being 0.64-cm thick after the removal of thatch layer. The subsamples were stored in sealed plastic bags at 5°C for later analysis.

The details of construction, establishment, and maintenance of the experimental putting greens were described by McClellan et al. (2007). Briefly, four USGA-specified putting greens were constructed in sequential years from 1997 to 2000. Within each green, two rootzone mixtures (RZM) and two establishment (EST) treatments were arranged in a randomized complete block design with three replications. The two RZMs were sand/sphagnum peat at 80:20 and sand/sphagnum peat/soil at 80:15:5 on volumetric basis. The sand component was calcareous with a pH value of 8.0, and the soil component was Tomek silty clay loam, fine smectitic and mesic Pachic Argiudoll. The two EST treatments were fertilization regimes (Table 1.1). All putting greens were seeded with 'Providence' creeping bentgrass (*Agrostis stolonifera* L.) at 7.5 g m $^{-2}$ in May of specified years.

The experimental greens were mowed at 0.32 cm and irrigated at 80% of the potential evapotranspiration. Other management practices included: 1) sand topdressing every 10 to 14 day (based on turfgrass growth rate) at a rate of 4.9 × 10^{-4} m^3 m^{-2} combined with vertical mowing; and 2) sand topdressing twice annually (spring and fall) at 1.96 × 10^{-3} m^3 m^{-2} combined with core cultivation with 1.6-cm o.d. hollow tines to 7.6-cm depth at 5-cm spacing. After the establishment year, an annual fertilization program was applied to all plots at 29, 19.5, and 29 g m^{-2} of N, P, and K, respectively, with liquid fertilizers. Simulated traffic was applied three times weekly using a device that has golf shoe spikes attached to the rollers of a modified greens mower.

Table 1.1. Two levels of the fertilization factor in the main plot treatments during the establishment year adapted from McClellan et al. (2007).

Timing of Application	Fertilization regime							
	Accelerated				Controlled			
	N	P	K	Micronutrient[†]	N	P	K	Micronutrient
	g m^{-2}							
Preplant[‡]	30.0	6.6	16.6	80.0	15.0	3.3	8.3	55.0
Postplant[§]	24.0	16.8	15.3	11.5	6.0	4.2	3.8	7.0
Total[¶]	54.0	23.4	31.9	91.5	21.0	7.5	12.1	62.0

[†] Micronutrient fertilizer with analysis of 12Mg-9S-0.5Cu-8Fe-3Mn-1Zn.

[‡] Preplant fertilizer was incorporated into the upper 8 cm of the rootzone mixture before seeding. Analyses for the fertilizers applied were (N-P-K) 16-11-10, 15-0-24, 38-0-0, and a micronutrient fertilizer.

[§] Postplant fertilizers were applied during the growing season at the full rate weekly for accelerated , and at the half rate every 2 wk for controlled. Analyses for fertilizers applied were 16-11-10 (N-P-K) and a micronutrient fertilizer.

[¶] Total application amounts during the establishment year.

Soil pH was determined in a 1:2 soil:water suspension (McClean, 1982) and EC was determined in a 1:5 soil:deionized water extracts (Rhoades, 1982). Cation exchange capacity was estimated using the ammonium acetate extraction method at pH 7

(Hendershot et al., 1993) followed by Kjeldahl steam distillation (Keeney and Nelson, 1982). Total organic C was analyzed by dry combustion at 1000 °C with non-dispersive infrared detection (Nelson and Sommers, 1982). Total N was determined using the Kjeldahl digestion method (Bremner, 1996). The 7-day short term anaerobic incubation method as described by Campell et al. (1993) was used to determine the potentially mineralizable N. Each soil sample was divided into two fractions, one was incubated under water logged conditions in an incubator at 40 °C for 7 days, the other was directly extracted with 2M KCl for assessment of initial ammonium (NH_4^+-N), and the NH_4^+-N contents after incubation or extraction were determined by Kjeldahl steam distillation. Potentially mineralizable N was calculated by subtracting the initial NH_4^+-N from the NH_4^+-N after incubation.

The experiment was a split-plot design with the main plot treatments being the four factorial combinations of two levels of RZM and two levels of EST, and the subplot treatments being the sampling depth. Analysis of variance was conducted using the PROC GLM procedure in SAS 9.2 version (SAS Institute Inc., Cary, NC) where the variances of replications nested within the greens were combined. Fisher's protected LSD at $P = 0.05$ was used to separate the treatment means.

Results and Discussion

There was no difference between the two levels of fertilization in EST treatments for total organic C, total N, PMN, CEC, EC, and pH (Table 1.2). No differences were found between the two RZMs for total organic C, total N, PMN, CEC and pH (Table 1.2). Soil depth had a significant effect on all the soil properties investigated. McClellan et al.

(2009) also reported a significant effect of depth on OM, TSS, pH and soil nutrient levels. The aging effect was not evaluated using the same statistical methods as other factors in this study because putting green age was not replicated (Table 1.2).

The two-way interaction between putting green age and soil depth had a significant effect on soil properties including total N, CEC and EC, but no effect on total organic C, PMN, and pH (Table 1.2). This result for CEC and EC agreed with study 2 of McClellan et al. (2009) in which soil samples were taken from 0-2.5, 2.5-10 and 10-20 cm. McClellan et al. (2009) speculated that the age and depth interaction for soil nutrient and chemical properties was likely caused by the presence of a mat layer, which increased in thickness over time. In addition to the mat layer, topdressing practices, which dilute thatch, might be another reason that attributed to the difference of soil properties in different soil depths. The three-way and four-way interactions were beyond the scope of this study for discussion.

Fertilization in EST treatments was expected to affect total organic C content because deposition of organic C was largely a result of growth of turfgrasses (Soper et al., 1988; Turgeon, 1991). McClellan et al. (2007) reported higher OM content of the accelerated than the controlled fertilization treatment in the grow-in year, but the treatment effect was not significant. Results from this study further showed that the accelerated fertilization during the establishment year had no effect on total organic C content 6 years later. Rootzone mixture of sand/peat/soil exhibited a higher EC value (0.16 dS m^{-1}) than sand/peat (0.15 dS m^{-1}). However, in previous study, McClellan et al. (2007) collecting

Table 1.2. Analysis of variance for soil chemical properties in USGA-specified putting greens.

Source of variation	df	pH	Electrical conductivity	Cation exchange capacity	Total organic C	Total N	PMN#
Age†	3	--	--	--	--	--	--
Replication (age)	8	**	***	***	NS	NS	*
RZM‡	1	NS	**	NS	NS	NS	NS
Age × RZM	3	NS	NS	NS	NS	NS	NS
EST§	1	NS	NS	NS	NS	NS	NS
Age × EST	3	NS	NS	NS	NS	NS	*
RZM × EST	1	NS	NS	NS	NS	NS	NS
Age × RZM × EST	3	NS	*	NS	NS	NS	*
Replication × age × RZM × EST	24	NS	**	***	*	**	***
Depth¶	11	***	***	***	***	***	***
Age × depth	33	NS	***	***	NS	**	NS
Replication × age × depth	88	**	NS	NS	***	NS	NS
Residual	264						
CV, %		7.72	18.4	16.5	21.7	26.7	97.1

* Significant at the 0.05 probability level.

** Significant at the 0.01 probability level.

*** Significant at the 0.001 probability level.

NS Nonsignificant at the 0.05 probability level.

† Putting green age at the time of sample collection. The four putting greens established in 1997, 1998, 1999, and 2000 were 6, 7, 8, and 9 years old, respectively.

‡ The two levels of rootzone mixtures were sand (calcareous sand with a pH value of 8.0)/sphagnum peat mixtures at 80:20 (v:v) and sand/sphagnum peat/soil (Tomek silty clay loam, fine smectitic, mesic Pachic Argiudoll) mixtures at 80:15:5 (v:v:v).

§ The two levels of establishment treatment were accelerated or controlled fertilization regime during the establishment year.

¶ Sampling depths from 0 to 7.62 cm. Soil cores were subdivided into 12 equal sections.

Potentially mineralizable N.

samples over a 6-yr period reported that no significant effect of RZM was observed for TSS. Total organic C, total N, PMN, CEC and EC decreased while soil pH increased with soil depth from 0 to 7.62 cm (Table 1.3). Total organic C decreased from 16.7 g kg^{-1} in the top layer to 5.4 g kg^{-1} in the bottom layer (Table 1.3). Higher total organic C content in the upper rootzone profile was likely a result of OM accumulation in the form of mat. Baker et al. (1999) reported that main concentration of OM in putting green rootzone was located in the upper 20 mm of the rootzone area and OM content decreased with soil depth.

