Soil Organic Matter Characterization and CO_2 Flux in Long-Term Experiments

by

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Abstract

Increasing global concentration of atmospheric CO_2 predating the beginning of industrial era mostly due to fossil fuel combustion, deforestation and changes in land management has necessitated studies that will quantify the relationship between soil organic matter fractions and CO_2 efflux from soils. Our studies evaluated the different fractions of soil organic matter (SOM) and CO_2 effluxes from known long-term experiments and chemically characterized functional groups of SOM from those plots. These long-term plots, the Old Rotation [c.1896] and the Cullars Rotation [c.1911] are located in Auburn University, Auburn, Alabama.

A two-year seasonal study was conducted to characterize fractions of SOM and determined carbon (C) and nitrogen (N) contents in Total, Light and Heavy SOM components. Efflux of CO_2 was also measured and SOM was chemically characterized. Total organic carbon (TOC) was determined by combustion. The Light component was determined by multiple extractions through a Millipore extraction set up with a 1.7 g cm^{-3} sodium iodide (NaI) solution and analyzed for TOC in the light fraction (LF). The passive and slow components that made up the heavy fraction (HF) were calculated by differences between the Total and the Light components. The CO_2 efflux was measured using

LiCOR 6200 placed on a ten centimeter polyvinyl chloride (PVC) pipes placed in between rows. The chemical characterization was performed through a sequential extraction of fulvic acid (FAs) component of SOM with 0.1 M sodium pyrophosphate. The extracted FAs were freeze-

dried and then kept refrigerated until ready to be analyzed. The analysis was done by Fourier Transform Infrared Analyzer (FTIR) to elucidate the functional groups in the samples.

Our study indicated that crop rotation and fertilizer application increased organic carbon accumulation in the soils. The Heavy fraction of carbon was ten times greater than the Light fraction. Plots with two to three year crop rotations in the Old Rotation had accumulated more organic matter fractions than the yearly and mono cropping systems. In the case of the chemical characterization, less transmittance intensities were seen for sodium pyrophosphate extractable organic functional groups in the 0-5 cm samples compared to 5-10 cm depth. In generally, treatments and crop rotations contributed to the presence of diverse organic functional groups. The CO_2 effluxes for the summer seasons were greater than their corresponding fall seasons for both years of the study. The summer 2010 CO_2 effluxes were greater than the summer 2008 effluxes for both locations. Soil CO_2 was affected by crop rotation and fertilizer treatments in both locations. In general, CO_2 effluxes were affected by factors that are interrelated and interdependent.

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CR	Cullars Rotation
DOM	Dissolved organic matter
FTIR	Fourier Transform Infrared
HF	Heavy Fraction
HFOC	Heavy Fraction Organic Carbon
HFON	Heavy Fraction Organic Nitrogen
LF	Light Fraction
LFOC	Light Fraction Organic Carbon
LFON	Light Fraction Organic Nitrogen
OR	Old Rotation
PYSOM	Pyrophosphate Extracted Soil Organic Matter
SOM	Soil Organic Matter
SF	Slow Fraction
TF	Total Fraction
TFON	Total Fraction Organic Nitrogen
TFOC	Total Fraction Organic Carbon
WSOM	Water Soluble Extracted Soil Organic Matter

Chapter 1: General Introduction and Literature Review

1.1 Introduction

Soil organic matter (SOM) is a basic, dynamic and very important component of a soil. SOM plays a major role in physical, chemical and biological properties of the soil. It significantly impacts soil productivity, serves as a terrestrial pool for carbon (C), and is a very sensitive and responsive soil property. SOM is a transitory component of the soil that is affected by soil property and management. Carbon dioxide (CO_2), which forms a major component of the greenhouse gases, can be sequestered through the accumulation of SOM in long-term conducive agricultural practices.

Apprehensions of current times with regards to global climate changes call for a critical look at decreasing atmospheric CO_2 by enhancing the storage of carbon in the soil by manipulation of soil management practices, land usage, climatic, edaphic and environmental influences. Soil organic carbon (SOC) pools had been proposed (Smith and Shuggart, 1993) as the longer term transient sink for much of anthropogenic carbon from the atmospheric CO_2. SOC pools play vital roles in modeling the anthropogenic changes that occur to the global carbon cycle. However, numerous human activities such as deforestation, conventional farming, biomass burning and other similar practices will accelerate CO_2 efflux from the SOM pool. In the past 15 to 20 years, different models have been proposed and used to predict soil carbon dynamics; each has its disadvantages and advantages depending on the circumstances under which they are used

Most of these SOC models use localized data and then extrapolate these data sets to meet regional and global scales. Notable among these models are the CENTURY (Parton et al., 1987); Rothamsted, EPIC (Sharpley and Williams, 1990); Woodruff Type (Woodruff, 1949); van Veen and Paul Models (van Veen and Paul, 1981). According to the CENTURY model the SOC can be grouped into five notable groups:

(i) Structural organic carbon – which is the carbon within woody tissues with three years as a turnover rate.

(ii) Metabolic carbon – plant based with 0.5 year as turnover rate

(iii) Active SOC – with 1.5 years turnover rate and mostly made of decomposing plant and animal residue in the soil.

(iv) Slow SOC – with not less than 25 years turnover rate and,

(v) Passive SOC - with over 1000 year's turnover rate.

A series of factors affect soil carbon pools and their distribution in the soil. Climatic factors such as temperature and precipitation exert much influence on the carbon inputs into soils as well as ensuring carbon within the soil is also recycled through the SOC and finally effluxes into the atmosphere as CO_2.

The dynamics of total organic carbon (TOC) can best be described by partitioning TOC into two or more fractions by physical fractionations method. Fractionation of TOC by physical methods is used to separate the specific carbon pools which are responsive to management and the physical control of the SOM (Cambardella and Elliot, 1993). Hence it is prudent to quantify these carbon pools by estimating their true values from soils under different soil treatments.

1.2 Literature Review

Allocation of SOC to different fractions and/or pools in the soil can be attributed to the changes in land usage and soil management procedures. Carbon fractions show different interactions and accessibilities (Sollins et al., 1996) as well as different rates of microbial and biochemical degradative processes (Stevenson, 1994). Numerous factors influence the capability of the soil to store SOM. Types of vegetation, climate, soil management practices, types of soil and landscape impact SOM.

The influence of vegetation differences can be attributed to carbon partitioning and fixing capability as well as capacity which result in differences such as root/shoot ratios, quantity of root exudates deposited and the thickness of roots and root biomass. The above-mentioned factors can impact SOM mineralization as well as accumulation in soils (Juma, 1993). Shifting vegetation usage can also directly influence SOM increment in soils, and highly fertilized plots have a higher rate of SOM accumulation, but this occurs at a “carbon” cost (Schlesinger, 1990). The impact of climate can be summarized as the interrelationship between the mean annual rainfall and temperature; warm climates enhance organic matter decomposition, whereas cool wet, climate delays decomposition and thereby enhance SOM accumulation (Cole et al., 1993; Tate, 1992). From a soil management point of view, results from long-term rotation experiments show increasing inputs of carbon in the form of plant residue can lead to a gradual accumulation of organic matter over time with particular emphasis on arable farming systems (Jenkinson, 1990).

Soil management practices also involved methods that make changes in microclimate such as reduced tillage and accumulation of mulches on the soil surfaces which are influenced by vegetation, or cropping practices. Beneficial effects of cover cropping of the soil cannot be underestimated, thus rendering winter cover cropping as one of the salient means of preventing soil erosion through cost effective and environmentally sound mechanisms (Lal et al., 1991; Recoisky and Forcella, 1998).

Different types or fractions of organic matter, namely particulate or macroorganic matter encompass recognizable parts of plant debris in the soil and constitute 18 to 40% of total organic matter with 1 to 5 years as turn-over periods (Gregorich et al., 1994; Parton et al., 1987). Carbohydrates and humic or fulvic acids make up the chemically sequestered organic matter, constituting 20 to 40% by total composition and their turn- over ranges between 1000-3000 years. The light fraction (LF) components constitute 10 to 30% of total SOC with 1 to15 years as turn over period (Parton et al., 1987). The light fraction is described as physically uncomplexed organic matter, and the heavy fraction is also described as the organic matter that is physically stabilized by soil minerals (McLauchlan and Hobbie, 2004; and Gregorich et al., 2006).

The light fraction of SOM is considered as a transitory pool between the stable organic matter, the humified and fresh plant and animal residues (Christensen, 1992); hence anything that affects its accumulation or degradation affects its accumulation and concentration in the soil. The concentration of LF in soils depends on the quantity, the accessibility of added residues, the chemical composition of the residue itself, moisture, temperature and nutritive contents which affect microbial degradation.

1.2.1 Decomposition Process of Carbon in the Terrestrial Agroecosystems

Many factors enhance carbon decomposition in SOM. Type of plant material and/or residue, the quality and quantity of the residue and temperature of the soil significantly affect carbon decomposition. These factors play a major role in organic matter (OM) decomposition to dissolved organic carbon (DOC), methane (CH_4) and CO_2 (Martens, 2000; Blanco-Canqui and Lal, 2004).With respect to the plant residue, the driving force behind the decomposition rate is primarily based on the type of carbon compounds within the plant (e.g. starches, celluloses, lipids, proteins and phenolic compounds). The ratio of the above classes of organic compounds in the plants/residue depends on the age of the plant, the type of plant and /or species of the plant. The turnover rates of these compounds depend solely on the C:N ratio as well as the class of carbon, which further strongly influences the decomposability of the residue. Among these classes of carbon compounds, lignified materials serve as the most recalcitrant carbon (Cheshire and Chapman, 1996; Martens, 2000). The quantity and quality of any plant residue are major determinants of the amount of carbon encapsulated within soil aggregates. Also, the physico-chemical protection of any SOM depends mostly on the capability of the encapsulation within stable aggregates.

Soil temperature specifically is one of the major factors that regulates the decomposition rate of SOM, with marked seasonal variations in higher CO_2 concentrations and DOC in the summer compared to corresponding winter seasons (Bonnett et al., 2006; Hope et al., 2004). However, temperature decomposition sensitivity is still debatable (Davidson et al., 2006) with some arguments that recalcitrant OM were shown not to be correlated with temperature sensitivity (Giardina and Ryan, 2000), whereas other studies showed that labile pools of SOM are less sensitive to temperature than the non-labile components (Knorr et al., 2005).

1.2.2 Soil Organic Matter under Cropland Ecosystems

The LF of SOM is the incomplete degraded plant and animal debris, and their associated microorganisms. LF is the relatively mineral-free component of the soil with density ranging between 1.5 to 2.0 gcm^{-3} with a relatively wide C:N ratio. It is biologically active and has a very rapid turnover rate (Sollins et al., 1984).

Initial cultivation of forest land and virgin lands culminates in significant loss of the LF loss of SOM. Greenland and Ford (1964) reported that the LF carbon is much more abundant in lateritic red soils under native vegetation as compared to cultivated arable land in the ratio of 4:1. However, the LF represents a smaller fraction of the TOC in cultivated arable soils than in virgin land soils. Skjemstad et al. (1986) reported that virgin soil had 9% of carbon from LF as compared to 1% from cultivated land. The loss of LF is seen to occur just after cultivation, which is indicative of the observation that LF is a highly decomposable and transitory. This loss was also reported and confirmed by Adams (1980) that most macro organic matter content of soils decomposed within the first three years of arable cropping on virgin land with subsequent decrease with usage. The placement of recent plant residues contributes a lot to the distribution of LF in the soil profile. Garwood et al. (1972) and Spycher et al. (1983) reported grassland and forest showed sharp declines in the amount of LF and organic carbon. The LF below the surface 2 to 3 cm consistently diminished within the soil profile.

The effects of winter cover crops on no-till corn (*Zea mays L*) and soybean (*Glycine max [L] Mer*r.) cropping systems have been widely reported, but without any report on soil quality (Villamil et al., 2006). The same authors reported on crop sequences including vetch or a mixture of rye, and vetch had the ability to increase the SOM content up to 30 cm below the soil surface. However, with no–tillage practices, residues placed on the soil surfaces seemed to have little lasting impact on the organic matter related soil properties. The humidified organic matter within the soil surface layers were enhanced by the continual addition and decomposition of residue, which also enhanced the aggregate stability of the soil and no-tillage practices stimulate soil carbon sequestration, especially during the initial stages of the no-tillage practice (Dick et al., 1997). With speculations about eventual carbon market underway, this phenomenal development could serve as an additional source of income to the farmers due to the enhancement of carbon sequestration (Ribaudo et al., 2007).

1.2.3 Chemical Composition of LF

The inputs of carbon are the primary factor that controls the chemical composition of LF and macroorganic matter, namely the extent, nature of decomposition processes in the soil and type of vegetation. LF is highly endowed with plant nutrients and organic carbon, where the concentrations of nitrogen and organic carbon range from 0.5 to 2.0% and 20 to 30% respectively, even though the LF occupies an insignificant portion of the mass. LF harbors a major amount of the total soil carbon (2 to 18 %) and of total nitrogen (1 to 12 %) (Janzen et al., 1992).

The enhanced loss of LF in virgin soils is attributed to several factors such as residue inputs, decomposition rates, soil disturbances due to tillage, and greater quantity of decomposable materials (Gregorich and Janzen, 1996). However, due to the small quantity of mineral matter in the LF, the carbon concentration in the LF is usually smaller than the plant tissues. It is noted that the organic matter in the LF is made up of plant debris.

Even though simple models have been used to describe long-term soil organic matter dynamics, the process of plant material decomposition can be described as very complex

(Jenkinson, 1990). The C: N ratio of the LF is usually an intermediate between the values of that of the whole soil. Whalen et al. (2000) suggested the LF component of SOM could be a major donor of mineralizable C and N since it shows a closer relationship to N mineralization rate (Barrios et al., 1996), proves to be a short term sink of N in magnitude rather than the heavy fraction (Compton and Boone, 2002) and then serves as fulcrum for soil respiration (Alvarez and Alvarez, 2000)

1.3 Soil Organic Matter Characterization

The operational definitions of SOM fractions based on solubility were first introduced by Sprengel (1837). Soil scientists classified humic acids (HAs) as humus materials that are soluble in aqueous alkaline solutions, but precipitate when the pH is adjusted to 1 (water scientists consider the precipitates at pH= 2 to be HAs) (Hayes, 2006).

SOM can be chemically characterized to different distinct components. The general name under which SOM can be classified is called humic substances (HSs) which is very heterogeneous in nature and based on their individual aqueous solubility properties. Stevenson (1994) also described HSs as the very dark, relatively very high molecular weight compounds formed through secondary synthesis reaction within the soil. Piccolo et al. (2001) considered HSs to be molecular associations formed by the self-assembly of supramolecular molecules arising from "the affinities of certain molecules in aqueous solutions."