Total N decreased from 1.4 g kg^{-1} in the top layer to 0.4 g kg^{-1} in the bottom layer and PMN decreased from 17 mg kg^{-1} to 1.54 mg kg^{-1} (Table 1.3). Development of the mat layer in the upper profile contributes to greater capacity of aging greens to store both organic N and inorganic N (mainly NH_4^+-N) (Nelson et al., 1980; Engelsjord et al., 2004). Potentially mineralizable N increased with the accumulation of total organic C and N in older turf (Shi et al., 2006). Therefore, both total N and PMN were higher in the upper rootzone profile. Cation exchange capacity decreased from 4.21 cmol$_c$ kg^{-1} in the top layer to 1.68 cmol$_c$ kg^{-1} in the bottom layer (Table 1.3). Accumulation of OM as mat in the upper rootzone profile contributes to greater CEC and nutrient retention (Turgeon, 1991; Carrow et al., 2001). Electrical conductivity decreased from 0.40 dS m^{-1} in the top layer to 0.07 dS m^{-1} in the bottom layer while soil pH increased from 5.36 to 6.66. Soil pH in putting green rootzone is determined by many factors including carbonate, organic acid, acidifying fertilizers and even topdressing materials (Beard, 1973; Waddington, 1992). Higher content of organic acid in top soils as a result of thatch/mat accumulation was one of the reasons that attributed to the lower pH.

Table 1.3. Soil chemical properties at different depths in USGA-specified putting greens. Results were combined across four putting greens that were 6, 7, 8, and 9 years old.

Layer †	pH	Electrical conductivity	Cation exchange capacity	Total organic C	Total N	PMN§
		dS m^{-1}	$cmol_c$ kg^{-1}	g kg^{-1}	g kg^{-1}	mg kg^{-1}
1	5.36d‡	0.40a	4.21a	16.7a	1.4a	17.0a
2	5.95c	0.27b	3.72b	14.1b	1.1b	12.9b
3	6.14b	0.23c	3.59b	13.1c	1.0c	11.0bc
4	6.08bc	0.19d	3.06c	11.2d	0.9d	8.0cd
5	6.22b	0.16e	2.84d	9.7e	0.8e	4.11de
6	6.35a	0.13f	2.53e	9.3ef	0.6f	3.10def
7	6.46a	0.10g	2.14f	8.6fg	0.5g	1.48efgh
8	6.43a	0.09h	1.97g	8.5g	0.4gh	0.43gh
9	6.51a	0.08hi	1.83gh	6.7h	0.4hi	0.59gh
10	6.56a	0.08i	1.74h	6.2hi	0.4hi	1.53efgh
11	6.48a	0.07i	1.70h	5.7i	0.4hi	0.69h
12	6.66a	0.07i	1.68h	5.4i	0.4hi	1.54efg

† Samples were collected from 0 to 7.62 cm and were partitioned into 12 layers with each layer being 0.64-cm thick. Layer 1 to 12 represents increasing soil depth with an increment of 0.64-cm.

‡ Means with the same letter within respective soil chemical properties are not significantly different according to Fisher's LSD test at P = 0.05.

§ Potentially mineralizable N.

Due to topdressing and other cultural practices, about 3.5 to 5 cm of new sand was added to the original rootzones. The cultural practice and root activities had a larger impact on the soil properties in the top 0 to 2 cm, while little changes for soil properties are reflected in the 6 to 8 cm depth (layer 9 to 12) (Table 1.3). The intermediate zone clearly showed differences as affected by green ages in the properties (Fig. 1.1 to 1.6). Shi et al. (2006) noted the age effect for PMN was more evident in the 0 to 5 cm soil than in the 5 to 15 cm. Shi et al. (2006) also reported that greater proportion of total N was mineralized during incubation in younger greens than older greens. Since the changes of chemical properties in the soil profile are not clearly defined and tend to be affected by cultural practices, any arbitrary classification of layers will not be sufficient for understanding of the changes in the rootzone.

Conclusions

The initial differences of soil chemical properties between rootzone mixtures of sand/peat at 80:20 (v:v) and sand/peat/soil at 80:15:5 (v:v:v), or between different levels of fertilization during establishment disappeared due to topdressing practice over a period of about 6 years at the top of the rootzone, especially in the 0 to 2 cm layer. A layer by layer evaluation of the soil rootzone in this study provided more information on changes in soil chemical properties over time, especially with respect to the impact of cultural practices.

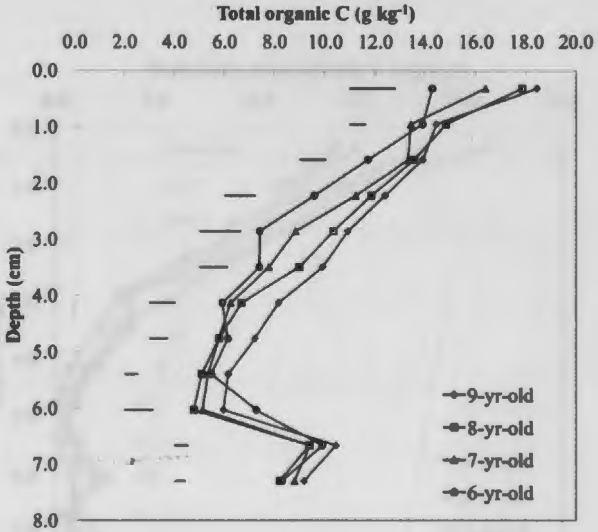

Fig. 1.1. Vertical changes of total organic C in USGA-specified putting green rootzone from 0 to 7.62 cm. Bars represent the standard deviation of means of the four putting greens at different ages.

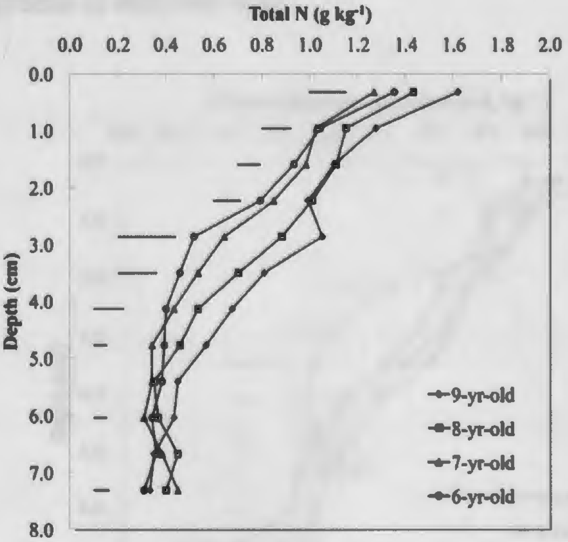

Fig. 1.2. Vertical changes of total N in USGA-specified putting green rootzone from 0 to 7.62 cm. Bars represent the standard deviation of means of the four putting greens at different ages.

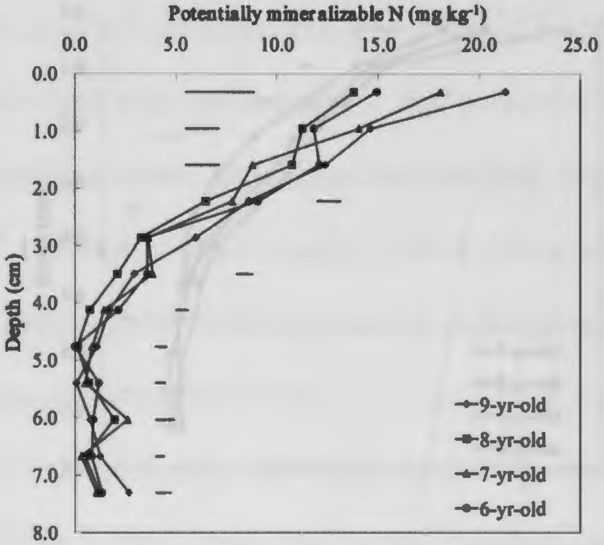

Fig. 1.3. Vertical changes of potentially mineralizable N in USGA-specified putting green rootzone from 0 to 7.62 cm. Bars represent the standard deviation of means of the four putting greens at different ages.

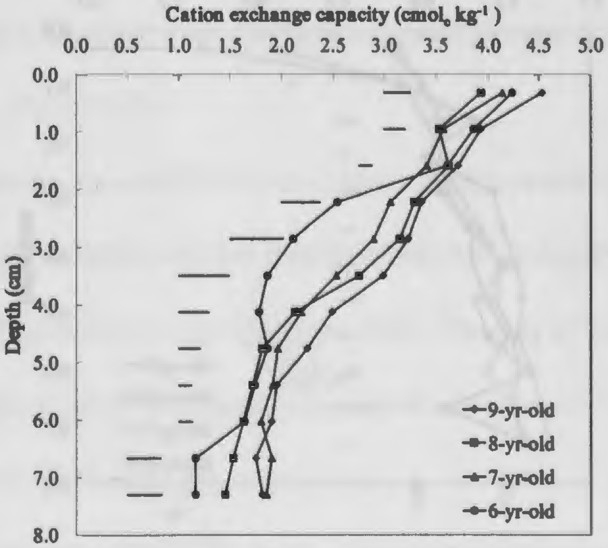

Fig. 1.4. Vertical changes of cation exchange capacity in USGA-specified putting green rootzone from 0 to 7.62 cm. Bars represent the standard deviation of means of the four putting greens at different ages.

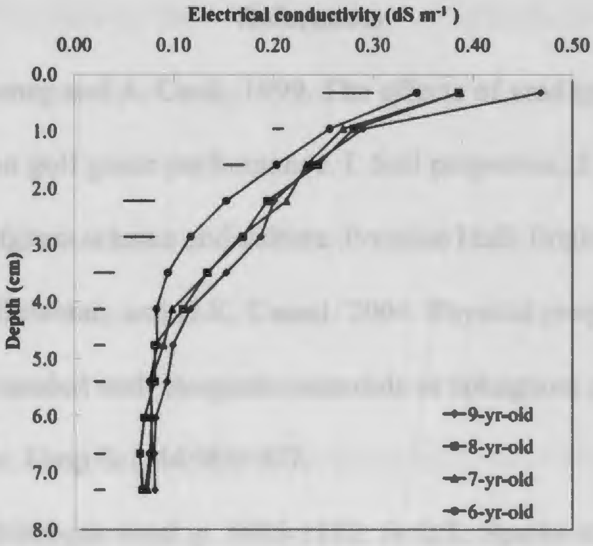

Fig. 1.5. Vertical changes of electrical conductivity in USGA-specified putting green rootzone from 0 to 7.62 cm. Bars represent the standard deviation of means of the four putting greens at different ages.

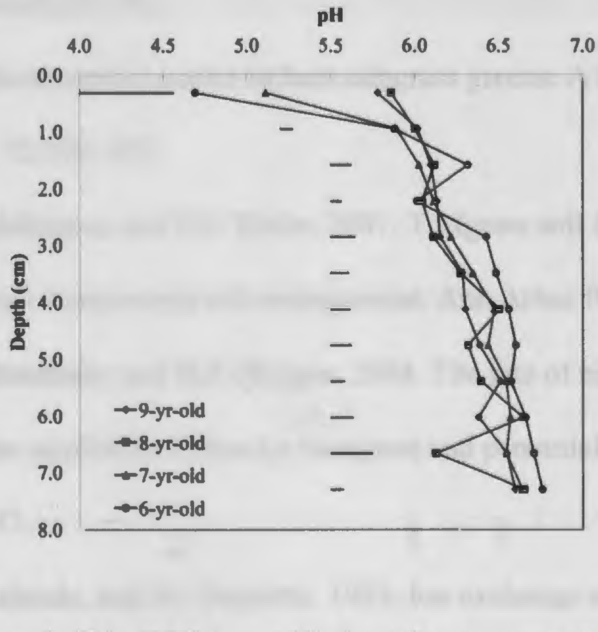

Fig. 1.6. Vertical changes of pH in USGA-specified putting green rootzone from 0 to 7.62 cm. Bars represent the standard deviation of means of the four putting greens at different ages.

References

Baker, S.W., S.J. Mooney and A. Cook. 1999. The effects of sand type and rootzone amendments on golf green performance. I. Soil properties. J. Turfgrass Sci. 75:2-17.

Beard, J.B. 1973. Turfgrass science and culture. Prentice Hall, Englewood Cliff, NJ.

Bigelow, C.A., D.C. Bowman, and D.K. Cassel. 2004. Physical properties of three sand-size classes amended with inorganic materials or sphagnum peat moss for putting green rootzone. Crop Sci. 44:900-907.

Bremner, J.M. 1996. Nitrogen-total. p. 1085-1122. *In* D.L. Sparks et al. (ed.) Methods of soil analysis. Part 3. SSSA Book Ser. 5. SSSA, Madison, WI.

Campbell, C.A., B.H. Ellert, and Y.W. Jame. 1993. Nitrogen mineralization potential in soils. p. 341-349. *In* M.R. Carter (ed.) Soil sampling and methods of analysis. Lewis Publ., Boca Raton, FL.

Carrow, R.N. 2004. Surface organic matter in bermudagrass greens: A primary stress? Golf Course Manage. 72:102-105.

Carrow, R.N., D.V. Waddington, and P.E. Rieke. 2001. Turfgrass soil fertility and chemical problems: Assessment and management. Ann Arbor Press, Chelsea, MI.

Engelsjord, M.E., B.E. Branham, and B.P. Horgan. 2004. The fate of nitrogen-15 ammonium sulfate applied to Kentucky bluegrass and perennial ryegrass turfs. Crop Sci. 44:1341-1347.

Hendershot, W.H., H. Lalande, and M. Duquette. 1993. Ion exchange and exchangeable cations, p. 167-176. *In* M.R. Carter (ed.) Soil sampling and methods of analysis. CRC Press, Boca Raton, FL.

Keeney, D.R., and D.W. Nelson. 1982. Nitrogen-inorganic forms. p. 643-687. *In* A.L. Page et al. (ed.) Methods of soil analysis. Part 2. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

Li, D., Y.K. Joo, N.E. Christians, and D.D. Minner. 2000. Inorganic soil amendment effects on sand-based sports turf media. Crop Sci. 40:1121-1125.

McClean, E.O. 1982. Soil pH and lime requirement. p. 199-224. *In* A.L. Page et al. (ed.) Methods of soil analysis. Part 2. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

McClellan, Ty.A., R.E. Gaussoin, R.C. Shearman, C.S. Wortmann, M. Mamo, and G.L. Horst. 2009. Nutrient and chemical characterization of aging golf course putting as impacted by soil depth and mat development. HortScience 44:452-458.

McClellan, Ty.A., R.C. Shearman, R.E. Gaussoin, M. Mamo, C.S. Wortmann, G.L. Horst, and D.B. Marx. 2007. Nutrient and chemical characterization of aging golf course putting greens: establishment and rootzone mixture treatment effects. Crop Sci. 47:193-199.

Nelson, D.W., and L.E. Sommers. 1982. Total carbon, organic carbon, and organic matter. p. 539-580. *In* A.L. Page et al. (ed.) Methods of soil Analysis. Part 2. 2nd ed. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

Nelson, K.E., A.J. Turgeon, and J.R. Street. 1980. Thatch influence on mobility and transformation of nitrogen carriers applied to turf. Agron. J. 72: 487-492.

Ok, C.-H., S.H. Anderson, and E.H. Ervin. 2003. Amendments and construction systems for improving the performance of sand-based putting greens. Agron. J. 95:1583-1590.

Rhoades, J.D. 1982. Soluble salts. p. 167-179. *In* A.L. Page et al. (ed.) Methods of soil analysis. Part 2. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

Rowland, J.H., J.H. Cisar, G.H. Snyder, J.B. Sartain., and A.L. Wright. 2009. USGA ultradwarf bermudagrass putting green properties as affected by cultural practices. Agron. J. 101:1565-1572.

Shi, W., H. Yao, and D. Bowman. 2006. Soil microbial biomass, activity and nitrogen transformations in a turfgrass chronosequence. Soil Biol. Biochem. 38:311-319.

Soper, D.Z., J.H. Dunn, D.D. Minner, and D.A. Sleper. 1988. Effects of clipping disposal, nitrogen, and growth retardants on thatch and tiller density in Zoysiagrass. Crop Sci. 28:325-328.

Turgeon, A.J. 1991. Turfgrass management. 3rd ed. Prentice Hall, Regents, NJ.

Waddington, D.V. 1992. Soils, soil mixtures, and scoil amendments. p. 331-383. *In* D.V. Waddington et al. (ed.) Turfgrass. Agron. Monogr. 32. ASA, CSSA, and SSSA, Madison, WI.

White, R.H., and R. Dickens. 1984. Thatch accumulation in bermudagrass as influenced by cultural practices. Agron. J. 76:19-22.