Under this major component, SOM could further be classified as Humic Acids (HAs) which are defined as the component of HSs and are insoluble in water under acidic pH conditions but soluble under alkaline pH conditions. Fulvic acids (FAs) also are defined as the fractions of HSs which are soluble under a very wide range of pH. FAs are also components that stay in solution if soil extracts are adjusted to very low acidic pH. Humin is the fraction that is insoluble in any aqueous media under any pH range (Aiken et al., 1985). The importance of HSs in soils cannot be overemphasized as they play very vital roles, including cation exchange for the release of nutrients such as potassium(K), calcium (Ca) and magnesium (Mg) as well as other nutrients such as N, P and S and serve as glue to enhance aggregate stability and hydraulic conductivity (Masri et al., 1996).

1.3.1 Separation Methods of LF

About 1 to 25% of SOM may be made of LF pools in cultivated agricultural soils, and these pools could serve as a labile source of mineralizable carbon and nitrogen (Greenland and Ford, 1964; Janzen et al., 1992); however, in forest soils, these values could be up to 63% of SOM (Strickland and Sollins, 1987; Boone, 1994). The LF component of soil is normally isolated through techniques of densimetry on liquid media of density ranges between 1.5 and 2.0 g/cm^3. This is the density ranges that had been found to yield a substantial amount of plant debris (Turchenek and Oades, 1979). On average, the density of soil minerals is around 2.65 g/cm^3 and hence any material with a lesser density will float in a liquid media with a lesser density than that of the soil mineral. Slight deviations in the density of the media could cause a big variation in the carbon concentration of the LF in range of 1.9 to 2.4 g/cm^3 (Richter et al.,1975).

A variety of liquid media whether organic or inorganic, has been employed in the separation of plant debris and LF from heavier soil minerals (Christensen 1992; Gregorich and Ellert, 1993). Some of the organic media come with toxicity problems, coagulation of suspended molecules, and contamination of separated carbon materials. However, most of these problems have been solved by the use of inorganic solvents such as potassium iodide (KI) and sodium iodide (NaI).

1.3 2 **Impact of Land Management Practices on CO_2 Efflux**

Increasing human concern over the possibility of global warming and its antecedent environmental outcries has pushed debate into scientific and political discussions from one protocol gathering to the other over the past many decades. The basis of these assertions are as a results of the increased emission of the greenhouse gases such as methane (CH_4), nitrous oxide (N_2O) and carbon dioxide (CO_2) from the surface of the soil into the atmosphere (Jabrow et al., 2008). Rastogi et al. (2002) reported that CO_2 accounts for almost 60% of the total greenhouse effect. Jensen (1993) reported soil as a major source and sink for CO_2 from the atmosphere. Measuring soil CO_2 flux is very important for accurate assessment of land management on carbon cycling and global warming effects.

Land management practices have a direct impact on soil moisture content and temperature that invariably influence CO_2 fluxes from the soil surface (Al-Kaisi and Yin, 2005; Amos et al., 2005). Usage of tillage implements on the land can lead to drying conditions whereas non-tillage practices such as conservation tillage leads to moisture retention in the soil and temperature reduction due to increased residue accumulation on the soil. Presence of residue on the soil surface leads to reduction in temperature due to fewer disturbances caused to the soil (Al-Kaisi and Yin, 2005; Curtin et al 2002).

Reicosky et al. (1999) found that on a short and cumulative basis of CO_2 effluxes, there is a decreased CO_2 efflux under no-tillage practices than their corresponding conventional tillage practices. Al-Kaisi and Yin (2005) also reported a 24% emission accumulation of soil CO_2 under no-tillage practices with residue than plots without residue in their 480 hours study.

Soil moisture content and temperature can be affected by soil management practices that invariably influence CO_2 flux (Parkin and Kaspar, 2003). Amos et al. (2005) reported that increased above and below ground level biomass production as well as deposition of crops can enhance the amount of residue deposition. This also leads to increase below ground deposition which further leads to increase CO_2 flux. The decomposition rate of the residue depends on residue quality in terms of C:N ratio (Kuo et al., 1997; Sainju et al., 2002).

Many studies consider the importance soil temperature plays on the various salient processes that occur in the carbon cycle. An increase in soil temperature has compounding effects on microbial and root activity, oxidation of OM, and mineralization processes of carbon which further enhances CO_2 production and efflux from the soil (Davidson et al., 1998). Boone et al. (1998) reported an exponential increase in CO_2 activity as a function of temperature.

Several studies report a linear, parabolic, quadratic and logarithmic relations between soil moisture content effect on water holding capacity, gravimetric or volumetric water content and matric potential (Davidson et al., 2000). Increasing soil moisture content impacts soil respiration by providing a better condition for microbial activities within the soil, which further enhances CO_2 production and its emission from the soil as a result of more oxygen consumption by soil inhabiting microbes (Buyanoski and Wagner, 1983). Reicosky and Lindstrom (1993) reported rapid physical release of CO_2 from the soil due to the tillage effect on a short-term basis that was due to the release of trapped CO_2 in the soil spaces and also keeping residue on the soil reduced CO_2 efflux rather than incorporating them into the soil. SOC has been found to be higher in conservation tillage than the corresponding conventional tillage in the surface 5 cm of the soil within four years of tillage on a loamy sand soil, but many of the differences among the tillage study were found within 1 cm (Reeves and Delaney, 2002).

The amount of CO_2 emitted into the atmosphere differed with the tillage type and the amount correlated with the degree of soil disturbance (Prior et al., 2000). Later Prior et al. (2004)

again reported no difference in CO_2 efflux between spring and fall tillage and the undisturbed soil; however, there was a higher CO_2 efflux in fall tillage as compared to the undisturbed soil. The marked difference could be attributed to temperature effects which further affect microbial activities within the soil. In contrast, Rochette et al. (1997) reported a higher spatial variability in spring and the variability decreased throughout the year. Enhanced SOM decomposition rates due to cultivation accounts for much of the carbon losses from agricultural soils. Much of the higher organic carbon losses occur through erosion (Ewert et al., 2005; Freibauer et al., 2004).

1.3.3 Impact of temperature and moisture on Soil CO_2 Efflux

Soil temperature and moisture serve as a major determinant in soil respiration, which also leads to CO_2 efflux from the soil based on enhanced microbial respiratory activities in the soil. Also, land management efforts in terms of Conservation Reserve Program (CRP) can also influence the soil moisture content as well as temperature which also leads to impact CO_2 efflux from the soil surfaces (Al-Kaisi and Yin 2005; Amos et al., 2005; Bajracharya et al., 2000; Curtin et al., 2002; Parkin and Kaspar, 2003). For example, minimal disturbance of the soil can accumulate much residue on the surface, conserve much moisture within the soil, and also reduce the temperature; however, the above named features could be increased by tillage.

An increase in soil temperature could directly be linked to faster and enhanced microbial activity, faster rate of organic matter decomposition as well as root activity, oxidation processes and carbon mineralization which could culminate in much soil respiration and CO_2 efflux. Studies have shown the relationship between soil moisture content and soil respiration. Davidson et al., (2000) in a pasture and forest soil study, reported an increment in soil respiration with respect to rising water in both locations. They further developed a regression equation showing “soil respiration as a function of soil matric potential and concluded that CO_2 flux correlated with soil matric potential in opposite directions.” The same authors described the relationship between soil moisture content and CO_2 efflux from the soil as linear, quadratic, parabolic and logarithmic equations.

Buyanowski and Wagner (1983) also reported the link between soil moisture content and soil respiration; asserting that higher moisture content of the soil provides conducive environments for the soil microbes, thereby increasing oxygen consumption as well as respiring greater CO_2 and efflux from the soil. Careful irrigation practices could also help in minimizing the emission of CO_2 to the atmosphere. Strip tillage and minimal and or no-tillage practices had been reported to effectively reduce CO_2 emission as perennial forage lands are being converted into annual crops (Jabrow et al., 2008).

1.4 Experimental Sites

1.4.1 Cullars Rotation (circa 1911)

The Cullars rotation experimental site is a 3-year rotational study started in 1911 primarily to study the impacts of long-term potassium, lime and other nutrient requirements on small grains such as cotton, corn, summer legumes, soybean and cowpea. The site has three tiers with fourteen plots per tier. Each plot within the tier is 6.7 x 33 m separated by 0.6 m to the next plot and 6.7 m between each tier. The experimental site was started with eleven plots numbered 1 through 11 with an additional three plots numbered, A, B, and C added in 1914 to see the impact of winter legumes in the rotation. The site is located within the Coastal Plains physiographic region and the soil is classified as a Marvyn loamy sand (fine –loamy, siliceous, thermic, Typic Kanhapludults) (Mitchell et al., 2005). This site is the fifth longest crop experiment in the US and the first to have treatment replications.

1.4.2 Old Rotation (circa 1896)

The Old Rotation, the oldest continuous cotton experiment site in the world, was started in 1896. The area of the experimental site serves as a boundary between Coastal Plain and Southern Piedmont Plateau physiographic region of the eastern part of Central Alabama. The site has an average annual rainfall of 1339 mm with annual temperature range around 18^{o}C. The site has an area of 1 hectare with 13 plots. The size of each plot is 6.5 m by 41.4 m. The soil at the site is classified as Pacolet fine sandy loam (clayey, kaolinitc, thermic, Typic Hapludults). The site has a three rotation systems with a 1- year, 2-year, and 3-year rotation including cotton, corn winter legumes, and soybeans or cowpea and small grains.

1.5 Research Justification

The increase in atmospheric CO_2 concentration from the 1850s from 260 ppm to 380 ppm (v/v) currently has prompted calls for concerted efforts from all fronts of human endeavor to lower the CO_2 concentration, in order to reduce global warming and climate change. One way is to successfully sequester the atmospheric C into the soil.

Enhanced photosynthetic activity will lead to more biomass production, thereby incorporating more plant residues into the soil, a practice which will further serve to reduce erosion. The OM formed as a result will serve as a binding agent or absorbent to hold moisture in the soil and increase soil particle aggregate stability. Assessing the different fractions of organic matter in the soil, characterizing the functional groups and also measuring the CO_2 efflux under different spans of rotations and fertility trials will enable us to better understand the impact of these factors on CO_2 efflux to reduce the atmospheric CO_2 concentration.

1.6 General Objectives

(i) To quantify soil organic fractions into light and heavy fraction pools by physical methods in the long-term experiments.

(ii) To measure the CO_2 effluxes under different crop and management systems in the long term experiments.

(iii) To determine the major functional groups of the extracted SOM in the long-term experiments.

(iv) To establish a relationship among the above parameters.

1.7 Dissertation Outline

Chapter One: Introduction and literature review.

Chapter Two: physical separation of soil organic matter into the three major pools seasonal and yearly variability of carbon, nitrogen, and C:N ratio.

Chapter Three: Seasonal fluctuations of the CO_2 efflux amongst the different treatments of the two long-term experimental plots.

Chapter Four: Chemical characterizations of SOM from these long-term experiments.

Chapter Five: Conclusion, summary and future studies.

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Chapter 2: Physical Soil Organic Matter Characterization in Long-term Experiments

Abstract

Sodium iodide (NaI) solutions were used to extract light density organic matter (LDOM) from seasonally sampled composite oven-dried soils from 2 long-term cropping experiments. Extracted LDOM and total soil were analyzed for nitrogen (N) and carbon (C). Their C:N ratios were calculated for the LDOM, heavy (slow and passive) and total. Our results indicated cropping system variability contributed to the differences among the different SOM fractions as well as among C, N and C:N ratio. Among the fractions in the Old Rotation, light fraction organic nitrogen (LFN) of the plot with inorganic ammonium nitrate fertilization treatment had 6.6% nitrogen in 2008, whereas there was more than 50% reduction for the 2009 corresponding value. In contrast, no nitrogen, and no winter legume treatment plots in 2009 had significantly greater nitrogen compared to the nitrogen treated plots and two-year crop rotated and winter legume treatments. Similar trend was observed for the light fraction organic carbon (LFC).

However, heavy fraction organic nitrogen fractions (HFN) for both 2008 and 2009 were not significantly different among the treatments. For heavy fraction organic carbon, only the inorganic nitrogen fertilizer treated plot were significantly different in 2008 and 2009. In Cullars Rotation, no nitrogen, and no winter legume treatments in addition to the no-potassium, and complete fertilization with micronutrients treatments showed a significantly different compared to the rest of the treatments for light fraction organic nitrogen in 2008. In 2009, no phosphorous treatment and complete fertilization treatments were significantly different from the other treatments. In 2008 and 2009, none of the

treatments in both years showed any significant difference for HFN. In 2008, no nitrogen, and no winter legume treatments showed very high significant difference followed by the no potassium and complete fertilization with micronutrients treatments compared to the rest of the treatments for LFC. However, in 2009, no fertilizer treatment, no nitrogen but winter legume treatments had a significant difference as compared to the rest of the treatments.

2.1 Introduction

Soil organic matter (SOM) is a transitory component of the soil with major impact on soil fertility and other soil properties. However, from the 1980s SOM has emerged as a major component of atmospheric CO_2 studies. This chapter will focus on the physical characterization of soil organic carbon (SOC) pools and their intrinsic major elements of carbon and nitrogen.

Most previous studies characterizing soil organic pools have been based on the assumptions of models that make use of local data sets and project such datasets onto regional and global scales. However, using long-term plots as a source of database will generate a historic contribution from these plots. Scientists of today should examine long- term plots with major focus of carbon sequestration potentials and then characterize these pools properly and exhaustively.

2.1.1 Factors Impacting Soil Organic Carbon Pools

Many factors influence SOM pools. Many researchers have examined the role of soil forming factors such as climate, soil organisms, and the others (Glinka 1927; Jenny 1941). Johnson et al., (1995) have suggested, but not limited to factors such as crop rotation instead of monocropping, changing soil inputs to enhance primary production, reduction in tillage intensity, fallowing of soils and using winter cover cropping to increase SOC.

2.1.2 Climate

Climate influences most ecosystem properties including soil carbon cycling by controlling composition from plant communities and their productivity. This further affects quality and quantity of SOC pools, decomposition activities, and microbial community composition (Holdridge, 1947). Jenny (1930) used differences in climate to explore the impact of moisture and temperature on SOM across the Great Plains and reported SOM concentration were lesser in hotter and drier southwest, whereas it was greater towards wetter and cooler northeast. Thus, high elevations and altitudes have greater carbon stocks than their corresponding lower elevations or tropical climate.

2.1.3 Soil Organisms

Soil organisms, which include soil inhabiting microbes, plants and animals, control the position and location as well as the chemical form of SOM. Jobbágy and Jackson (2000) reported a significant correlation by analyzing over 2700 soil profiles between the vegetation types with SOC and its distribution along the soil profile. They further reported that vegetation exerts an influence on soil carbon in many ways and forms. This correlates with climate. The net primary production (NPP), which depends on plant community and species, shows the impact in the amount of carbon inputs into the soil. However, for soils with the same rate of decomposition, plants with more vegetation production will sequester a greater quantity of organic carbon. The conversion of forest ecosystems to arable agriculture and/or pasture could lead to a significant loss of carbon due to the reduction in the NPP (Trumbore et al., 1995).