CHAPTER 3. ANALYSIS OF SOIL CHEMICAL PROPERTIES OF SAND-BASED TURFGRASS ROOTZONE USING FOURIER TRANSFORM INFRARED SPECTROSCOPY

Abstract

Soil samples collected from sand-based golf putting greens were analyzed for total organic C, total N, cation exchange capacity (CEC), electrical conductivity (EC) and pH using diffuse reflectance Fourier transform infrared (DRIFT) spectroscopy in conjunction with partial least square regression (PLSR) analysis. Analysis by DRIFT was conducted in the near-infrared (NIR) (4000-10000 cm^{-1}) and mid-infrared (MIR) (600-4000 cm^{-1}) region. Mid-infrared and NIR calibration models built through PLSR and leave-one-out cross validation for total organic C, total N, CEC, and EC produced $R^2 > 0.80$. Mid-infrared and NIR spectroscopy achieved similar calibration accuracy for total organic C, total N, CEC, EC, and pH. The whole sample set was grouped into subsets based on factors that might contribute to variations in soil constituents. Mid-infrared calibration model was built for each subset and mutual prediction was performed within a group to test model robustness as affected by those influential factors. Subsets grouped by rootzone mixture (sand-peat vs sand-peat-soil) and putting green age (6-yr-old green vs 9-yr-old green) were calibrated and predicted with reasonable accuracy. However, subsets grouped by sampling depth (0-3.8 cm vs 3.8-7.6 cm) failed to be calibrated and predicted within the group. Results of this study confirmed the applicability of DRIFT-NIR and -MIR to predict chemical properties of sand-based turf soil through modeling. Model robustness could be largely affected by sampling depth, which is mostly attributed to the inner discrepancy in the amount and nature of soil organic matter in the upper and lower rootzone profile.

Introduction

Soil analysis is vital to turfgrass establishment and maintenance. Besides the basic soil fertility test, turfgrass troubleshooting, in many cases, requires determination of many soil properties at a time (Stowell and Gelernter, 2001). Moreover, because of the temporal and spatial nature of many soil properties, such as moisture content, pH and nitrate levels, frequent scouting of the soil conditions are needed in precision turfgrass management (Carrow et al., 2009). Conventional analytical methods cannot meet the demand of the requirements as mentioned above, not only because they are time consuming and expensive, but also because of the hazards that are involved in many wet chemistry used in analysis (Janik et al., 1998). Vibrational infrared spectroscopy technique has been recognized as a promising tool to replace conventional analytical methods to generate accurate results of soil properties rapidly and cost-effectively (Dalal and Henry, 1986; Janik et al., 1998; Reeves et al., 2001).

Vibrational infrared spectroscopy (VIS) is based on the transition of energy levels of bonded atoms induced by matching infrared radiations. The frequency of absorption is corresponding to the vibrational modes of bonds within molecules (Coleman, 1993). Thus, vibrational infrared spectroscopy is able to provide rich information on structures and compositions of soil minerals and soil organic matter (SOM) (Johnston and Aochi, 1996).

Quantitative analysis of soil properties using VIS depends on the proportional relationship between absorption intensity and concentration of molecules, and is affected by basic soil constituents. Empirical calibration models are first built by regressing laboratory determined soil properties with spectral features of soil constituents. Prediction of several unknown soil properties then can be made from the established models with the input of results from a single spectral scanning. Multivariate regression techniques including multiple linear regressions (MLR), principle component regression (PCR), and partial least square regression (PLSR) are commonly used in building calibration models (Westerhaus et al., 2004). The PLSR technique is especially useful in dealing with sample sets that have significantly less dependent variables than spectral predictors or have collinearity problems with spectral predictors. The superiority of PLSR over PCR and stepwise-MLR in quantitative infrared studies was demonstrated from the findings by Bolster et al. (1996) and Vasques et al. (2008).

The application of VIS in soil analysis uses both near-infrared (NIR) (4000–10000 cm^{-1}) and mid-infrared (MIR) (400-4000 cm^{-1}) regions. The two are complementary with MIR spectrum more informative than NIR of important soil properties. The MIR region features fundamental vibrational modes from functional groups of soil minerals and SOM while NIR region is dominated by overtones and combinations of fundamental vibrations due to C–H, N–H and O–H groups (Coleman, 1993; Reeves et al., 2001; Malley et al., 2004).

Diffuse reflectance Fourier transform infrared (DRIFT) spectroscopy is one of the VIS techniques that are especially suitable for screening solid soil samples. With careful sample preparation and dilution using an inert salt, some of the limitations associated with DRIFT can be alleviated, such as nonlinearities due to absorptions, specular reflection, and sample uniformities. Coupled with multivariate regression techniques, recent studies have shown that accurate predictions of soil properties can be achieved by MIRS (Reeves et al., 2001).

Many soil chemical properties have been successfully calibrated and predicted using NIRS together with multivariate regression. Dalal and Henry (1986) used dispersive spectrometer of DR-NIRS-MLR to simultaneously determine moisture content, organic C and total N in soil samples of different size fractions. Organic C and total N were predicted using three wavelengths as predictors, both with R^2 of 0.86. The author found that prediction accuracy was affected by soil particle size. Morra et al. (1991) later modeled total C and N with $R^2 > 0.80$ in silt and clay fractions using DR-NIRS-MLR. The silt fraction exhibited higher prediction accuracy of total C and N than the silt plus coarse clay fraction. Ben-Dor and Banin (1995) used DRIFT-NIR-MLR to analysis soil collected from different climate zones in Israeli. Cation exchange capacity was modeled with $R^2 = 0.82$ and predicted with $R^2 = 0.64$, which was considered sufficient accuracy of NIRS to be used for rapid field and laboratory measurement. However, SOM was poorly calibrated ($R^2 = 0.69$) and predicted ($R^2 = 0.69$) with bias in this study, which was likely attributed to the heterogeneous nature of SOM. A thorough analysis of soil chemical, biological and physical properties by NIRS-PCR over large geographical regions in the US was conducted by Chang et al. (2001). Results showed that total C, total N, CEC and Mehlich-3 Ca were successfully predicted with $R^2 > 0.80$ while pH, Mehlich-3 Fe, K, Mg, Mn were less successfully predicted with R^2 between 0.5 and 0.8.

Recent studies showed that MIRS could perform better than NIRS in predicting many soil properties. Analyzing farm soils from Maryland using DRIFT-PLSR with both

MIRS and NIRS, Reeves et al. (2001) concluded that accurate calibrations can be developed for total C, total N, pH ($R^2 > 0.80$), and that pH was better predicted with MIRS than with NIRS. Both Madari et al. (2006) and McCarty et al. (2002) reported that MIRS outperformed NIRS in predicting total, organic, and inorganic C using DRIFT-PLSR. In analyzing repository soils in Australia by DRIFT-NIRS and -MIRS, Minasny and McBratney (2008) noted that MIRS generally performed better than NIRS in predicting total C, total N, CEC and clay.

Although previous NIRS and MIRS studies have covered a great diversity of soil types sampled from large geographic regions or agricultural fields, few studies on sand-based turf soil exist. Couillard et al. (1997) applied NIRS-PLSR in analyzing sand-based turf soils collected from 10-yr-old golf putting greens and reasonable prediction was reported for soil properties such as moisture content, SOM, particle size fractions, and pH with $R^2 > 0.80$. However, there is a lack of separate prediction procedure in this study. In a qualitative manner, Shi et al. (2006) utilized FTIR-MIR to characterize SOM fractions from sand-based turf soil by detecting the changes of featured functional groups of SOM as turf aged. Therefore, more work is needed in investigating the applicability of DRIFT-MIR and -NIR technique in quantitative analysis of sand-based turf soil.

Deposition of organic C in sand-based turfgrass rootzone is a central issue associated with changes of physical conditions and soil fertility status as turf mature. Along with accumulation of organic C, chemical properties such as plant available nutrients, CEC and pH are also modified over time. The objective of this research was to evaluate the performance of DRIFT in the NIR and MIR region in conjunction with PLSR analysis in calibrating and predicting organic C and selected chemical properties of sand-based turf soil.

Materials and Methods

Site Description and Soil Sampling

Four experimental putting greens were established in sequential years from 1997 to 2000 at the University of Nebraska-Lincoln John Seaton Anderson Turfgrass Research Facility located near Mead, NE (41°11' N, lat. 96 ° 28' W). A detailed description of putting green construction, establishment and maintenance were given by McClellan et al. (2007). In brief, the four USGA-specified golf putting greens were covered with 'Providence' creeping bentgrass (*Agrostis stolonifera* L.). Within each green, the treatments were combinations of two levels of rootzone mixtures (RZM) and two levels of establishment (EST) treatments in randomized complete block design with three replications. The two RZMs were sand/sphagnum peat at 80:20 and sand/sphagnum peat/soil at 80:15:5 on volumetric basis. The sand component was calcareous with pH value of 8.0, and the soil component was Tomek silty clay loam, fine smectitic, mesic Pachic Argiudoll. The two EST treatments were accelerated and controlled fertilization regimes during the establishment year. Besides nutritional and maintaining programs, other management practices included sand topdressing every 10 to 14 day combined with vertical mowing and sand topdressing twice annually (spring and fall) combined with hollow-tine core cultivation.

Soil sampling was conducted in June 2006 on four putting greens that were 6, 7, 8 and 9 years old. The soil cores were retracted using a 10.2-cm diameter cup cutter at 0 to

7.62 cm depth and transported in a coolant to the laboratory at North Dakota State University, where each soil core was subdivided into 12 equal cross sections (each section being 0.64-cm thick) after the removal of thatch layer. The subsamples were stored in sealed plastic bags at 5°C for later analysis.

Determination of Reference Values

Soil pH was determined in a 1:2 soil:water suspension (McClean, 1982) and EC was determined in a 1:5 soil:deionized water extracts (Rhoades, 1982). Cation exchange capacity was estimated using the ammonium acetate extraction method at pH 7 (Hendershot et al., 1993) followed by Kjeldahl steam distillation (Keeney and Nelson, 1982). Total organic C was analyzed by dry combustion at 1000 °C with non-dispersive infrared detection (Nelson and Sommers, 1982). Total N was determined using the Kjeldahl digestion method (Bremner, 1996).

Spectral Analysis

Soil samples used for DRIFT analysis were air dried, grounded using a hammer mill and then passed through a 100-mesh sieve. Soil samples were then diluted to 50% (by weight) with potassium bromide (KBr) powder and further grounded with an agate mortar and pestle. Spectral scanning was performed by a Bruker Optic Tensor 27 FTIR spectrometer (Bruker Optics Inc. Billerica, MA) equipped with a germanium-coated KBr beam splitter. Soil samples were scanned in the MIR region from 600-4000 cm^{-1} (16666 nm-2500 nm) with the spectrometer set to a high density global source and a liquid nitrogen cooled wide-band mercury-cadmium-tel-lurid (MCT) detector. Soil samples were scanned in the NIR region from 4000-10000 cm^{-1} (2500 nm-1000 nm) with the spectrometer set to an In GaAs detector. All spectra were collected at a resolution of 4 cm^{-1} with 64 co-added scans per spectra in a diffuse reflectance mode and two scans were taken for each sample.

Calibration and Validation

Duplicate readings of each sample were first averaged. Spectral data of all samples was transformed from AB (absorbance) to log (1/R) (R is the reflectance) using KBr as the background reference and preprocessed with baseline correction, mean centering and variance scaling. Model-building was performed by PLSR and leave-one-out cross validation with which spectral data was regressed against laboratory-determined reference values. The maximum number of PLSR factors was set to 15 and the optimum number of factors selected in building the final calibration model was evaluated by the predicted residual sum of squares (PRESS). Calibration models of the whole sample set consisted of 576 samples were developed with NIRS and MIRS spectral data.

Calibration robustness is affected by variations in the amount and chemical composition of soil minerals and SOM among sample sets (Reeves et al., 2001; Sorensen and Dalsgaard, 2005). Therefore, based on influential factors that may contribute to those variations, the whole sample set was grouped into subsets in three manners: 1) upper-profile (0-3.81cm depth) and lower-profile (3.81-7.62 cm depth) subsets based sampling depth in putting green rootzone; 2) Sand-peat and sand-peat-soil subsets based rootzone mixture treatment; 3) 6-yr-old and 9-yr-old putting green subsets based on putting green age. A calibration model was built for each subset by PLSR and leave-one-out cross validation. Then, mutual prediction was performed to test the calibration robustness within a group. All analyses of subsets were only preformed with the MIRS spectra data.

Accuracy of calibration and prediction was evaluated by: coefficient of determination (R^2) and root mean square errors (RMSE). Correlation between the predicted value and the reference value with R^2 in the range of 0.90-0.70 was considered reasonable and with $R^2 > 0.90$ was considered accurate in this study. A correlation with an $R^2 > 0.70$ could be used as a surrogate for laboratory-based analysis according to the suggestion by Janik et al. (1998) in a review of MIRS. Descriptive statistical and PLSR analyses were carried out using SAS 9.2 version (SAS Institute, Inc., Cary, NC).

Results and Discussion

Calibration of the Whole Sample Set

Mid infrared spectroscopy and NIRS calibrations for total organic C, total N, CEC and EC resulted in $R^2 > 0.80$ (Table 2.1). Among the five soil properties, total N was calibrated with the highest accuracy ($R^2 = 0.87$ by MIRS and $R^2 = 0.86$ by NIRS) (Table 2.1, Fig. 2.1). Only pH value failed to be calibrated with reasonable accuracy ($R^2 < 0.60$ by both NIRS and MIRS); however, the ability of NIRS and MIRS to model soil pH with reasonable accuracy has been confirmed by previous studies (Reeves et al., 2001; Malley et al., 2004). The poor calibration was most likely attributed to the high variance of the laboratory reference values. Results of pH were still presented for purpose of demonstrating the general trend but would not be further discussed.

Table 2.1. Near-infrared and mid-infrared calibration results of the whole sample set using partial least square regression and leave-one-out cross validation.

	Mid-infrared spectroscopy					Near-infrared spectroscopy				
	Calibration by leave-one-out cross-validation			Final calibration		Calibration by leave-one-out cross-validation			Final calibration	
Soil property	Factors	R^2	RMSE†	R^2	RMSE	Factors	R^2	RMSE	R^2	RMSE
pH	7	0.47	0.18	0.51	0.18	4	0.43	0.19	0.46	0.19
EC‡	12	0.81	0.04	0.81	0.04	4	0.82	0.04	0.82	0.04
CEC§	11	0.84	0.34	0.85	0.33	5	0.82	0.36	0.85	0.34
Total organic C	12	0.82	0.17	0.82	0.17	5	0.80	0.18	0.81	0.17
Total N	15	0.86	0.01	0.87	0.01	5	0.85	0.01	0.86	0.01

† Root mean square error.

‡ Electrical conductivity.

§ Cation exchange capacity.

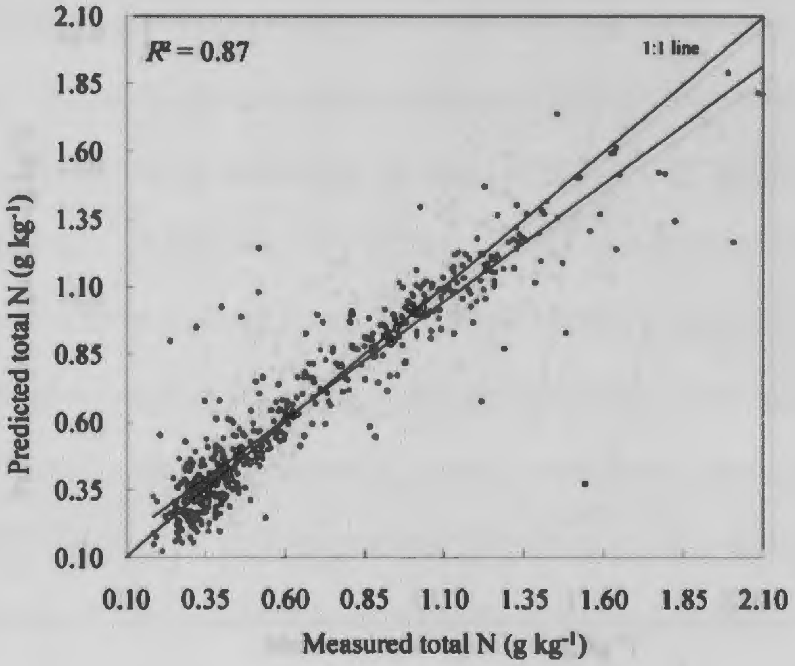

Fig. 2.1. Mid-infrared calibration for total N with the whole sample set. Calibration model was built using partial least square regression and leave-one-out cross validation.

Better calibration result for total organic C with MIRS could be achieved by acid pretreatment of samples to remove soil carbonate because bands due to carbonate could mask featured bands that are responsible for determining total organic C (McCarty et al., 2002). Since calcareous sand was the dominating matrix of soil samples in this study, calibration accuracy for total organic C with MIRS ($R^2 = 0.82$) might be undermined by the presence of carbonate (Fig. 2.2).