2.1.4 Soil Organic Matter

Soil organic matter is defined as the "the organic fraction of the soil exclusive of undecayed plant and animal residues" (SSSA, 1997). This term is similar in meaning to "humus." However, Nelson and Sommers (1982) defined SOM as organic materials accompanying soil particles passed through 2 mm sieves. It occupies up to 5% of the total volume of soil and has several advantages such as being a source of essential plant nutrients such as carbon, nitrogen, phosphorous, sulfur and micro nutrients for plant growth and nutrient cycling. SOM enhances aggregate stability, soil porosity, water- holding capacity, soil tilth, crop production and overall soil sustainability (Bauer and Black, 1994; Lal et al, 1997; Reeves, 1997).

An increase or decrease in SOM could be attributed to agricultural management practices. The practice of optimizing agricultural management for SOC increment could lead to enhanced atmospheric CO_2 sequestration (Sampson and Scholes, 2000). As a result of the numerous advantageous effects of SOM on nutrient status, soil structure, and water holding capacity, it is very desirable to maintain the organic matter content of lands intended for long-term usage (Allison, 1973).

2.1.5 Soil Organic Matter Fractionation Process

There are several methods of separating SOM fractions namely size, aggregation and density with the goal of isolating SOC pools. The density approach takes advantage of the differences among the densities of the mineral linked organic matter and particulate organic matter (POM) by the basic method of floatation of the light fraction and the heavier fraction sinking in a dense liquid (Strickland 1987; Sollins et al. 1999). Gregorich et al., (1996) suggested the light fraction is partially degraded of more recent source C than the carbon in the heavy fraction (Trumbore and Zheng, 1996). Other studies undertaken by Rasmussen et al. (2005) and Swantson et al. (2005) showed that radiocarbon measurements revealed separated light fractions have slower mean residence time as compared to the heavy fraction. Other than the above mentioned factors, litter quality and quantity, plant biomass as well as human influence impact organic matter pools.

2.1.5.1 Soil Organic Matter Fractions

There are three distinct fractions of organic matter in soils namely passive, active and the slow components. Each of these fractions has different mean residence time (MRT) or turnover rates, depending on their chemical and biochemical constitutions. About two thirds of carbon in the terrestrial ecosystem is said to be SOC in active exchange with the atmosphere (Baes et al., 1977).

2.1.5.2 Passive and Slow Fractions

The passive fraction of the SOC constitutes the resistant pool and has mean residence time of centuries to millennia (Fortuna et al., 2003). The slow fraction (SF) of SOC has turnover time from years to decades, and is considered the pool which constitutes the recalcitrant C pool. The passive and the slow fractions constitute the heavy fraction (HF) component of SOM. The HF has contributed more to net nitrogen mineralization as compared to the light fraction (LF) since HF makes up greater proportion of total SOM (Boone, 1984; Strickland and Sollins, 1987). Again the HF of SOM has a more narrow C:N ratio than the LF and tends to be more difficult to decompose easily as the latter. Soil texture and land use impact differently on the relative contributions of the various fractions of SOM to nitrogen mineralization (Strickland and Sollins, 1987; Hassink 1995; Barrios et al., 1996).

2.1.5.3 Active Fraction

Several SOC turnover simulation models have been used to forecast changes with changing management and environmental conditions. Other studies have also suggested biosphere carbon is accumulating but values out of these studies are primarily estimates. Golchin et al. (1994) posited that active fraction (AF) has molecular chemistry resembling fungal and faunal compounds under various stages of degradation even though the bulk of it comes from young and partially decomposed plant materials. The AF of SOC pool has a limited mean residence time of days to months and can also be referred to as the LF fraction. Within this fraction, two distinct types of carbon from SOM, namely particulate and occluded carbon, are noted. Due to its short turnover time, LF is very sensitive to soil management changes as compared to whole soil (Swantson et al., 2002). Light fraction accounts for 2 to 5% of total soil organic carbon (Sohi et al., 2005). Carbon and nitrogen within LF have been found to be proportional to active microbial biomass (Hassink, 1995) as well as C and N content of the LF material (Janzen et al., 1992; Barrios et al., 1996). Additionally, Boone, (1994) suggested seasonality of litter inputs affects N mineralization in the LF pool, and the net N mineralization was greater in HF than LF (Sollins et al., 1984).

2.1.6 Total Carbon and Nitrogen in SOM

SOM is the N reservoir for organic farming and other well-managed agronomic farms, although it is made up of biologically inert and recalcitrant materials with turnover times in hundreds and thousands of years (Stevenson, 1994). If N-fixers are part of a rotation system or introduced into the systems, they have the tendency to increase soil carbon (Johnson and Henderson, 1995). Soil carbon declines with repeated cultivation of arable lands when there is not much return of residues back into the soil. Degradation of SOM and oxidation of SOC or a combination of any of the two factors are shown to decrease SOC (Follett, 2001; Paustian et al., 2000). The goals for this study are (i) physical fractionation of SOM among the major pools in long-term experiments, and (ii) quantify the N and C as constituents of these pools.

2.2. Materials and Methods

2.2.1 Site Description

These studies were started in 2008 on the historic Old Rotation (circa, 1896) and Cullars Rotation (circa 1911) of Auburn University, Auburn, Alabama. The Old Rotation is located at the boundary between Coastal Plain and Southern Piedmont Plateau Physiographic regions of the Eastern part of Central Alabama. The soil type at this location is Pacolet fine sandy loam (clayey, kaolinitic, thermic, and Typic Hapludults) within latitude 32^{o} 35′ and longitude 85^{o} 29′. The Cullars Rotation is located in the Coastal Plain Physiographic region and the soil is classified as Marvyn loamy sand (fine–loamy, siliceous, thermic, Typic Kanhapludults) within latitude 32^{o} 35′ and longitude 85^{o} 28′ (Mitchell et al., 2005). The Old and Cullars Rotations consist of 13 and 14 plots, respectively. Each plot in the Old rotation is 6.5 m wide by 41.4 m long, with 1 m alley separating each plot. The Cullars Rotation is made up of three similar blocks in dimension. Each plot within the block is 6.7 m x 33 m separated by 0.6 m to the next plot and 6.7 m separating each block (Hubbs et al., 1998).

2.2.2 Sampling and Extraction

Twenty core samples up to ten centimeter (cm) depth were randomly taken from each plot in the middle tier seasonally in 2008 and 2009, except the winter seasons. Each sample was separated between the depths of 0-5 cm and 5-10 cm, respectively. They were mixed separately and a composite sample was taken and oven–dried and then ground in Braun Pulverizer Type UA-53 (Braun Corp. Los Angeles, USA). Fifty grams of each oven-dried and milled sample was weighed into 250 mL centrifuge bottles and 100 mL sodium iodide (NaI) of density 1.7 g cm^{-3} was added (Gregorich and Ellert, 1993). The mixture was shaken for 15 minutes and centrifuged for another 15 minutes at a speed of 3500 revolution per second. The centrifuged samples were then separated between the suspended light density organic matters (LDOM) and the heavy (HDOM) settled. The light mixture was then gently decanted through a Millipore with 0.45 µm filter paper under water suction. This process was repeated three times to ensure all the available LDOM was separated from the soil. The NaI was saved for reuse unless the density fell below 1.7g cm^{-3}. The extracted samples were then washed thoroughly using 100 mL each of 0.1M calcium chloride ($CaCl_2$) solution to take off all the adherent salts on the LDOM and with deionized water. The final LDOM samples on the filter paper were dried in the oven at 50 ^oC overnight.

2.2.3 Elemental Analysis

The dried LDOM sample was prepared by weighing 0.1 g of the sample into an aluminum foil. An equivalent weight of tungsten powder was added to each sample to aid combustion in the Vario Macro CNS Elementar Analyzer GmbH (Elemental Analyzer Elementar American Inc., NJ). Carbon and nitrogen were measured in percentage based on the actual weight of the sample. Similarly, SOC was also measured by weighing 0.1 g soil sample and 0.1 g of tungsten and analyzed at 1150 ^oC. The components representing the Heavy components were calculated by subtracting the corresponding values of Light from the Total SOC.

2.2.4 Statistical Analysis

The data set for the three different SOM pools with their constituent elements were analyzed using the Repeated Measures procedure in the mixed model of statistical analysis system (SAS Institute Inc. Cary, NC.). A full model was developed with all the class statement variables such as depth of sampling, treatment, rotation, year; and then with 2- and 3-way interactions between the variables. Seasonal measurement and year were considered as repeated measures, treatment, depth and rotations of each plot combination as the main plot variable and fixed effect. Similarly, data sets for carbon and nitrogen under Light, Heavy and Total fractions with their constituent elements as well as C:N ratio were analyzed using the same mixed procedure described above. Compound symmetry covariant structures were imposed on the analysis with the assumption that all pairs of measurement are the same for each experimental unit. Protected least significant difference tests were performed to separate the means of all response variables of interest to us at $P<0.05$ significance level. In addition t-test for response variables among the treatments was compared.

2.3 Results and Discussions

2.3.1. Soil Organic Nitrogen Fractions

2.3.1.1 Old Rotation

Total soil organic nitrogen (TSON) in Old Rotation showed a lot of variability among the sampled treatments. A no-rotation with winter legume and two-year cropping rotation with inorganic nitrogen fertilizer and winter legume treatment were greater in 2008 compared to the other treatments (Table 2.4). In 2009, the one year winter legume treatment rotation was greater than the 3-year rotation treatments and the ammonium fertilizer treatment on the no rotation cotton was the least. The above treatments in 2009 were very significantly different from the rest of the treatments. As expected, no nitrogen and no winter legume treatments had the lowest TSON values and the values of 2009 were lower compared to the corresponding 2008. This could be due to the excessive rainfall in 2009, which could have enhanced more leaching than 2008. Under heavy fraction organic nitrogen (HFON), again winter legume under no- rotation treatment, 2-year rotation with inorganic nitrogen source and winter legume treatments in addition to 3-year rotation treatments had higher values compared to the other treatments. In 2009, the same no rotation with winter legume treatment showed a higher significant difference followed by the 3-year rotation treatment (Table 2.4). The trend seen was similar to Sollins et al., 1984 studies.

2.3.1.2 Cullars Rotation

In Cullars Rotation, irrespective of the type of fraction, the TFON values were similar for 2008 and 2009 values (Table 2.8). The TFON, the no-nitrogen and winter legume treatments, no-potassium treatment in addition to complete fertilization with micronutrient inclusive treatment showed marginally higher absolute values compared to no-treatment and no-potassium treatment in 2008. However, in 2009, the significant differences of the latter description were only seen with the no phosphorous treatment. The HFON was lowest for no treatment (Plot C) in 2008 and 2009. However, variability in the absolute values was seen among treatments in both years. In the case of LFON, though the absolute values were very low, the no potassium treatment and complete fertilization with micronutrient treatment were greater than the rest of the sampled treatments in 2008. For reasons unknown to us, the no-nitrogen and no-winter legume treatment, which is plot B, had a marginally greater absolute values increment over some of the inorganic fertilizer treated plots in both 2008 and 2009. Across the fractions, the same treatments showed some differences in SON we measured.

2.3.2 Soil Organic Carbon Fractions

2.3.2.1 Old Rotation

Soil organic carbon is a good measure for soil quality due to its influence on nutrient cycling, enhancement of water holding capacity of the soil, ensuring aggregate stability and soil structure. Soil organic carbon is correlated with nitrogen and can be said to be involved in the nitrogen cycle (Korschens, 1997). Generally, plots with no multiple cropping rotation and fallowing treatment showed less carbon accumulation (Potter et al., 1997). Fallowing is found to limit organic carbon sequestration. Our results indicated similar trend where neither the no-nitrogen nor winter legume inclusion showed the least accumulation of carbon for the different fractions of carbon. The total fraction organic carbon (TFOC) is directly related to the plant root mass and biomass production since plants contain greater than 40% carbon on dry basis. The

TFOC ranged between 8.4 g C kg^{-1} for the no-rotation treatment to 17.5 g C kg^{-1} in 2-year rotation treatment with inorganic fertilizer application and winter legume in the rotation in 2008 (Table 2.5). However, in 2009, the 3-year rotation with cotton-corn and soybean with winter legume showed the highest absolute values as compared to the rest of the treatments. It is no surprise to us to see the no-nitrogen and no-winter legume treatment under no rotation showed the least accumulation of the different fraction of organic carbon. With the exception of the no-rotation treatments with inorganic ammonium nitrate treatments and the 3-year rotation treatment in 2009, all the 2008 values were marginally greater than in 2009 (Table 2.5). The HFOC, except a 2-year rotation with winter legume and no nitrogen, the rest of the treatments had similar values among treatments in 2008. Again, all the treatments were greater than the No-N/No-winter legume treatment. However, in 2009, most of the 3-year rotation treatments were greater than the rest of the treatments. Among the rest of the treatments, the 2–year rotation with winter legume and no-rotation with winter legume had similar values that are different from the rest of the treatments. Again, within treatments and between 2008 and 2009, there was very high treatment variability. On the average, the light fraction organic carbon (LFOC) was between 10 to 15 times lower in term of magnitude as compared to TFOC and HFOC. In 2008, the ammonium fertilization treatment under no rotation had a greater value compared to the rest of the treatments for LFOC. A similar trend was seen in 2009; however, the absolute values in 2008 were greater than the corresponding 2009 values. This marked difference could be due to the excessive rainfall in 2009 in the study area.

Plots treated with higher rates of N fertilizer, winter legume and 2- or 3-year rotation of crops had higher accumulation of carbon (Table 2.2). This situation confirms assertions in the literature that multiple crop rotations coupled with winter cover crop cultivation add a lot C into the soil. The absolute values of TSOC in 2008 and 2009 were far greater than those of 1988 and 1992 as reported by Mitchell and Entry (1998) (Table 2.2). This indicates enhanced carbon sequestration under well managed cultural practices. This could also be due to the benefits of conservation practices started in 1997 in both locations of the study by changing the experiment from conventional tillage to strip tillage. Other reasons could be due to the method of organic carbon determination changes as well as different plant varieties that have better photosynthetic CO_2 consumption, leading to better biomass production and accumulation.

2.3.2.2 Cullars Rotation

The general trends seen in the Cullars Rotation among fractions of carbon (TFOC, and HFOC) were similar to the trends of fractions of nitrogen. The absolute values of TFOC and HFOC in Cullars Rotation were lower than their Old Rotation (Table 2.9). This could be due to the general nature of sandy soil texture in that location which has lower capacity of holding soil organic matter. The TFOC, in 2008, no N plus winter legume treatment was greater than the rest of the treatments (Table 2.10). The no treatments obviously showed the least in terms fractions of organic carbon accumulation except in 2009 (Table 2.10). In 2009, again, the no-nitrogen but winter legume and no potassium treatments had relatively higher values in terms of carbon accumulation compared to the rest of the treatments. The least in terms of carbon accumulation was rather seen in the no phosphorous treatment. The trend in allotment of soil organic carbon amongst the three different pools, TFOC, LFOC, and HFOC components, depends on the balances between rates of residue inputs, humus formation, and mineralization process in the soil. Our results were similar to results reported by Mitchell and Entry (1998) in the Old Rotation.

Increment in the HFOC could be due to increased yearly biomass production, residue input, and less decomposition activities. However, reduction in SOC could be attributed to higher SOM mineralization and less annual plant inputs. This scenario is shown in no nitrogen but winter legume and no nitrogen and no winter legume in the Old Rotation which showed the least amount of carbon among the three fractions, compared to the rest of the treatments in both locations.

2.3.3 C:N Ratio

2.3.3.1 Old Rotation

Generally, C:N ratio for total soil falls within the generally reported ranges of 9.5 in the no rotation with winter legume to 13.2 also within no rotation and no winter legume in 2008 (Table 2.6). In 2009, the values ranged between 10 in the 2-year rotation with winter legume as the least to 11.7 again within no rotation with no nitrogen and no winter legume treatment. There C:N values were similar for 2008 and 2009 for all the treatments within carbon fraction and years. With respect to the heavy fraction C:N ratio, the 2008 and 2009 treatments of no rotation with no nitrogen and no winter legume only were different. However, between treatments within and between each year of the study, there were no mean differences among them. These values are within ranges of C:N ratio in literature.

The LF C:N ratio for all the treatments ranged 18.2 under no rotation with winter legume treatment to 22.7 under 3-year rotation treatments (Table 2.6). However, the 3-year rotation treatment was different from the rest of the treatments. Though there were differences between the C:N ratio of 2008 and 2009; the high absolute values for 2009 light fraction C:N could be attributed the very low values of light fraction nitrogen in 2009 due to excessive rainfall that occurred in 2009. The high C:N ratio for the light fraction for both years could be attributed to the nature and quantum of the LDOM.

2.3.3.2 Cullars Rotation

The total fraction C:N ratio for all the treatments under Cullars Rotation for both years of the study fell within the range of 8.5 in complete fertilization and micronutrient inclusive and 11.0 in the no nitrogen but legume treatment in 2008 (Table 2.11). However, in 2009 it ranged from 9.5 in the no treatment to 10.7 in the no-nitrogen and no winter legume treatment. Except in 2008, where the complete fertilization and micronutrients and no nitrogen but winter legume had different values from the rest of the treatments. The HFOC C:N ratio for 2008, there were differences in treatments, but the most conspicuous differences were seen in the no nitrogen but winter legume and the complete fertilization with micronutrient. The rest of the treatments did not show much difference among themselves. Curiously, for reasons we cannot explain the no treatment had high C:N values in both years of the study under light fraction compared to the other treatments. Complete fertilization treatment showed the least C:N ratio of 14.0 and the no treatment showed the highest of 23.6. However, it is of significant interest to note that, the no-nitrogen but winter legume, no-nitrogen and no-winter legume and no treatment treatments showed the highest C:N ratios in 2008 and they were actually different from the inorganic fertilizer applied treatments. Almost the same trend was seen in 2009, except the no-nitrogen and no-winter legume treatment deviated from the norm.

2.4 Summary and Conclusions

The LFON and LFOC were less than HFON and HFOC in both the Old Rotation and The Cullars Rotation. The C:N of the Old Rotation and the Cullars Rotation were similar even though the C and N in the Old Rotation were greater than the Cullars Rotation. This difference could due to the sandy soil at the Cullars Rotation and the sandy loam at the Old Rotation. This study has shown that varying factors such as fertilizer treatments, crop rotations and or combination of the two, which are interrelated and interdependent, have impacted the different fractions of SOM differently. Carbon and nitrogen contents significantly decreased with depth in all locations. Organic carbon content of the two study sites increased over time for treatments that yielded more biomass. Fertilizer treatments, crop rotation and management practices have measurable impacts on SOC that can be invaluable for soil and carbon sequestering.

Table 2.1: Cropping system and fertilizer usage in the Old Rotation, Auburn University, Auburn, Alabama

Treatment or Cropping system	Plots	summer 2008	winter 2008	winter 2009	summer 2009	Nutrients applied/rotation ($N-P_2O_5-K_2O$) kg ha^{-1}
No Rotation						
No N, No winter legume	1, 6	Cotton	Nothing		Cotton	0 -90-67
+ winter legume	2, 3 & 8	Cotton	Crimson clover		Cotton	0-90-67
+ Fert. N	13	Cotton	Nothing		Cotton	134 – 90 - 67
2-Yr Rotation						
+ winter legume	4, 7	Cotton	Crimson clover		Corn/Cotton	0 – 180 -134
+ Fert. N + winter legume	5, 9	Cotton/Corn	Crimson clover		Corn	268 – 180 - 134
3-Yr Rotation	10, 11 & 12	Wheat/SB	Crimson clover (10) Wheat (11)/Nothing (12)		Corn (10)/SB (11) Cotton(12)	330 – 180 – 134
Cotton (Legume)- corn-Wheat/soybean						

Mean (SE):- Mean ± standard error. 2-Yr and 3-Yr: - Two and three - year rotations respectively in the Old Rotation, Auburn University, Auburn, Alabama. 2008-2009.SB:- Soybean

Table 2.2: Total soil organic carbon in the Old Rotation from 1988 to 2009, Auburn University, Auburn, Alabama

Treatment or Cropping system	Plots	--------------------total soil organic carbon (g C kg^{-1} soil)-----------------------				
		1988*	1992*	1994*	2008	2009
No Rotation						
No N, No winter legume	1, 6	5.5	5.0	3.0	9.0	9.4
+ winter legume	2, 3 & 8	12.0	8.7	10.0	17.4	15.4
+ Fert. N	13	8.0	10.0	9.0	13.7	17.4
2-Yr Rotation						
+ winter legume	4, 7	10.5	10.0	10.0	15.5	14.7
+ Fert. N + winter legume	5, 9	13.5	11.6	10.5	17.7	15.1
3-Yr Rotation Cotton (Legume) - corn-Wheat/soybean	10, 11 & 12	14.7	13.3	10.7	17.0	18.4

2-Yr and 3-Yr: - Two and three - year rotations respectively in the Old Rotation, Auburn University, Auburn, Alabama.
Fert. – Fertilization. *Values of 1988 to 1992 were based on 0-20 cm depth of sampling (Source: Mitchell and Entry, 1998) whereas others were based on 0 -10 cm depth in 2008 and 2009. In 1997, the tillage system was changed from conventional to strip tillage.

Table 2.3: Percentage composition of organic fractions in the Old Rotation, Auburn University, Auburn, Alabama

Treatment or Cropping system	Plots	% LFN 2008	% LFN 2009	% HFN 2008	% HFN 2009	% LFC 2008	% LFC 2009	%HFC 2008	%HFC 2009
		…………………………………….. Mean (SE)……………………………………							
No Rotation									
No N, No winter legume	1, 6	2.2(0.5)	3.6(0.6)	97.8(1.4)	96.4(0.6)	6.5(0.4)	9.9(2.0)	93.5(1.4)	90.1(2.0)
+ winter legume	2, 3,8	4.0(0.6)	2.7(0.8)	96.0(0.5)	97.3(0.8)	7.5(0.9)	6.5(1.7)	92.5(0.9)	93.5(1.7)
+ Fert. N	13	6.6(1.5)	3.1(1.0)	93.4(1.5)	96.9(1.1)	12.3(2.6)	7.4(1.9)	87.7(2.6)	92.7(1.9)
2-Yr Rotation									
+ winter legume	4, 7	4.2(0.7)	2.3(0.6)	95.8(0.7)	97.7(0.6)	8.7(1.4)	5.8(1.5)	91.3(1.4)	94.2(1.5)
+ Fert. N + winter legume	5, 9	4.3(1.0)	2.3(0.4)	95.7(1.0)	97.7(0.4)	7.8(1.9)	5.5(0.9)	92.2(1.9)	94.5(0.9)
3-Yr Rotation Cotton (Legume)- corn-Wheat/soybean	10,11,12	3.5(0.6)	1.7(0.3)	96.5(0.5)	98.4(0.3)	7.3(0.9)	7.5(0.9)	92.7(0.9)	92.3(0.6)

Mean (SE):- Mean ± standard error. 2-Yr and 3-Yr: - Two and three - year rotations respectively in the Old Rotation, Auburn University, Auburn, Alabama. 2008-2009. Fert. – Fertilization.

Table 2.4: Fractions of nitrogen in the Old Rotation, Auburn University, Auburn, Alabama

Treatment or Cropping system	Plots	Light Fraction N 2008	Light Fraction N 2009	Heavy Fraction N 2008	Heavy Fraction N 2009	Total Fraction N 2008	Total Fraction N 2009
		……Mean (SE)…… g N kg^{-1} soil					
No Rotation							
No N, No winter legume	1, 6	0.04(0.01)	0.03(.006)	1.2(0.13)	1.12(0.12)	1.28(0.12)	1.15(0.11)
+ winter legume	2, 3, 8	0.07(0.01)	0.04(.007)	1.6(0.3)	1.76(0.3)	1.73(0.12)	1.74(0.17)
+ Fert. N	13	0.09(0.02)	0.05(0.02)	1.4(0.1)	1.5(0.1)	1.46(0.11)	1.59(0.14)
2-Yr Rotation							
+ winter legume	4, 7	0.06(0.01)	0.02(0.006)	1.5(0.14)	1.4(0.12)	1.52(0.14)	1.44(0.12)
+ Fert. N + winter legume	5, 9	0.06(0.01)	0.03(0.004)	1.6(0.12)	1.38(0.11)	1.66(0.12)	1.40(0.11)
3-Yr Rotation	10, 11, 12						
Cotton (Legume)- corn-Wheat/soybean		0.05(0.007)	0.03(0.004)	1.6(0.1)	1.63(0.1)	1.61(0.1)	1.6(0.1)

Mean (SE):- Mean ± standard error. 2-Yr and 3-Yr:- Two and three - year rotations respectively in the Old Rotation, Auburn University, Auburn, Alabama. 2008-2009.
Fert. – Fertilization.

Table 2.5: Fractions of carbon in the Old Rotation, Auburn University, Auburn, Alabama

Treatment or Cropping system	Plots	Light Fraction C 2008	Light Fraction C 2009	Heavy Fraction C 2008	Heavy Fraction C 2009	Total Fraction C 2008	Total Fraction C 2009
		……… Mean (SE) ………					
		-------- $g\ C\ kg^{-1}$ soil --------					
No Rotation							
No N, No winter legume	1, 6	1.1(0.2)	0.9(0.1)	7.5(0.8)	8.6(0.8)	8.4(0.8)	9.5(0.8)
+ winter legume	2, 3 & 8	1.3(0.2)	1.0(0.2)	15.3(1.7)	15.6(1.6)	16.5(1.9)	16.6(1.5)
+ Fert. N	13	1.8(0.42)	1.44(0.4)	16.1(1.0)	14.0(1.5)	15.0(1.7)	17.4(1. 2)
2-Yr Rotation							
+ winter legume	4, 7	1.3(0.2)	0.7(0.09)	13.9(1.4)	16.3(1.4)	15.2(1.6)	14.7(1.4)
+ Fert. N + winter legume	5, 9	1.2(0.2)	0.7(0.09)	16.2(1.4)	14.3(1.3)	17.5(1.4)	15.0(1.3)
3-Yr Rotation Cotton (Legume)- corn-Wheat/soybean	10, 11 & 12	1.1(0.1)	0.7(0.1)	15.8(1.2)	17.7(1.4)	16.9(1.2)	18.4(1.4)

Mean (SE):- Mean ± standard error. 2-Yr and 3-Yr: - Two and three - year rotations respectively in the Old Rotation, Auburn University, Auburn, Alabama. 2008-2009.
Fert. - Fertilization

Table 2.6: Fractions of carbon-nitrogen ratio in the Old Rotation, Auburn University, Auburn, Alabama

Treatment or Cropping system	Plots	Light Fraction C: N 2008	Light Fraction C: N 2009	Heavy Fraction C: N 2008	Heavy Fraction C: N 2009	Total Fraction C: N 2008	Total Fraction C: N 2009
		……… Mean (SE)………					
No Rotation							
No N, No winter legume	1, 6	19.7(2.9)	32.7(6.3)	9.0(0.7)	10.9(0.6)	13.2(3.2)	11.7(0.6)
+ winter legume	2, 3 & 8	18.2(0.7)	27.6(3.1)	9.2(0.3)	10.1(0.4)	9.5(0.4)	10.5(0.4)
+ Fert. N	13	19.0(1.0)	31.3(7.8)	9.5(0.6)	10.7(0.8)	10.2(0.6)	11.2(0.7)
2-Yr Rotation							
+ winter legume	4, 7	0.4(1.4)	28.2(3.0)	9.5(0.4)	9.7(0.4)	9.9(0.4)	10.0(0.3)
+ Fert. N + winter legume	5, 9	19.6(0.8)	31.7(4.7)	10.1(0.4)	10.3(0.5)	10.5(0.4)	10.7(0.5)
3-Yr Rotation Cotton (Legume)- corn-Wheat/soybean	10, 11 & 12	22.7(0.9)	30.7(3.7)	10.1(0.3)	10.7(0.3)	10.5(0.3)	11.0(0.3)

Mean (SE):- Mean ± standard error. 2-Yr and 3-Yr: - Two and three - year rotations respectively in the Old Rotation, Auburn University, Auburn, Alabama. 2008-2009.

Table 2.7: Cropping system and fertilizer usage in the Cullars Rotation, Auburn University, Auburn, Alabama

Treatment or rotation	Plots	summer	winter		summer	Nutrients applied/ 3-Yr
Cropping system		2008	2008	2009	2009	(N-P_2O_5-K_2O) kg ha^{-1}
No N/+ winter legume	A	Cotton	Crimson clover		Corn	0 -224-190
No N/No winter legume	B	Cotton	No Crimson clover		Corn	0-224-190
No Treatment	C	Cotton	No Crimson clover		Corn	0 - 0 - 0
No Phosphorous	2	Cotton	Crimson clover		Corn	168 - 0 - 190
Complete Fert.	3	Cotton	Crimson clover		Corn	168 -224 - 190
No Potassium	6	Cotton	Crimson clover		Corn	168 - 224 - 0
Complete Fert. + micronutrients	10	Cotton	Crimson clover		Corn	168-224- 190

Three-year rotations sampled treatments in the Cullars Rotation, Auburn University, Auburn, Alabama; 2008-2009
Fert. - Fertilization

Table 2.8: Fractions of nitrogen in the Cullars Rotation, Auburn University, Auburn, Alabama.