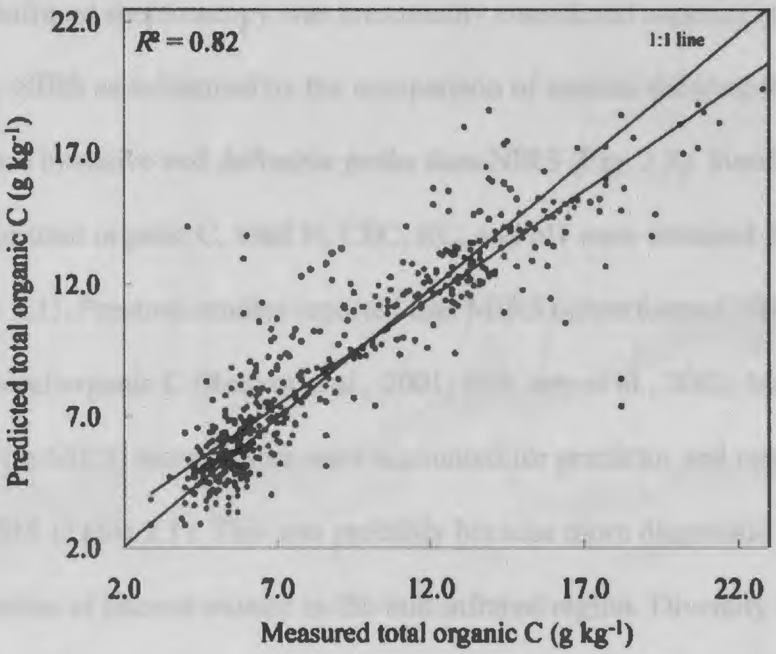

Fig. 2.2. Mid-infrared calibration for total organic C with the whole sample set. Calibration model was built using partial least square regression and leave-one-out cross validation.

Results of this study showed that EC values of sand-based turf soils could be calibrated with reasonable accuracy ($R^2 = 0.81$ by MIRS and $R^2 = 0.82$ by NIRS). However, calibration models of soil EC established by infrared analysis were considered less reliable because EC values tended to be related to chemistry of the soil solution and depend more on transient criteria (Janik et al., 1998). In the study by Minasny et al. (2009), EC was also successfully modeled with $R^2 = 0.94$ using MIRS-PLSR, but validation of this calibration model by soils from other locations resulted in R^2 value being only 0.08 and 0.26.

Therefore, calibration models of EC based on sand-based turf soil might be soil-type limited.

Mid infrared spectroscopy was presumably considered superior in quantitative analysis than NIRS as evidenced by the comparison of spectra showing that MIRS exhibited more intensive and definable peaks than NIRS (Fig. 2.3). Similar accuracy of calibration for total organic C, total N, CEC, EC, and pH were obtained between MIRS and NIRS (Table 2.1). Previous studies reported that MIRS outperformed NIRS in predicting soil pH and total organic C (Reeves et al., 2001; McCarty et al., 2002; Madari et al. 2006). Compared with NIRS, more factors were accounted for predictor and response variations in results of MIRS (Table 2.1). This was probably because more diagnostic bands responsible for the properties of interest existed in the mid infrared region. Diversity in soil composition could also affect the number of calibration factors (Reeves et al., 2001).

Rootzone Mixture Based Subsets

It was earlier postulated that compositional differences between the calibration set and prediction set might influence calibration robustness. So, the whole sample set was separated into two subsets of different rootzone mixtures. The robustness of the calibration model built using one subset was tested by the other subset.

Mid infrared spectroscopy calibrations for total organic C, total N, CEC and EC were developed with an R^2 in the range of 0.78-0.90 using the two subsets (Table 2.2). Better calibration models of total organic C, total N, CEC and pH were developed using the sand-peat subset compared with the sand-peat-soil subset (Table 2.2). Improved calibration accuracy was observed for the sand-peat subset compared with the whole sample set

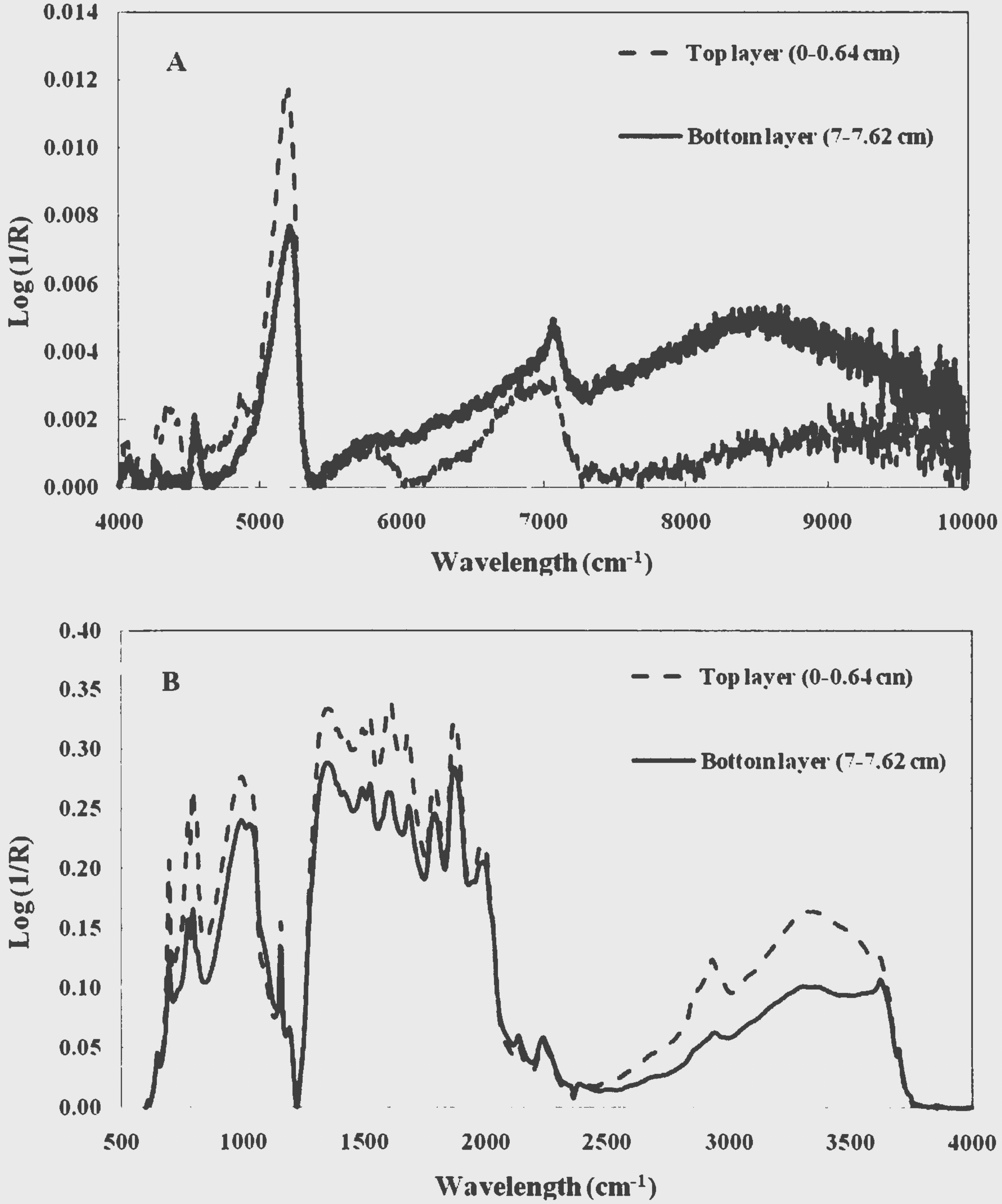

Fig. 2.3. Comparison of (A) near-infrared spectra (4000-10000 cm^{-1}) and (B) mid-infrared spectra (600-4000 cm^{-1}) of a top layer (0-0.64 cm) and bottom layer (7-7.62 cm) sample collected from USGA-specified putting green rootzone.

Table 2.2. Mid-infrared calibration and mutual prediction results of the two subsets separated based on rootzone mixture.

	Sand-peat†			Sand-peat-soil‡			Sand-peat-soil by sand-peat		Sand-peat by Sand-peat-soil	
Soil property	Factors	R^2	RMSE§	Factors	R^2	RMSE	R^2	RMSE	R^2	RMSE
pH	6	0.57	0.18	5	0.46	0.18	0.43	0.23	0.48	0.15
EC¶	11	0.82	0.04	12	0.85	0.04	0.78	0.05	0.72	0.05
CEC#	10	0.89	0.31	10	0.85	0.32	0.81	0.45	0.83	0.32
Total organic C	12	0.87	0.15	7	0.78	0.19	0.73	0.25	0.78	0.18
Total N	11	0.90	0.01	9	0.81	0.02	0.80	0.02	0.88	0.01

† Subset of rootzone mixture of sand and peat at 80:20 (v:v).

‡ Subset of rootzone mixture of sand, peat and soil at 80:15:5 (v:v:v).

§ Root mean square error.

¶ Electrical conductivity.