Treatment or Cropping system	Plots	Light Fraction N 2008	Light Fraction N 2009	Heavy Fraction N 2008	Heavy Fraction N 2009	Total Fraction N 2008	Total Fraction N 2009
		…… Mean (SE) ……					
		----g N kg^{-1} soil ----					
No N/+ winter legume	A	0.05(0.009)	0.04(0.007)	1.1(0.2)	0.96(0.2)	1.12(0.2)	1.02(0.2)
No N, No winter legume	B	0.05(0.01)	0.04(0.01)	0.85(0.2)	0.99(0.2)	0.92(0.2)	0.93(0.1)
No treatment	C	0.03(0.009)	0.02((0.006)	0.65(0.07)	0.65(0.08)	0.73(0.1)	0.9(0.2)
No phosphorous	2	0.04(0.008)	0.03(0.006)	0.0.83(0.1)	0.77(0.13)	0.83(0.1)	0.64(0.1)
Complete Fert.	3	0.04(0.01)	0.02(0.004)	0.94(0.1)	1.0(0.2)	0.95(0.1)	0.94(0.08)
No potassium	6	0.07(0.01)	0.03(0.006)	0.95(0.1)	0.95(0.2)	1.0(0.1)	1.1(0.2)
Complete Fert. + micronutrient	10	0.06(0.007)	0.04(0.01)	0.96(0.09)	1.05(0.1)	0.99(0.07)	1.01(0.2)

Mean (SE):- Mean ± standard error. The Cullars Rotation, Auburn University, Auburn, Alabama; 2008 – 2009, Fert. - Fertilization

Table 2.9: Percentage composition of organic fraction in the Cullars Rotation, Auburn University, Auburn, Alabama

Treatment or Cropping system	Plots	% LFN 2008	% LFN 2009	% HFN 2008	% HFN 2009	% LFC 2008	% LFC 2009	%HFC 2008	%HFC 2009
No N/+ winter legume	A	5.5(1.7)	4.4(0.6)	94.5(1.7)	96.7(0.6)	10.8(2.9)	10.8(2.6)	89.2(2.9)	89.1(2.6)
No N, No winter legume	B	6.2(1.5)	4.1(0.8)	93.8(1.5)	95.9(0.7)	16.2(4.3)	8.6(1.0)	83.8(4.3)	91.4(1.0)
No treatment	C	4.1(1.3)	3.1(1.0)	95.9(1.3)	96.9(1.0)	8.9(2.2)	11.7(2.6)	87.1(2.5)	91.1(2.2)
No phosphorous	2	5.3(2.2)	5.0(2.0)	95.5(1.5)	94.7(2.0)	11.7(2.6)	9.1(2.5)	88.3(2.6)	90.9(2.5)
Complete Fert.	3	4.5((1.6)	2.7(0.6)	95.5(1.6)	97.3(0.6)	10.8(3.4)	7.3(1.1)	89.2(3.4)	92.7(1.1)
No potassium	6	6.4(0.9)	3.2(1.2)	93.6(0.9)	96.8(1.2)	14.3(1.2)	7.2(2.1)	85.7(1.2)	92.8(2.1)
Complete Fert. + micronutrient	10	6.0(1.3)	3.3(0.8)	94.0(1.3)	96.7(0.8)	13.8(2.3)	7.6(1.2	86.2(2.3)	92.41.2)

Mean (SE):- Mean ± standard error. The Cullars Rotation, Auburn University, Auburn, Alabama. 2008 – 2009. Fert. - Fertilization

Table 2.10: Fractions of carbon in the Cullars Rotation, Auburn University, Auburn, Alabama

Treatment or Cropping system	Plots	Light Fraction C 2008	Light Fraction C 2009	Heavy Fraction C 2008	Heavy Fraction C 2009	Total Fraction C 2008	Total Fraction C 2009
		Mean (SE) $g\ N\ kg^{-1}$ soil					
No N/+ winter legume	A	1.1 (0.1)	1.09(0.2)	11.4(3.2)	9.7(1.6)	12.5(3.3)	10.2(1.7)
No N, No winter	B	1.2(0.1)	0.9(0.2)	8.01(2.0)	10.2(2.3)	9.6(1.9)	9.9(1.2)
No treatment	C	0.83(0.2)	0.52(0.1)	5.3(0.6)	5.5(0.7)	7.0(1.1)	8.8(2.6)
No phosphorous	2	0.88(0.1)	0.64(0.1)	7.2(0.8)	7.3(1.0)	7.8(0.6)	6.5(0.9)
Complete Fert.	3	0.89(0.2)	0.7(0.2)	8.5(1.2)	9.8(2.2)	8.6(1.3)	9.0(0.8)
No potassium	6	1.3(0.1)	0.6(0.1)	8.2(1.0)	9.2(1.6)	9.9(1.1)	10.7(2.3)
Complete Fert. + micronutrient	10	1.1(0.1)	0.8(0.2)	7.6(0.9)	9.2(1.5)	8.5(0.8)	9.5(1.6)

Mean (SE):- Mean ± standard error. The Cullars Rotation, Auburn University, Auburn, Alabama. Fert. - Fertilization

Table 2.11: Fractions of C:N Ratio in the Cullars Rotation, Auburn University, Auburn, Alabama

Treatment or Cropping system	Plots	Light Fraction C:N 2008	Light Fraction C:N 2009	Heavy Fraction C: N 2008	Heavy Fraction C: N 2009	Total Fraction C: N 2008	Total Fraction C: N 2009
		……………… Mean (SE) ………………					
No N/+ winter legume	A	22.5(3.0)	17.0(5.9)	10.4(1.2)	10.3(0.45)	11.0(1.1)	10.2(0.5)
No N, No winter legume	B	22.1(5.7)	16.6(5.8)	9.1(0.9)	10.1(0.3)	10.5(0.8)	10.7(0.3)
No treatment	C	23.6(8.9)	25.8(11.9)	8.2(0.6)	8.5(0.3)	9.5(0.7)	9.5(0.7)
No phosphorous	2	18.9(4.7)	14.5(5.1)	8.9(0.5)	9.7(0.4)	9.6(0.6)	10.4(0.4)
Complete Fert.	3	16.9(5.3)	17.9(6.8)	9.1(1.2)	9.9(1.0)	8.9(0.3)	9.7(1.0)
No potassium	6	17.1(7.0)	14.0(4.2)	8.5(0.4)	9.8(0.5)	10.1(0.9)	10.0(0.5)
Complete Fert. + micronutrient	10	14.0(4.2)	16.7(5.8)	7.8(0.4)	8.7(0.5)	8.5(0.4)	9.7(0.9)

Mean (SE):- Mean ± standard error. Fert. – Fertilization. The Cullars Rotation, Auburn University, Auburn, Alabama.

Table 2.12 Fixed effect and their interactions for carbon for Cullars Rotation

Test of fixed effects and their interactions for fraction of nitrogen and carbon

-------------------------------------- Pr > F---

Effect	N Light	N Heavy	N Total	C Light	C Heavy	C Total
Depth	<0.0001	<0.0001	< 0.0001	<0.0001	<0.0001	<0.0001
Year	< 0.0001	0.057	NS	0.0001	NS	NS
Treatments	0.012	0.04	0.1	0.018	0.0184	0.1
Year*Depth	NS	NS	NS	NS	NS	NS

(P≤0.05); NS denotes not significant

Table 2.13 Fixed effect and their interactions for fractions of nitrogen and carbon in the Old Rotation

Test of fixed effects and their interactions for fractions of nitrogen and carbon

-------------------------------------- Pr > F---

Effect	N Light	N Heavy	N Total	C Light	C Heavy	C Total
Depth	NS	< 0.0001	< 0.0001	<0.0001	0.0002	<0.0001
Year	NS	NS	NS	<0.0001	NS	NS
Treatments	NS	< 0.0001	< 0.0001	0.04	<0.001	<0.0001
Year*Depth	NS	NS	NS	0.013	NS	NS

(P≤0.05); NS denotes not significant

Table 2.14: Fixed effect and their interactions for C:N ratio for Old Rotation

Test of fixed effects and their interactions for C:N Ratio			
-- Pr > F---			
Effect	Light C:N	Heavy C:N	Total C:N
Depth	0.1	NS	NS
Year	<0.0001	NS	NS
Treatments	0.02	NS	NS
Year*Depth	0.007	NS {0.05 (Y *T)}	NS

(P≤0.05); NS denotes not significant and (Y*T) denotes Year and Treatment interaction

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Chapter 3: Carbon Dioxide Flux in Long-term Experiments

Abstract

Increasing atmospheric carbon dioxide (CO_2) concentration has necessitated the need to study CO_2 efflux under varied agronomic cultural practices. Carbon dioxide constitutes a major component of the greenhouse gases that could lead to global warming. Soil serves as a major sink for carbon sequestration. Carbon dioxide efflux was measured in the summer and fall of 2008, and summer 2010, in two long-term, historic crop rotation experiments, using a LICOR 6200 gas chamber. The gas chamber was placed on 10 cm diameter polyvinyl chloride (PVC) pipes, which were placed firmly into the soil for at least 3 days prior to measurement for equilibration. Summer CO_2 efflux measurements were significantly higher than the fall values. An intensive 3-year rotation - of cotton-corn- wheat- soybean had significantly less CO_2 efflux than a corresponding 2-year rotation of cotton and corn. In Cullars Rotation, with the exception of the no-nitrogen but winter legume, and no nitrogen nor winter legume treatments, the summer 2010 effluxes were greater than their corresponding summer 2008. In the fall of 2008, only plots CRA and CRB showed some appreciable increment. The summer 2010 and 2008 annual efflux values for the Old Rotation were about 58 and 56 tons $ha^{-1}yr^{-1}$, respectively, whereas the least in the fall 2008 was about 27 tons $ha^{-1}yr^{-1}$. In Cullars Rotation, the annual average efflux ranged between 37 and 42 tons $ha^{-1}yr^{-1}$ with the least being around 28 tons $ha^{-1}yr^{-1}$. In fall 2008, inorganic fertilized treated plots with no phosphorous, with complete fertilization, with no potassium and the treatment with complete fertilization in addition to micronutrient had less efflux than the unfertilized plots of no-nitrogen but winter legume (Plot A), and no-nitrogen nor

winter legume treatment (plot B), with the exception of the no-treatment (plot C). However, in the summer 2008, the trend was reversed with inorganic fertilizer treated plots showing greater efflux values compared to unfertilized plots. In the summer 2008, the absolute efflux values were greater for each plot, with the plot with the treatment of neither no-nitrogen nor winter legume showing efflux of 3.9 $\mu molm^{-2}s^{-1}$. In general CO_2 efflux is affected by many interacting and interdependent factors.

3.1 Introduction

Increasing concentration of atmospheric CO_2 has been associated to climate changes. There is concern that most frequent natural disasters of large magnitude like floods, fires, and drought are due to climate change and global warming effects. Global warming has been associated with an accumulation of greenhouse gases such as CO_2, CO, CH_4, N_2O and ozone that form a blanket in the stratosphere. This blanket impedes the reflectance of the rays and heat from the sun back into the atmosphere (Lashof and Ahuja, 1990). Schlesinger (1977) posited that soil CO_2 flux may increase due to increases in atmospheric CO_2. Even though, the nature and magnitude of change cannot be readily verified and ascertained with a high degree of certainty, the use of well-managed soil ecosystems could act as potential sinks for atmospheric CO_2 (Ceulemans et al., 1999; Jenkinson et al., 1991; and Nakayama et al., 1994).

Most CO_2 impact studies have depended on aboveground tree responses (Bazzaz, 1990) and have showed that increasing concentrations of atmospheric CO_2 may lead to changes in forest ecosystems (Ceulemans et al.1999). However, there have been few reports on long-term agronomic experimental studies in the literature. Different factors impact soil CO_2 efflux, notably temperature, moisture, quality and quantity of residue in the soil. Edwards (1975) showed variations in CO_2 efflux of forest floor litter and soil in a temperate deciduous forest. He indicated soil moisture had the highest influence on rates of CO_2 efflux and took temperature as an annual indicator of soil CO_2 efflux. Billings et al. (1998) also studied how soil moisture and temperature impact soil respiration in boreal forest. They believed any future climatic change could result in deeper thawing which could also change the soil moisture content and invariably affects the soil microbial composition and root respiration. Rayment and Jarvis (2000) concluded that soil temperature predominantly affected CO_2 respiration, and soil moisture had little effect.

Agricultural activities contribute at least 25% of the overall anthropogenic evolutions of CO_2 (Duxbury 1994; 1995). The CO_2 in the atmosphere is converted into photosynthate by plants which are stored in soils as residue and SOM. Management practices such as cropping intensity, rotation, tillage practices can either speed up CO_2 emission or sequestration, depending on the management activity. Reicosky and Lindstrom (1993) suggested that tillage disrupts soil clods/aggregates that enhance aeration and plant residue incorporation (Beare et al., 1994). This induces microbial oxidation of SOM to give off CO_2 (Jastrow et al., 1996). Rapid cropping intensity (Lal et al., 1995) coupled with either minimal tillage or no-tillage enhances soil carbon storage (Paustian et al., 1995). Minimal tillage is seen as one of the most efficient agricultural methods to reduce CO_2 emission and sequester atmospheric C in the soil (Kern and Johnson, 1993; Lal and Kimble, 1997; Curtin et al., 2000; Al-Kaisi and Yin, 2005).

Soil inhabiting living organisms and plant roots serve as significant contributors of CO_2 during respiration (Rochette and Flanagan, 1997; Curtin et al. 2000). Also, the evolution of CO_2 from the soil surface into the atmosphere was recognized as the main means of soil carbon loss (Parkin and Kaspar, 2003). In contrast, Roberts and Chan (1990) suggested an increase in tillage intensity correlated with CO_2 emission due to increased soil disturbance and aeration. This same scenario was reported by Reicoscky and Lindstrom (1993) and Jackson et al. (2003). These disturbances of the soil could serve as an early mechanism for carbon emission if changes in SOC as a result of management practices are not detected quickly (Fortin et al.1996; Grant, 1997). Sherrod et al. (2003) and Sainju et al. (2006) estimated that increased cropping intensity and nitrogen fertilization (Gregorich et al., 1996) could result in enhanced SOC.

Little information is available on the long-term impact of long-term crop rotation and tillage on CO_2 efflux. U.S. agricultural practices have seen 11% reduction in conventional tillage practice from 1990-2004 and 17% increase in no-tillage. There is much room for improvement by implementing conservation tillage practices which may continue to enhance carbon sequestration (CTIC, 2004). Soil CO_2 is a major part of the carbon in soil. Organic carbon in soils is a major reservoir that is in constant exchange with the atmospheric CO_2. On a time scale of human concerns, SOC serve as a potential greenhouse gases source and sink simultaneously (Fischlin and Gyalistras, 1997). After the Kyoto Protocol, where it was first noticed that CO_2 can be sequestered into soils to help reduce the trend of global warming and its climate change effects; many questions have been posed with regards to the paradigm shift in research concerning the usage and managements of soil for purposes of atmospheric carbon sequestration. Some of the questions asked include the following:

(i) Are soils now the source and sink of greenhouse gases?

(ii) Do soils now play the role of amplifier or natural modulators with respect to global warming and climate change?

(iii) How do researchers and scientist sequester atmospheric CO_2 and have the carbon stabilized as a result?

(iv) What effective management approaches are there to enhance these mechanistic processes?

(v) Can rotations and tillage practices help to enhance these efforts?

The above questions and others have been at the forefront of driving studies into finding answers, and they require very clear understanding of where and how carbon is stored within the soil matrix (Torn et al., 2009).

3.1.1 SOC loss and Mitigation on U.S. Cropland

The cropland areas of US have been relatively constant in the 20th century. From the 1910s, a total area of 134 Mha had been cultivated, increasing to 152 Mha between the World War I and II era, then to 154 Mha during the early 1970s and then declining to 134 Mha since the 1980s due to diversions from production as a result of federal farm programs (Lal et al.1999). Careful management of croplands can enhance carbon sequestration potential. There are five classifications of U.S. croplands, (a) harvested croplands, constituting 63% of the total from which crops are continually harvested; (b) land on which crops failed to grow even though crops were sown (1%) and were not harvested; (c) cropland held for summer fallow (7%); (d) idle croplands constituting lands in cover and not cropped for physical and economic gains (15%), and (e) cropland used for pasture in rotations with crops (Lal et al.1999). Rasmussen and Collins (1994) suggested virgin soils which are in equilibrium with native vegetation can be classified as soils with much potential for large SOC reserves. It had been estimated that the total U.S. cropland had lost almost 5,000 million metric tons of carbon as a result of cultivation of the soil, but with prudent adoption of recommended practices of agriculture, there can be up to 75% of the lost carbon sequestered, which can be attained within a 25-50 year period (Lal et al. 1998).

Several mechanistic approaches can be adopted to mitigate carbon emission due to agricultural practices. Some of the methods are as follows: (i) intensification of agricultural practices by employing conservation tillage practices and residue management on prime agricultural lands. (ii) soil erosion management, which can be achieved through leaving much residue and vegetation cover on susceptible lands and (iii) marginal agricultural land conversion to non-agricultural restoration uses such as forestry and grasslands (Paustian et al., 1992).

The objectives for this study were to (1) determine the effects of fertilizer and rotation and seasons of sampling on soil CO_2 efflux, and (2) to compare CO_2 effluxes at different seasons in the long-term agricultural systems.

3.2 Materials and Methods

3.2.1 Site description

The Old Rotation (OR) (circa 1896) and the Cullars Rotation (CR) (circa 1911) long-term are among North America's oldest continuous crop experiments. The OR is the oldest continuous cotton experiment in the world, whereas the CR is the oldest soil fertility experiment in the Southeastern United States. It is also the first replicated long-term experiments. The CO_2 efflux study started in May 2008 at the Old and Cullars Rotations of Auburn University in Auburn, Alabama. Measurements were taken in summer 2008, from late May to August and fall 2008, from September to middle of November. No measurements were taken in 2009 due to excessive moisture from rainfall. Measurements were also taken in the summer 2010, again from late May to August. The OR is located at the boundary between Coastal Plain and Southern Piedmont Plateau Physiographic regions of the eastern part of Central Alabama, within latitude 32^o 35′ and longitude 85^o 29′. The nearby CR is located at the Coastal Plains Physiographic region and the soil is classified as a Marvyn loamy sand (fine-loamy, siliceous, thermic, Typic Kanhapludults) and located within latitude 32^o 35′ and longitude 85^o 28′ (Mitchell et al., 2005). The Old Rotation consists of 13 plots with 6 different treatments. Each plot in the OR is 6.5 by 41.5 meters with a meter (1 m) alley separating each plot (Hubbs et al., 1998). Originally, each plot represented a separate treatment, but today, the experiment consists of 6 cropping systems (Table3.1) The Cullars Rotation consists of three similar sets of blocks with 14 different treatments, in each tier. Four different crops with winter legumes (e.g. Crimson clover) used as winter cover crop.

Cotton, corn, and wheat and soybeans are planted seasonally in rotation (Table 3.2). Our study was limited to the middle tier in the Cullars rotation.

3.2.2 CO_2 Efflux Sampling

CO_2 efflux was measured on weekly intervals using a portable system Li-6200 (LICOR, Inc., Lincoln, Nebraska) during summer or fall seasons of 2008 and 2009. An LI-09 soil gas chamber was attached to the LICOR system and placed on a 10 cm PVC collars and equilibrated between 260-280 ppm of ambient CO_2 concentration before taking measurement. Each plot had 4 collars randomly placed between rows. The space between the soil surface and the edge of a collar was 5 cm. The console and the gas chamber combo operate on the basis of gas exchange principles to measure the CO_2 efflux. Carbon dioxide effluxes were taken between 8.00 am and 12.00 pm on sampling days except on days of excessive moisture, during which sampling was conducted in the afternoons. Soil temperature was simultaneously measured with a digital soil thermometer during CO_2 efflux measurements. Data presented are means of all observations during summer 2008, fall 2008, and summer 2010.

3.2.3 Soil moisture and temperature

Moisture content of the soil was measured once only just for comparison of relative moisture capacity of the plots. Moisture was taken days after a saturating rainfall in order to approximate field capacity. The gravimetric moisture content was determined by taking core samples per plot, which were oven-dried at 105^{o}C for twenty-four hours. The volumetric moisture content was then calculated from the product of the gravimetric moisture content and the bulk density of the soil. The bulk density was determined by determining the dry weight and the volume of soil.

3.3 Results and Discussions

3.3.1 Old Rotation

The soil pH averagely ranged between 5.73 in the no rotation cropping with winter legume and 6.05 in the 3-year cropping rotation (Table 3.3) in the Old Rotation. The lowest bulk density measurement of 1.19 gcm^{-3} was observed in the same treatment as pH_s and the highest among the treatments was 1.36 gcm^{-3} under the 2-year rotation with winter legume inclusion. There was no significant difference in the temperature measured but some variability was shown as depicted in (Table 3.3). The lowest temperature we measured was on average in plot A 26.6°C under the 2-year rotation with winter legume and inorganic ammonium nitrate fertilized treatment, and the highest was 28.5°C under the no nitrogen and no winter legume inclusive treatment (Table 3.3). Volumetric moisture content ranged between 11.4 under the no nitrogen and no winter legume inclusive treatment to 23.9 under the 3-year rotation making up of plots OR10, OR11, and OR12. Efforts were made to maintain a water solution pH (pH_w) between 5.8 and 6.5 through the application of ground agricultural limestone.

3.3.2 Cullars Rotation

Among the sampled treatments, the no nitrogen but winter legume inclusive treatment gave the lowest pHs value of 5.95, whereas the highest average was found among the no treatment, complete fertilization and complete fertilization with micronutrient inclusive treatments of 6.20. Bulk density ranged from 1.15 gcm^{-3} under the complete fertilization with micronutrients up to 1.43 g cm^{-3} under the no-nitrogen but winter inclusive treatment. The volumetric moisture content though far less in terms of quantity to the Old Rotation, ranged from the 1.5 under the complete fertilization treatment to 8.7 under the complete fertilization with micronutrient inclusive treatment (Table 3.4). The sharp contrast in the amount of moisture content between the two locations could be due to the soil textural classes of the locations. Since Cullars Rotation is predominantly sandy texturally, it has less tendency to hold much organic matter which further affects its water holding-capacity and hence less moisture content. The Old Rotation is predominantly loamy in nature and has an appreciable amount of kaolinitic clay as constituent and hence holds more moisture than the former.

3.3.3 CO_2 efflux in the Old Rotation

Season and treatments, interdependently and interrelated significantly affected the CO_2 efflux. In summer 2008, treatments with winter legume inclusive between the no rotation and 2 year cropping rotation showed an averagely appreciable CO_2 efflux. The 2-year cropping rotation with winter legume had the highest efflux of 5.44 μ mol $m^{-2}s^{-1}$ (plots 4 and 7) and significantly followed by the same cropping rotation but with an additional ammonium nitrate source (plots 5 and 9). However, fall 2008 effluxes were appreciably lesser than their corresponding summer 2008 effluxes. Except the no nitrogen and no winter legume inclusive treatments (plots of 1 and 6), summer 2010 measured effluxes were higher than the former two seasons of sampling. Again, winter legume's inclusive treatments showed significant effluxes of 5.12, 6.0 and 4.2 μ mol $m^{-2}s^{-1}$ respectively under the no rotation cropping system with winter legume (Plots 2,3,8); the 2-year rotation with winter legume (Plots 4 and 7) and the same treatment with additional nitrogen source (Plots 5 and 9), respectively (Table 3.5). Except the no rotation cropping system with only inorganic nitrogen fertilizer source and the control plot with no-nitrogen and no-winter legume cultivation which served as the control for the adjustment of multiple comparison test, all the other treatments were highly significant (Table 3.6). Season, cropping rotation treatments and their respective interaction showed very high significant differences. Even though, these values averagely seemed to be high compared to Cullars Rotation; in their entirety, they are far less compared to other studies conducted in the southeastern United States, specifically in Belle Mina, Alabama and four different locations in Georgia (Rifai et al., 2010)

3.3.4 CO_2 efflux in Cullars Rotation

In general, CO_2 efflux measurements in the fall of 2008 were lower than the summer 2008 and 2010 (Table 3.7). In fall 2008, plots with mineral fertilizer treatments; except plot C which had neither inorganic nor organic nitrogen fertilizer treatment, were much lower than their corresponding no inorganic nitrogen fertilizer treatments plots of A and B (Table 3.7). In summer 2008, the opposite trend described above was seen to be prevailing. The inorganic fertilizer treatments had higher CO_2 efflux than the no treatment plot of C as well as the nitrogen but winter legume inclusive and no nitrogen with winter legume exclusive plots A and B, respectively. However, in summer 2010, the general trend as compared to summer 2008, was higher in magnitude in all the treatments except the no treatment (plot C) (Table 3.7). In general, there was much variability of CO_2 efflux among the treatments with the no nitrogen treatments (Plots B and A) showing the highest effluxes of 3.86 and 3.28 μ mol m^{-2} s^{-1}, respectively. This trend is similar to one seen by Yavitt et al. (1995) who reported about CO_2 efflux in agricultural fields. It can also be said that CO_2 effluxes may have also been affected by factors such as fertility, crops, season of sampling, and soil temperature that varied in interrelations and interdependence. Again, all treatments were highly significantly different from each other except the no treatment which was used as the control and the no potassium treatment (Table 3.8).

3.4 Summary and Conclusions

With respect to the objectives of this study, the following conclusion can be drawn from the results.

(i) Soil CO_2 effluxes were affected by crop rotation and fertilizer treatments.

(ii) Season of sampling has significant difference on CO_2 efflux. The summer 2008 efflux values were greater than their corresponding fall 2008.

(iii) Summer 2010 CO_2 effluxes were greater than summer 2008 as well as fall 2008.

(iv) Soil temperature was observed not to have any influence on the CO_2 effluxes.

(v) In the Old Rotation, treatments with legume had greater CO_2 efflux values in the summer of 2008 and 2010 compared to fall season sampling. Also, winter legume treatments showed significantly greater CO_2 efflux compared to the no-legume treatments.

In general, CO_2 efflux is dependent on soil conditions that include soil moisture, organic matter content, microbial activity and temperature. Temporal and spatial variability could play a role on the magnitude of the CO_2 efflux.

Table 3.1: Cropping system and fertilizer usage in the Old Rotation, Auburn University, Auburn, Alabama

Treatment or Nutrients applied/rotation	Plots	summer	winter		summer
Cropping system ($N-P_2O_5-K_2O$) kg ha^{-1}		2008	2008	2009	2009
No Rotation					
No N, No winter legume 0 -90-67	1, 6	Cotton	Nothing		Cotton
+ winter legume 0-90-67	2, 3 & 8	Cotton	Crimson clover		Cotton
+ Fert. N 134 – 90 - 67	13	Cotton	Nothing		Cotton
2-Yr Rotation					
+ winter legume 0 – 180 -134	4, 7	Cotton	Crimson clover		Corn/Cotton
+ Fert. N + winter legume 268 – 180 - 134	5, 9	Cotton/Corn	Crimson clover		Corn
3-Yr Rotation (11) 330 – 180 – 134 Cotton (Legume)- corn-Wheat/soybean	10, 11 & 12	Wheat/SB	Crimson clover (10) Wheat (11)/Nothing (12)		Corn (10)/SB Cotton (12)

2-Yr and 3-Yr: - Two and three - year rotations respectively in the Old Rotation, Auburn University, Auburn, Alabama. 2008-2009.

Table 3.2: Cropping system and fertilizer usage in the Cullars Rotation, Auburn University, Auburn, Alabama

Treatment or Nutrients applied/ Cropping system (N-P_2O_5-K_2O) kg ha^{-1}	Plots 3-Yr rotation	summer 2008	winter 2008 2009	summer 2009
No N/+ winter legume 0 -224-190	A	Cotton	Crimson clover	Corn
No N/No winter legume 0-224-190	B	Cotton	No Crimson clover	Corn
No Treatment 0 - 0 - 0	C	Cotton	No Crimson clover	Corn
No Phosphorous 168 - 0 - 190	2	Cotton	Crimson clover	Corn
Complete Fert. 168 -224 - 190	3	Cotton	Crimson clover	Corn
No Potassium 168 - 224 - 0	6	Cotton	Crimson clover	Corn
Complete Fert. 168-224- 190 + micronutrients	10	Cotton	Crimson clover	Corn

Three-year rotations sampled treatments in the Cullars Rotation, Auburn University, Auburn, Alabama. 2008-2009.Fert. – Fertilization

Table 3.3: Physical parameters measured in Old Rotation, June 2009. Auburn University; Auburn, Alabama.

Treatment or Cropping system	Plots	pH	Bulk Density (g cm^{-3})	Gravimetric Moisture (Θ_g)	Volumetric Moisture (Θ_v)	Temperature ^{o} C
<u>No Rotation</u>						
No N, No winter legume	1, 6	5.93	1.27	9.2	11.4	28.5
+ winter legume	2, 3, 8	5.73	1.19	14.7	17.3	27.8
+ Fert. N	13	5.95	1.27	11.5	14.5	28.0
<u>2-Yr Rotation</u>						
+ winter legume	4, 7	5.98	1.36	11.1	15.1	27.6
+ Fert. N + winter legume	5, 9	5.85	1.27	10.3	13.1	26.6
<u>3-Yr Rotation</u> Cotton/Legume - corn-Wheat/soybean	10, 11, 12	6.05	1.25	19.2	23.9	27.7

2-Yr and 3-Yr: - Two and three - year rotations respectively in the Old Rotation, Auburn University, Auburn, Alabama.
Fert. – Fertilization. pHs – pH determined in 0.1M $CaCl_2$ solution.

Table 3.4: Physical parameters measured in Cullars Rotation, June 2009. Auburn, Alabama.