Cation exchange capacity.

whereas this was not the case for the sand-peat-soil subset (Table 2.1 and 2.2). Janik and Skjemstad (1995) noted that a wider range of reference values with larger sample sets might cause nonlinearity using DRIFT-MIRS; small subsets with narrow range tend to improve prediction linearity and precision. But in this case, ranges of reference values of the two subsets separated based on rootzone mixture were not necessarily narrower than the whole sample set (Table 2.3 and 2.4). Morra et al. (1991) reported that accuracy of calibration model for total C and N was improved by using only the silt fraction subsets in model development. Therefore, the author speculated that the improved accuracy might be attributed to the increased similarity in the chemical composition of the C and N pools. Likewise, less complexity in soil composition of the sand-peat subset might be the reason of the the improved calibration accuracy.

Table 2.3. Reference values of the whole sample set. Values were determined using conventional analytical methods.

Soil property	Mean	Min	Max	SD†
pH	6.33	3.60	7.19	0.37
EC‡, dS m^{-1}	0.16	0.04	0.60	0.10
CEC§, $cmol_c$ kg^{-1}	2.56	0.98	5.86	0.93
Total organic C, g kg^{-1}	9.2	2.9	26.1	4.4
Total N, g kg^{-1}	0.7	0.2	2.1	0.4

† Standard deviation.
‡ Electrical conductivity.
§ Cation exchange capacity.

Table 2.4. Reference values of the two subsets separated based on rootzone mixture. Values were determined using conventional analytical methods.

	Sand-peat mixture†				Sand-peat-soil mixture‡			
Soil property	Mean	Min	Max	SD§	Mean	Min	Max	SD
pH	6.33	5.14	7.13	0.36	6.34	3.60	7.19	0.39
EC¶, dS m^{-1}	0.15	0.04	0.56	0.10	0.16	0.05	0.60	0.10
CEC#, $cmol_c$ kg^{-1}	2.55	1.13	5.86	0.96	2.58	0.98	5.13	0.90
Total organic C, g kg^{-1}	9.1	2.9	26.1	4.3	9.3	3.5	25.3	4.5
Total N, g kg^{-1}	0.7	0.2	2.1	0.4	0.7	0.2	2.1	0.4

† Rootzone mixture of sand and peat at 80:20 (v:v).
‡ Rootzone mixture of sand, peat and soil at 80:15:5 (v:v:v).
§ Standard deviation.
¶ Electrical conductivity.
# Cation exchange capacity.

Mutual prediction for total organic C, total N, CEC and EC using calibration models built with each subset resulted in $R^2 > 0.70$, which indicated that at least 70% of the variation of the prediction set could be explained by the calibration model (Table 2.2). This result indicated that calibration models built with rootzone materials comprised of sand-peat (80:20 v:v) or sand-peat-soil (80:15:5 v:v:v) might be generalized with each other. Though it was speculated that parent material in the rootzone mixture might impact model robustness, differences in rootzone mixtures in this study might not be significant enough to cause reduction in model robustness.

Prediction of sand-peat subset using the calibration models developed by sand-peat-soil subset generally performed better than prediction of sand-peat-soil subset using calibration models developed by sand-peat subset (Table 2.2). Range of reference values in sand-peat-soil subsets did not necessarily exceed that of sand-peat subset (Table 2.4).

Therefore, this result was probably because that incorporation of silty clay loam in the sand-peat-soil subset brought more complexity in soil mineralogy.

Putting Green Age Based Subsets

Mid infrared spectroscopy calibrations for total organic C, total N, CEC and EC were developed with an R^2 between 0.69 and 0.90 using the two subsets that were separated based on putting green age (Table 2.5). Better calibration models for total organic C, total N, CEC and EC were developed using the 9-yr-old putting green subset than the 6-yr-old putting green subset (Table 2.5).

Subsets of this group generally had narrower range of reference values compared to the whole sample set (Tables 2.3 and 2.6). As previously discussed, both subsets were supposed to have improved calibration accuracy compared to the whole sample set. However, improved calibration accuracy was only observed for the 9-yr-old putting green subset whereas this was not the case for the 6-yr-old putting green subset (Table 2.5).

Results of using calibration models developed based on 6-yr-old putting green subset to predict 9-yr-old putting green subset were better than using calibration models developed based on 9-yr-old putting green subset to predict 6-yr-old putting green subset (Table 2.5). Previous studies found that soil samples differed greatly in decomposition stage and functional groups of SOM between the calibration and prediction samples resulted in poor prediction performance (Ben-Dor and Banin, 1995; Reeves et al., 2001). Given that the range of reference values did not differ greatly between the two subsets (Table 2.6), it was therefore speculated that younger greens might exhibit greater diversity in the nature of organic matter.

Table 2.5. Mid-infrared calibration and mutual prediction results of the two subsets separated based on putting green age.

	9-yr-old putting green†			6-yr-old putting green‡			6-yr-old by 9-yr-old putting green		9-yr-old by 6-yr-old putting green	
Soil property	Factors	R^2	RMSE§	Factors	R^2	RMSE	R^2	RMSE	R^2	RMSE
pH	5	0.49	0.17	5	0.53	0.18	0.35	0.17	0.43	0.24
EC¶	10	0.85	0.04	8	0.82	0.03	0.46	0.08	0.75	0.04
CEC#	6	0.89	0.31	8	0.84	0.31	0.68	0.42	0.87	0.31
Total organic C	10	0.90	0.14	8	0.69	0.19	0.27	0.64	0.74	0.18
Total N	10	0.90	0.01	8	0.84	0.01	0.70	0.02	0.80	0.02

† The putting green was constructed in 1997 and samples were collected in 2006.

‡ The putting green was constructed in 2000 and samples were collected in 2006.

§ Root mean square error.

¶ Electrical conductivity.

Cation exchange capacity.

Table 2.6. Reference values of the two subsets separated based on putting green age. Values were determined using conventional analytical methods.

	9-yr-old putting green†				6-yr-old putting green‡			
Soil property	Mean	Min	Max	SD§	Mean	Min	Max	SD
pH	6.27	5.14	6.85	0.34	6.45	5.24	7.19	0.36
EC¶, dS m^{-1}	0.17	0.06	0.60	0.11	0.14	0.05	0.42	0.09
CEC#, $cmol_c$ kg^{-1}	2.82	1.44	5.86	0.98	2.27	0.98	4.64	0.84
Total organic C, g kg^{-1}	10.1	4.4	26.1	4.5	8.4	3.9	25.2	4.1
Total N, g kg^{-1}	0.8	0.2	2.0	0.4	0.6	0.2	2.1	0.4

† The putting green was constructed in 1997 and samples were collected in 2006.
‡ The putting green was constructed in 2000 and samples were collected in 2006.
§ Standard deviation.
¶ Electrical conductivity.
# Cation exchange capacity.

Depth Based Subsets

Mid infrared spectroscopy calibrations for total organic C, total N, CEC, and EC of the upper- profile subset produced R^2 between 0.69 and 0.78 while the results of the lower-profile subset were in the range of 0.25-0.48 (Table 2.7). Calibration accuracy of the upper-profile subset was better than the lower- profile subset. Generally, mutual prediction failed to explain variations of the counterpart for both subsets (Table 2.7). Calibration models developed based on the upper-profile subset failed to predict soil properties in the lower-profile subset (Table 2.7).

Examples of the MIRS and NIRS spectra of the top layer (0-0.64 cm depth) and bottom layer (7-7.62 cm depth) samples was presented in Fig. 2.3. Visually, there were differences in absorption intensity and peak position between the top layer and bottom layer samples indicating variations in the concentration and composition of soil

Table 2.7. Mid-infrared calibration and mutual prediction results of the two subsets separated based on soil depth.

	Upper-profile†			Lower-profile‡			Lower-profile by upper-profile		Upper-profile by lower-profile	
Soil property	Factors	R^2	RMSE§	Factors	R^2	RMSE	R^2	RMSE	R^2	RMSE
pH	7	0.41	0.16	5	0.25	0.01	0.01	0.15	0.48	0.01
EC¶	9	0.69	0.05	9	0.45	0.16	0.05	0.04	0.62	0.28
CEC#	6	0.69	0.36	3	0.25	0.07	0.18	0.38	0.50	0.09
Total organic C	15	0.76	0.17	13	0.48	0.01	0.07	0.26	0.72	0.01
Total N	10	0.78	0.01	5	0.25	0.01	0.21	0.02	0.48	0.01

† Soil samples collected from 0-3.81 cm depth.

‡ Soil samples collected from 3.81-7.62 cm depth.

§ Root mean square error.

¶ Electrical conductivity.

Cation exchange capacity.

constituents. The upper-profile subset generally had a wider range of reference values than the lower-profile subset (Table 2.8). Shi et al. (2006) reported that chemical composition of SOM varied at the 0- 5 and 5-15 cm depth in putting green rootzones. In accordance, the upper-profile subset was different in SOM composition with the lower-profile subset. As a result of the diversity in both the range and chemical composition of SOM, spectral signatures of the prediction set might lie outside the calibration set, which subsequently resulted in a poor prediction performance (Janik et al., 2009).