Treatment/ Cropping system	Plot	pHs	Bulk Density	Gravimetric Moisture (Θ_g)	Volumetric Moisture (Θ_v)	Temperature °C
No N/ WL	A	5.95	1.43	4.2	6.0	26.7
No N / No WL	B	6.0	1.34	2.3	3.1	27.1
No Treatment	C	6.2	1.42	2.3	3.3	27.7
No Phosphorous	2	6.15	1.37	2.8	3.9	27.3
Complete Fert.	3	6.2	1.18	1.3	1.5	27.4
No Potassium	6	6.1	1.13	5.2	5.8	28.0
Complete Fert.	10	6.2	1.15	7.5	8.7	27.9

Fert. – Fertilization. pHs – pH determined in 0.1M $CaCl_2$ solution. WL: – Winter legume

Table 3.5: CO_2 efflux variations in the Old Rotation, Auburn University; Auburn, Alabama

Treatment or Cropping system	Plots	summer 2008	fall 2008	summer 2010
		CO_2 Efflux (μ Mol m^{-2} s^{-1}) Mean (SE)		
No Rotation				
No N, No winter legume	1, 6	3.69(0.17)	1.3(0.06)	2.15(0.12)
+ winter legume	2, 3, 8	4.02(0.11)	2.2(0.09)	5.12((0.15)
+ Fert. N	13	3.02(0.13)	1.47(0.1)	3.39(0.43)
2-Yr Rotation				
+ winter legume	4, 7	5.44(0.23)	1.76(0.06)	6.00(0.23)
+ Fert. N + winter legume	5, 9	4.14(0.14)	1.91(0.09)	4.20(0.14)
3-Yr Rotation Cotton/Legume - corn- Wheat/soybean	10, 11, 12	3.65(0.09)	2.02(0.08)	3.76(0.12)

2-Yr and 3-Yr: - Two and three - year rotations respectively in the Old Rotation, Auburn University, Auburn, Alabama.
Mean (SE):- Mean ± standard error. Fert. – Fertilization.

Table 3.6: Treatment effect of CO_2 efflux LS MEAN in the Old Rotation

Treatment or Cropping system	Plots	LSMEAN	CO_2 efflux $Pr > \lvert t \rvert$	$LSD_{0.05}$
No Rotation				
No N/ No winter legume	1, 6	2.38	---------	--- -----
+ winter legume	2, 3, 8	3.77	<0.0001	1.39
+ Fert. N	13	2.62	NS	0.25
2-Yr Rotation				
+ winter legume	4, 7	4.40	<0.0001	2.02
+ Fert. N + winter legume	5, 9	3.42	<0.0001	1.03
3-Yr Rotation Cotton /Legume - corn-Wheat/soybean	10, 11, 12	3.14	<0.0001	0.77

2-Yr and 3-Yr: - Two and three - year rotations respectively in the Old Rotation, Auburn University, Auburn, Alabama.
Fert. – Fertilization.

Table 3.7: CO_2 efflux variations in summer 2008, fall 2008 and summer 2010 in the Cullars Rotation, Auburn University; Auburn Alabama

Treatment or Cropping system	Plots	summer 2008	fall 2008	summer 2010
		-------------------- CO_2 Efflux (μ Mol m^{-2} s^{-1}) Mean (SE) -----		-----------------
No N/+ winter legume	A	2.36(0.14)	2.87(0.3)	3.28(0.16)
No N, No winter	B	2.02(0.16)	2.29(0.18)	3.86(0.17)
No treatment	C	2.29(0.5)	1.19(0.09)	1.80(0.13)
No phosphorous	2	2.94(0.25)	1.63(0.08)	3.06(0.18)
Complete Fert.	3	2.97(0.1)	1.87(0.1)	2.72(0.08)
No potassium	6	2.69(0.1)	1.83(0.1)	2.44(0.08)
Complete Fert. + micronutrient	10	3.25(0.14)	1.87(0.08)	3.20(0.14)

Mean (SE):- Mean ± standard error. The Cullars Rotation, Auburn University, Auburn, Alabama.
Fert. - Fertilization

Table 3.8: Treatment effect of CO_2 efflux LS MEAN in the Cullars Rotation

Treatment or Cropping system	Plots	LSMEAN	CO_2 efflux Pr > | t |	$LSD_{0.05}$
No N/+ winter legume	A	2.83	<0.0001	1.08
No N, No winter	B	2.72	<0.0001	0.96
No treatment	C	1.76	--------	------
No phosphorous	2	2.54	<0.0001	0.77
Complete Fert.	3	2.52	<0.0001	0.76
No potassium	6	2.32	0.0061	0.56
Complete Fert. + micronutrient	10	2.77	<0.0001	1.01

Cullars Rotation, Auburn University, Auburn, Alabama. Fert. - Fertilization

Figure 3.1. Average CO_2 efflux in each season and location in (Tons ha^{-1} yr^{-1})

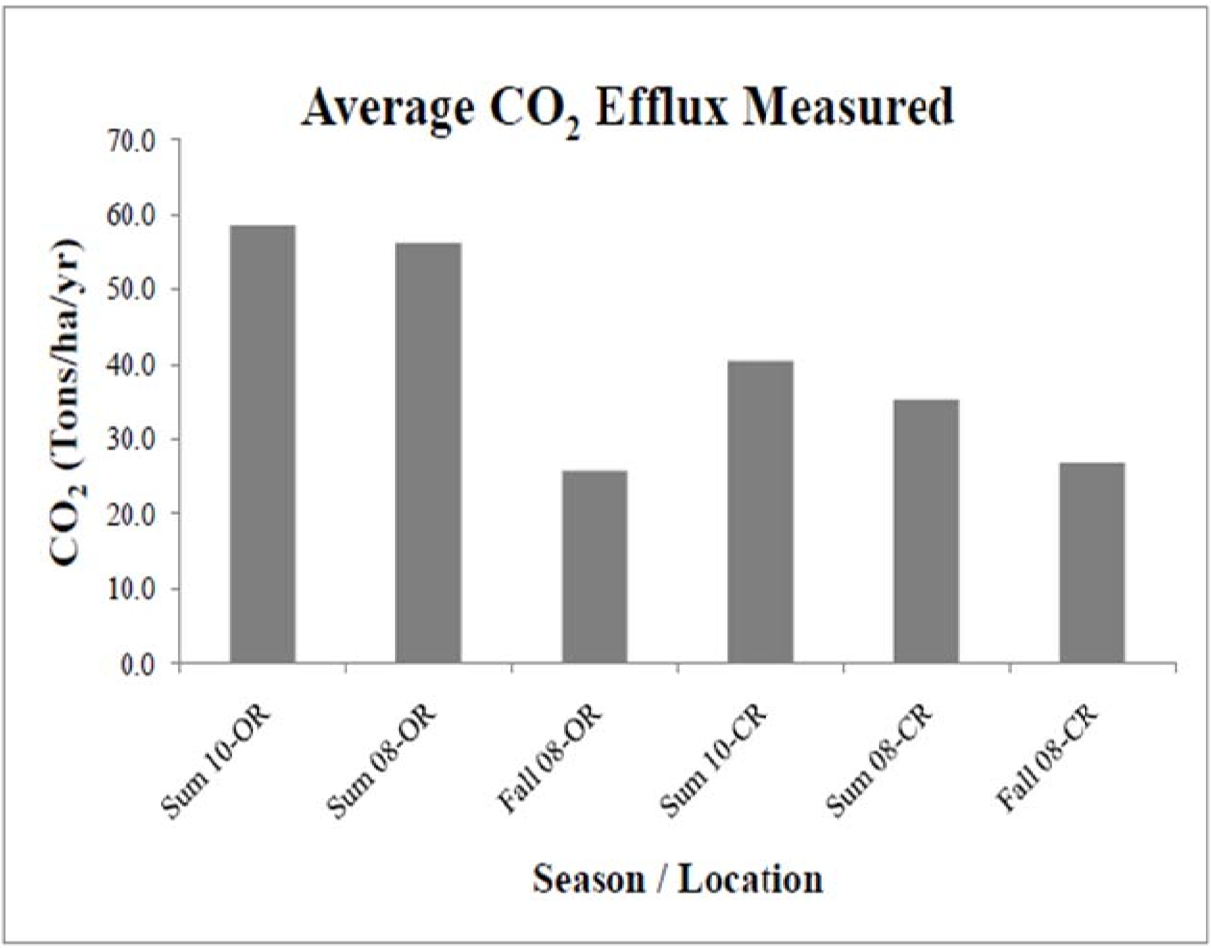
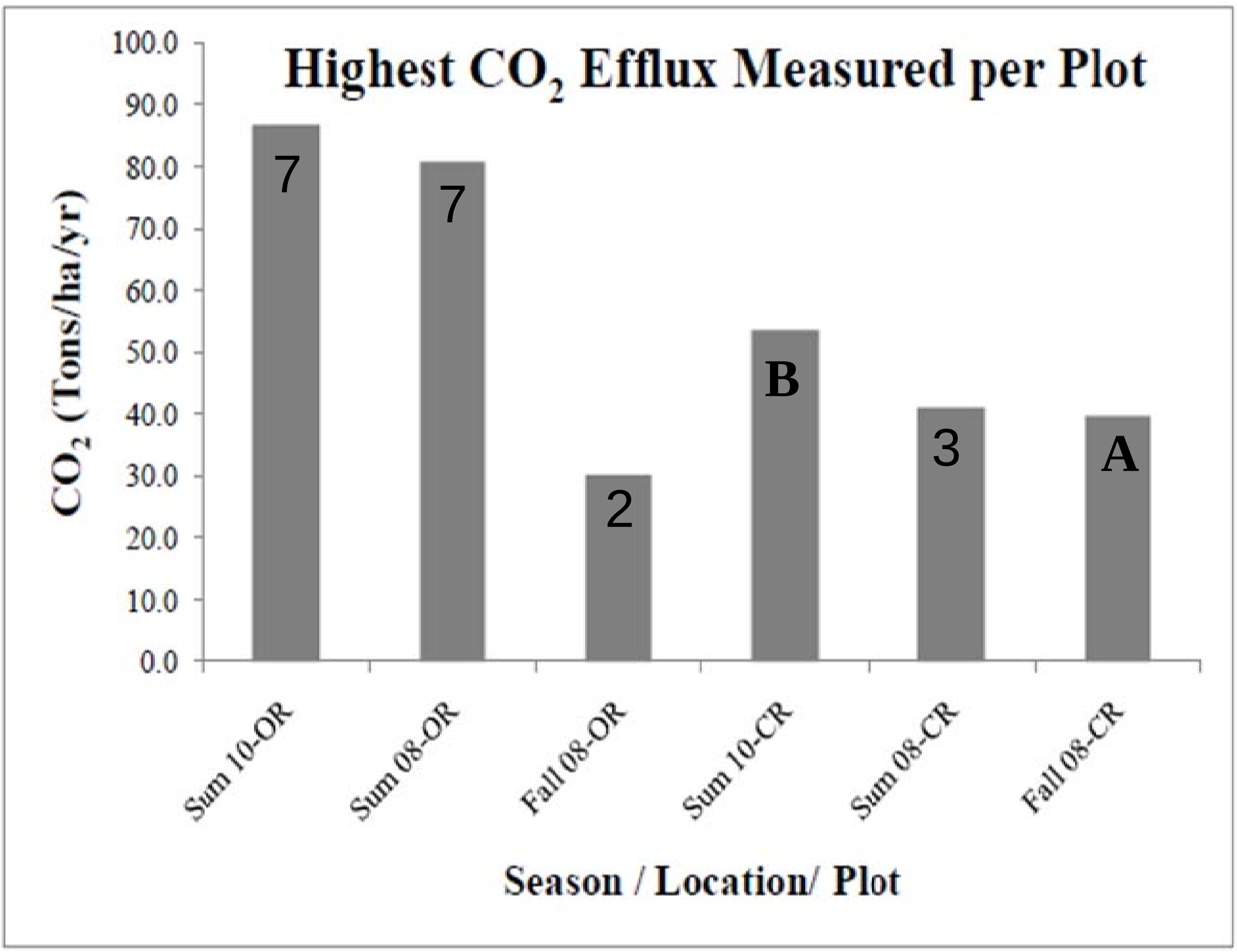


Figure 3.2. Highest CO_2 efflux per plot in each season and location in (Tons ha^{-1} yr^{-1})



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Chapter 4: Chemical Fractionation of Soil Organic Matter in Long-term Experiments

Abstract

Fourier transform infrared (FTIR) spectroscopy was used to identify the complex functional groups of SOM in two long-term cropping experiments at Auburn University in Alabama, the Old Rotation (circa 1896) and from some selected plots in the Cullars Rotation (circa 1911). Elucidating the chemical organic functional groups within soil organic matter (SOM) will aid in understanding the roles rotation and fertilizers play on stabilizing SOM under different management conditions. Soluble organic compounds were sequentially extracted by deionized water and 0.1 M sodium pyrophosphate solutions, respectively.

The extracted samples were frozen and subjected to freeze drying. The freeze-dried samples were placed in a desiccator with copper sulfate to remove traces of moisture. Potassium bromide (KBr) was used as background to identify different organic functional groups within soils for 0-5 and 5-10 cm depths. Once the peaks of each functional group were measured, they were compared to known organic functional group for qualitative identification.

Similar functional groups such as alkyl groups (CH_2, CH_3), carboxylic acid derivatives(C=O), and stretching vibrations of aldehydes and ketones (C-O) were found in all extracts in both long-term experiments. However, dissolution of SOM is less pronounced in the sodium pyrophosphate extracts. There were lower transmittance values in spectral graphs showing peaks extracted in the sodium pyrophosphate medium compared to deionized water extracted peaks. Only a few treatments from the Cullars Rotation showed peaks with stretching

vibrations due to methyl and methylene groups under both symmetric and asymmetric vibrations. There were no differences due to cropping system and fertilizer treatments on functional groups.

4.1 Introduction

Paustian et al. (2000) reported SOM should be considered as a vital component in the terrestrial carbon cycle globally. Soils accumulate and store over 80% of active carbon from organic sources (Wattel-Koekkoek et al., 2001). In assessing changes in SOM as a result of management, carbon turn-over models are normally used (Smith et al., 1997; Gabrielle et al., 2002). Most models are based on only two pools, labile and stable pools (Powlson et al., 1996; Stevenson, 1994; Wattel-Koekkoek et al., 2003). However, some studies indicate a major drawback in these models (Powlson et al 1996; Pennock and Frick 2001; Wattel-Koekkoek et al. 2003). There are no verifiable linkages between the experimentally extracted organic matter fractions and the conceptual pools.

Based on measurable carbon pools, Sohi et al.(2001) suggested the mechanistic approach to density fractionation would serve as a means for SOM mean residence models; despite the low amount (up to 5% of the total organic carbon) of SOM extracted by these means. There is lack of knowledge about the basic concepts of SOM stabilization in the two long-term cultivated experiments located at Auburn University, the Cullars and the Old Rotations with respect to organic carbon pools and their chemically extracted functional groups. Gaps in general knowledge have been identified, which gave Powlson et al., (1996) the uncertainties and doubts when models are applied to long-term experiments.

Among the possibilities of understanding SOM transformation is the association between polyvalent cations and SOM (Gillet and Ponge, 2002; Gregorich et al., 2003;

Gleixner et al., 2002; Wattel-Koekkoek et al., 2003). Soil particle aggregations and particle sizes are important consideration when studying SOM solubility. For analytical purposes, SOM can be partitioned among variable components with respect to their solubility, which also depends on the associations between SOM, soil mineral surfaces and polyvalent cations (Sposito, 1989; Stevenson, 1994). West and Post (2002) suggested management and land use, soil texture and climate influence not only SOM content but also the composition of the SOM as well.