Table 2.8. Reference values of the two subsets separated based on soil depth. Values were determined using conventional analytical methods.

	Upper profile†				Lower profile‡			
Soil property	Mean	Min	Max	SD§	Mean	Min	Max	SD
pH	6.12	3.60	7.19	0.35	6.54	3.87	7.13	0.31
EC¶, dS m^{-1}	0.23	0.06	0.60	0.10	0.08	0.04	0.14	0.02
CEC#, $cmol_c$ kg^{-1}	3.29	0.98	5.86	0.77	1.84	1.13	2.99	0.33
Total organic C, g kg^{-1}	12.2	4.1	26.1	4.0	5.9	2.9	15.1	1.5
Total N, g kg^{-1}	1.0	0.2	2.1	0.3	0.4	0.2	1.5	0.1

† Soil samples collected from 0-3.81 cm depth.

‡ Soil samples collected from 3.81-7.62 cm depth.

§ Standard deviation.

¶ Electrical conductivity.

Cation exchange capacity.

Conclusions

Results of this study confirmed the applicability of DRIFT in the MIR and NIR region in conjunction with PLSR in building reliable models to predict chemical properties of sand-based turf soil. The calibration and mutual prediction process using subsets of the whole sample provided evidence about factors that might influence the robustness of calibration models for sand-based turf soil. Subsets grouped by rootzone mixture and putting green age generally resulted in successful calibration and reasonable prediction. However, subsets grouped by sampling depth failed in calibration and prediction, suggesting that calibration robustness could be largely affected by sampling depth. The inner reason that explains calibration robustness is the diversity in soil constituents among samples of different depths.

In sum, the DRIFT-PLSR method requires simple sample preparation and is able to rapidly analyze multiple properties from a single scanning. Once the calibration model is built, soil samples of similar type and origin can be predicted with reasonable accuracy. For sand-based turf soil, especially putting greens constructed following USGA specifications with similar sources of parent materials, generalization of calibration models would be possible. Further efforts could concentrate on adding more representative samples from sand-based turf soil into building the calibration model to increase the overall robustness and prediction accuracy.

References

Ben-Dor, E., and A. Banin. 1995. Near infrared analysis as a method to simultaneously evaluate several soil properties. Soil Sci. Soc. Am. J. 59:364-372.

Bolster, K.L., M.E. Martin, and J.D. Aber. 1996. Determination of carbon fraction and nitrogen concentration in tree foliage by near infrared reflectance: a comparison of statistical methods. Can. J. For. Res. 26:590-600.

Bremner, J.M. 1996. Nitrogen-total. p. 1085-1122. *In* D.L. Sparks et al. (ed.) Methods of soil analysis. Part 3. SSSA Book Ser. 5. SSSA, Madison, WI.

Carrow, R.N., J. Krum, J. Hartwiger. 2009. Precision turfgrass management: A new concept for efficient application of inputs. USGA Turfgrass Environ. Res. Online. 8:1-12.

Chang, C.W., D.A. Laird, M.J. Mausbach, and C.J. Hurburgh. 2001. Near infrared reflectance spectroscopy-principal component regression analyses of soil properties. Soil Sci. Soc. Am. J. 65:480-490.

Coleman, P.B. 1993. Theoretical considerations. p. 1-10. *In* P.B. Coleman (ed.) Practical sampling techniques for infrared analysis. CRC Press, Boca Raton, FL.

Couillard, A., A.J. Turgeon, J.S. Shenk, and M.O. Westerhaus. 1997. Near infrared reflectance spectroscopy for analysis of turf soil profiles. Crop Sci. 37:1554-1559.

Dalal, R.C., and R.J. Henry. 1986. Simultaneous determination of moisture, organic carbon, and total nitrogen by near infrared reflectance spectrophotometry. Soil Sci. Soc. Am. J. 50:120-123.

Hendershot, W.H., H. Lalande, and M. Duquette. 1993. Ion exchange and exchangeable cations. p. 167-176. *In* M.R. Carter (ed.) Soil sampling and. methods of analysis. CRC Press, Boca Raton, FL.

Janik, L.J., S.T. Forrester, and A. Rawson. 2009. The prediction of soil chemical and physical properties from mid-infrared spectroscopy and combined partial least-squares regression and neural networks analysis. Chem. and Intell. Labor. Syst. 97:179-188.

Janik, L.J., R.G. Merry, and J.O. Skjemstand. 1998. Can mid infrared diffuse reflectance analysis replace soil extractions ? Austr. J. Exp. Agric. 38:681-696.

Janik, L.J., and J.O. Skjemstad. 1995. Characterization and analysis of soils using mid-infrared partial least-squares: II. Correlations with some laboratory data. Aust. J. Soil Res. 33:637-650.

Johnston, C.T., and Y.O. Aochi. 1996. Fourier transform infrared and Raman spectroscopy. p. 269-321. *In* D.L. Sparks (ed.) Methods of soil analysis. Part 3. SSSA Book Ser. No. 5. SSSA, Madison, WI.

Keeney, D.R., and D.W. Nelson. 1982. Nitrogen-inorganic forms. p. 643-687. *In* A.L. Page et al. (ed.) Methods of soil analysis. Part 2. Chemical and microbiological properties. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

Madari, B.E., J.B. Reeves III., P. Machado, E. Torres, C.M. Guimaraes, and G.M. McCarty. 2006. Mid- and near-infrared spectroscopic determination of soil compositional parameters and structural indices in tow Ferralsols. Geoderma 136:245-259.

Malley, D.F., P.D. Martin, and E. Ben-Dor. 2004. Application in analysis of soils. p. 729-784. *In* C.A. Roberts et al. (ed.) Near-infrared spectroscopy in agriculture. Agron. 44. ASA, CSSA, and SSSA, Madison, WI.

McCarty, G.W., J.B. Reeves, V.B. Reeves, R.F. Follett, and J.M. Kimble. 2002. Mid-infrared and near-infrared diffuse reflectance spectroscopy for soil carbon measurement. Soil Sci. Soc. Am. J. 66:640-646.

McClean, E.O. 1982. Soil pH and lime requirement. p. 199-224. *In* A.L. Page et al. (ed.) Methods of soil analysis. Part 2. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

McClellan, Ty.A., R.C. Shearman, R.E. Gaussoin, M. Mamo, C.S. Wortmann, G.L. Horst, and D.B. Marx. 2007. Nutrient and chemical characterization of aging golf course putting greens: establishment and rootzone mixture treatment effects. Crop Sci. 47:193-199.

Minasny, B., A.B. McBratney. 2008. Regression rules as a tool for predicting soil properties from infrared reflectance spectroscopy. Chemom. Intell. Lab. Syst. 94:72-79.

Minasny, B., G. Tranter, A.B. McBratney, D.M. Brough, and B.W. Murphy. 2009. Regional transferability of mid-infrared diffuse reflectance spectroscopic prediction for soil chemical properties. Geoderma 153:155-162.

Morra, M.J., M.H. Hall, and L.L. Freeborn. 1991. Carbon and nitrogen analysis of soil fractions using near infrared reflectance spectroscopy. Soil Sci. Soc. Am. J. 55:288-291.

Nelson, D.W., and L.E. Sommers. 1982. Total carbon, organic carbon, and organic matter. p. 961-1010. *In* D.L. Sparks et al. (ed.) Methods of soil analysis: Part 3. No. 5. ASA and SSSA, Madison, WI.

Reeves, III, J.B., G.W. McCarty, and V.B. Reeves. 2001. Mid infrared diffuse reflectance spectroscopy for the quantitative analysis of agricultural soils. J. Agric. Food Chem. 49:766-772.

Rhoades, J.D. 1982. Soluble salts. p. 167-179. *In* A.L. Page et al. (ed.) Methods of soil analysis. Part 2. Agron Monogr. 9. ASA and SSSA, Madison, WI.

Shi, W.E., D.B. Dell, and K. Iyyemperumal. 2006. Soil enzyme activities and organic matter composition in a turfgrass chronosequence. Plant Soil 288:285-296.

Sørensen, L. K., and S. Dalsgaard. 2005. Determination of clay and other soil properties by near infrared spectroscopy. Soil Sci. Soc. Am. J. 69:159-167.

Stowell, L. J., W.D. Gelernter. 2001. Diagnosis of turfgrass diseases. Annu. Rev. Phytopathol. 39:135-55.

Westerhaus, M., J. Workman, Jr., J.B. Reeves III, and H. Mark. 2004. Application in analysis of soils. p. 133-174. *In* C.A. Roberts et al. (ed.) Near-Infrared spectroscopy in agriculture. Agronomy 44. ASA, CSSA, and SSSA, Madison, WI.