Bascomb (1968), and Greenwood and Earnshaw (1984) were part of the initial researchers who reported and affirmed the capability of pyrophosphate anions to remove cations from SOM by the formation of complexes of the cation-pyrophosphate. This leads to easy solubilization of OM and extraction. With the use of pyrophosphate, isolation of stable SOM could be achieved. This will allow assessment of carbon pools in carbon models like the Rothamsted model (Ellerbrock and Kaiser, 2005). Similarly, the same authors found that composition and stability of the extracted OM by FTIR depends on the components of the soil minerals as well as climatic conditions prevailing within the soil in general. The usage of the word "composition" refers solely to the functional groups within the extracted SOM (e.g. alkyl, phenol groups, carboxylic acid groups, ketones, aldehydes etc). Almendros (1995); Gressel et al. (1995) also reported on the strong impact on SOM functional groups as influenced by the sorption characteristics such as cation exchange capacity (CEC).

Among a variety of techniques, FTIR can be used in assessing the differences in composition of SOM (Capriel et al., 1995; Gerzabek et al., 1997) in addition to nuclear magnetic resonance (NMR) (Gonzalez-Villa et al., 1976). As recent as 2005, a synchrotron-based FTIR was successfully used by Solomon et al. (2005) to assess the composition of SOM from both silt and clay fractions from soils.

4.2 Materials and Methods

4.2.1 Chemical Characterization of Extracted Soil Organic Matter (SOM)

The samples for these studies were taken in 2008 and 2009 from two long-term crop experiments the Old Rotation (circa 1896) and Cullars Rotation (circa 1911) of Auburn University in Auburn, Alabama, within latitude 32^{o} 35′ and longitude 85^{o} 29′. The Old Rotation is located at the boundary between Coastal Plain and Southern Piedmont Plateau Physiographic regions of the Eastern part of Central Alabama. The soil type on the Old Rotation is Pacolet fine sandy loam (Clayey, Kaolinitc, Thermic, and Typic Hapludults).

The Cullars Rotation is located in the Coastal Plain Physiographic region and the soil is a Marvyn loamy sand (fine-loamy, siliceous, thermic, Typic Kanhapludults) (Mitchell et al., 2005). The Old Rotation consists of 13 plots. Each plot in the Old Rotation is 6.5 by 41.5 meters with 1 meter alley separating each plot (Hubbs et al., 1998). The Cullars Rotation is made up of three blocks with 14 different treatments, with each block having the same sets of treatments for the three different crops (cotton, winter legume, corn, and wheat/rye and soybeans). Each block treatment is a different crop rotation sequence involving cotton. However our study was limited to only the middle tier in the Cullars Rotation. The treatments sampled are listed in table 4.1 and 4.2, respectively, for the Old Rotation and the Cullars Rotation. The Old Rotation is the oldest continuous cotton experiment in the world (cf. 1896) and the Cullars Rotation is the oldest soil fertility experiment in the southeastern United States.

4.2.2 Sampling, Sample Preparation and Two Step Sequential Extractions

Soil samples were randomly taken from individual plots of study at both locations similar to the previous studies and were air dried for 72 hours. Using the modified method of Kaiser and Ellerbrock (2005), 10 g of each sample was weighed into a 250 mL centrifuge bottles. One hundred mL of deionized water was added to each sample and securely tightened and then shaken for 24 hours. Thereafter, the thoroughly shaken mixture was centrifuged at a speed of 3500 revolutions per second for 35 minutes. Water soluble organic fractions are assumed to be dissolved in the water and referred to as"water soluble organic matter" (WSOM) according to Nierop and Buurman (1998). The centrifuged sample was then filtered through 0.45 µm filter paper using the Millipore filtration set up. One hundred milliliters (100 mL) of 0.1 M sodium pyrophosphate solution was then added to the remaining soil residue in the bottle and shaken for another six hours and filtered through the same Millipore set up. At this stage, all the organic components of the dissolvable organic compounds in the soils are believed to be dissolved into the 0.1M sodium pyrophosphate solution. The filtrates were then decanted into a clean beaker and then acidified with a 1N hydrochloric acid (HCl) solution to pH 2. The acidification causes the recalcitrant humic acid components to settle at the bottom of the beaker leaving the fulvic acid component in suspension. The tinged colored fulvic acid part otherwise known as the "pyrophosphate extracted organic matter" (PYSOM) was carefully decanted into a clean centrifuge bottle again and centrifuged again. The centrifuged dissolved organic compounds were then filtered again through the same set up and frozen. Both the WSOM and PYSOM frozen samples were freeze dried and samples kept frozen until ready to be analyzed.

4.2.3. WSOM and PYSOM Chemical Characterization

The chemical characterizations of the freeze dried samples were done according to the KBr methodology described by Capriel et al., (1995) and Celi et al., (1997). A 0.5 mg of each sample was weighed and added to 80 mg potassium bromide (KBr). This was kept in a dessicator filled with a copper sulfate desiccant ($CuSO_4$) for at least 12 hours to standardize the moisture content in all the samples. Varying moisture content of the samples could interfere with the interpretations of the spectral peaks as a result of the O-H bonds in water. The desiccated samples were then ground in an agate mortar into a fine powder and hydraulically pressed into a fine, thin transparent pellet. The pellet was then placed in the FTIR, and its transmittance was measured through the peaks formed from each particular chemically extracted sample in the range of 400 to 4000 cm^{-1}, resolution of 1 cm^{-1}, 16 scans, square triangle apodization (Celi et al., 1997). Each particular peak of the spectral corresponds to a particular functional group of organic compound in the fulvic acid component. Before any sample reading was taken, a background was read on the FTIR using a standardized pure KBr pellet. If there was a negative peak spectral due to air interference, the background was changed to air.

4.2.4. Peak Assignments for the FTIR Spectra

There are many functional compounds that can be found in extracted soil organic matter, but of much particular interest to our study are those of functional groups with multiple carbon chains and of aromatic composition within wave numbers between 2000 - 4000 cm^{-1} (see Table 4.1).

4.3 Results and Discussions

Similar functional groups were found in both water and sodium pyrophosphate extracted dissolved organic compounds. However, C-H groups found among some of the Cullars Rotation extracts (Figures 4.1 to 4.5) could be attributed to stretching vibrations of ketones and aldehydes. In entirety, the percent transmittances of the sodium pyrophosphate extract were higher than their water extractable samples, ranging between 19 to 28.5%. However, Figure 4.8 showed the opposite scenario, with water extract showing marginally higher transmittance than the sodium pyrophosphate extracts. These functional groups are products of SOM incorporation and treatments. Generally, dissolution of SOM functional groups in sodium pyrophosphate is more pronounced than in deionized water (e.g. Figures 4.1 and 4.3). This is as a result of the anionic part of the pyrophosphate ($P_2O_7^-$) that gets attached to the dissolvable organic compounds in the soil in solution with sodium pyrophosphate and thereby is dissolved in solution (Kaiser and Ellerbrock, 2005).

Comparing these spectral graphs to the trends seen in the carbon fractions, carbon and its products are sequestered into the heavy fraction of carbon. The main reasons for these developments could be attributed to minimal tillage implements usage due to the change in management of the experiments from conventional tillage to strip tillage. Also, it is of much importance to note that spectral graphs resulting from sodium pyrophosphates extracts (PYSOM) also showed less transmittance as depicted in the peak heights as compared to water extractable ones (WSOM). Thus, WSOM spectral graphs had higher percentage transmittance than their corresponding PYSOM extracts with a few exception such as (Figure 4.1 CRA 0-5, CRA 5-10,

Figure 4.2 CRB 0-5 and 5-10 respectively; Figure 4.12; OR9 5-10 and Figure. 4.14; OR11 0-5) cm. These spectral graphs with their shown individual functional groups again confirm much more functional groups within the dissolvable organic compounds are neither breaking up much nor dissolving in solution enough, hence their absence in sodium pyrophosphate extracts. These could be attributed to their quick transformation into the inert chemically organic compounds. Sodium pyrophosphate has the tendency to dissolve soluble organic compounds in fulvic acids. Only some Cullars Rotation extracted samples have showed peaks due to vibrations of methyl and methylene of both of which are symmetric and asymmetric vibrations between the wave numbers of 2860 to 2960 cm^{-1} and a few others such as amide peaks (CN) in the Old Rotation extracted samples. Even though the expected peaks within the wave number range of 2000 to 4000 cm^{-1} was inconspicuous and those that did were just a small quantity of the total in terms of percentage transmittance. Conservation tillage, crop rotation, and continuous cultivation practices coupled with sound management practices encouraged carbon sequestration into the soil. Irrespective of location of sampling, all spectral graphs indicated the presence of similar functional groups, namely carboxylic acid derivatives (C=O), methyl and ethyl groups–alkyl groups (CH_3, CH_2) and stretching vibration from ketones, cyclic and acyclic aldehydes (C-O).

4.4 Summary and Conclusions

Water and pyrophosphate extracted organic compounds with different transmittance. Methyl, hydroxyl, methylene, carboxylic, alkyl, and other organic functional groups were present in the soils at both depths. Results from this study indicated the absence of dissolvable organic compound of multiple carbon chains and aromatic compounds of higher molecular weights within wave numbers ranges of 2000 to 4000. These organic compounds could have the potential of disintegrating and being given off as carbon dioxide under the conditions of conventional tillage practices. These developments could indicate their inaccessibility, which could imply they are being held intact in the soil. This is clearly seen in both extracts spectral graphs and by the low transmittance values shown by spectral graphs.

Table 4.1 Peak assignments

Functional group	Wave number (cm^{-1})	Compound classes
CH_3, CH_2	700-900	Alkyl groups
O-H	1250-2000	Moisture
C=O or COO^-, C=C (conjugated), N-H	1600-1613	Unsaturated ketones, carboxylic acids, amides
C=O	1600-1640	Carboxylic acid anions
C=O …………………………………………	1698-1740	Stretching vibrations for ketones, cyclic and acyclic aldehydes and carboxylic acids.
CO_2 peak	2250-2400	carbon dioxide
C-H (symmetric)	2860	stretching vibrations for methyl and methylene groups
C-H (asymmetric)	2960	stretching vibrations for methyl and methylene groups
O-H	3500-4000	moisture

Adapted from Organic chemistry 5th (ed) by John McMurry. Chapter 12, Pp. 458 and Organic structure spectroscopy by Lambert et al., 1998. Chapter 6. Pp. 189-192.

Table 4.2: Cropping system and fertilizer usage in the Old Rotation, Auburn University, Auburn, Alabama

Treatment or Cropping system	Plots	summer 2008	winter 2008	winter 2009	summer 2009	Nutrients applied/rotation ($N-P_2O_5-K_2O$) kg ha^{-1}
No Rotation						
No N, No winter legume	1, 6	Cotton	Nothing		Cotton	0 -90-67
+ winter legume	2, 3 & 8	Cotton	Crimson clover		Cotton	0-90-67
+ Fert. N	13	Cotton	Nothing		Cotton	134 – 90 - 67
2-Yr Rotation						
+ winter legume	4, 7	Cotton	Crimson clover		Corn/Cotton	0 – 180 -134
+ Fert. N + winter legume	5, 9	Cotton/Corn	Crimson clover		Corn	268 – 180 - 134
3-Yr Rotation	10, 11 & 12	Wheat/SB	Crimson clover (10) Wheat (11)/Nothing (12)		Corn (10)/SB (11) Cotton (12)	330 – 180 – 134
Cotton (Legume)- corn-Wheat/soybean						

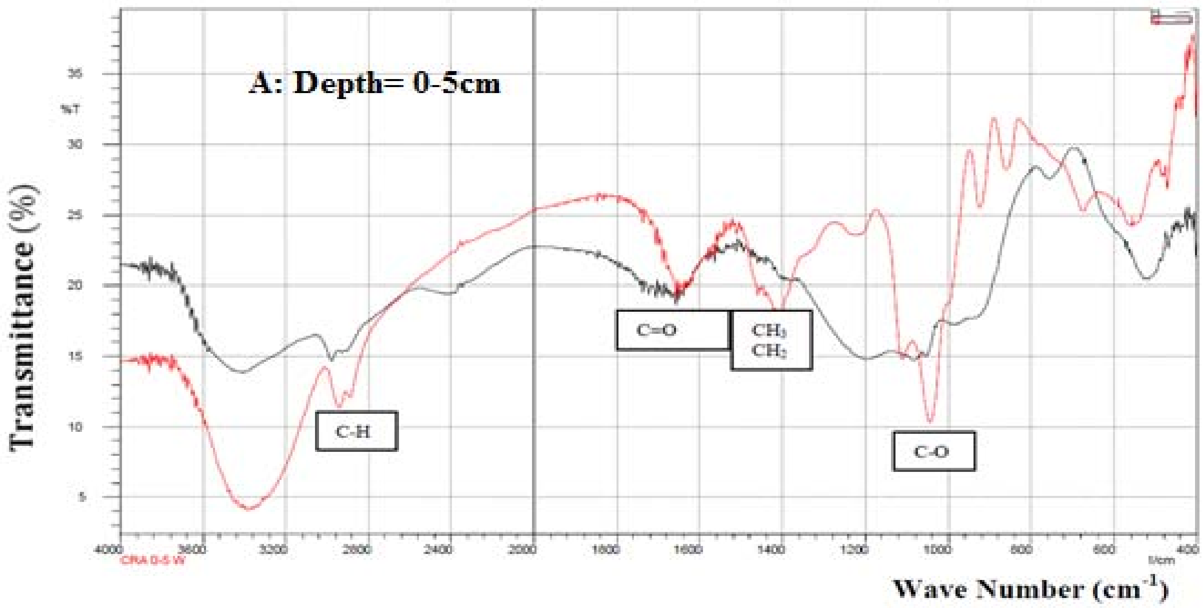
2-Yr and 3-Yr: - Two and three - year rotations respectively in the Old Rotation, Auburn University, Auburn, Alabama. 2008-2009.

Table 4.3: Cropping system and fertilizer usage in the Cullars Rotation, Auburn University, Auburn, Alabama

Treatment or rotation	Plots	summer	winter		summer	Nutrients applied/ 3-Yr
Cropping system		2008	2008	2009	2009	(N-P_2O_5-K_2O) kg ha^{-1}
No N/+ winter legume	A	Cotton	Crimson clover		Corn	0 -224-190
No N/No winter legume	B	Cotton	No Crimson clover		Corn	0-224-190
No Treatment	C	Cotton	No Crimson clover		Corn	0 - 0 - 0
No Phosphorous	2	Cotton	Crimson clover		Corn	168 - 0 - 190
Complete Fert.	3	Cotton	Crimson clover		Corn	168 -224 - 190
No Potassium	6	Cotton	Crimson clover		Corn	168 - 224 - 0
Complete Fert. + micronutrients	10	Cotton	Crimson clover		Corn	168-224- 190

Three-year rotations sampled treatments in the Cullars Rotation, Auburn University, Auburn, Alabama. 2008-2009
Fert. – Fertilization

Figures:



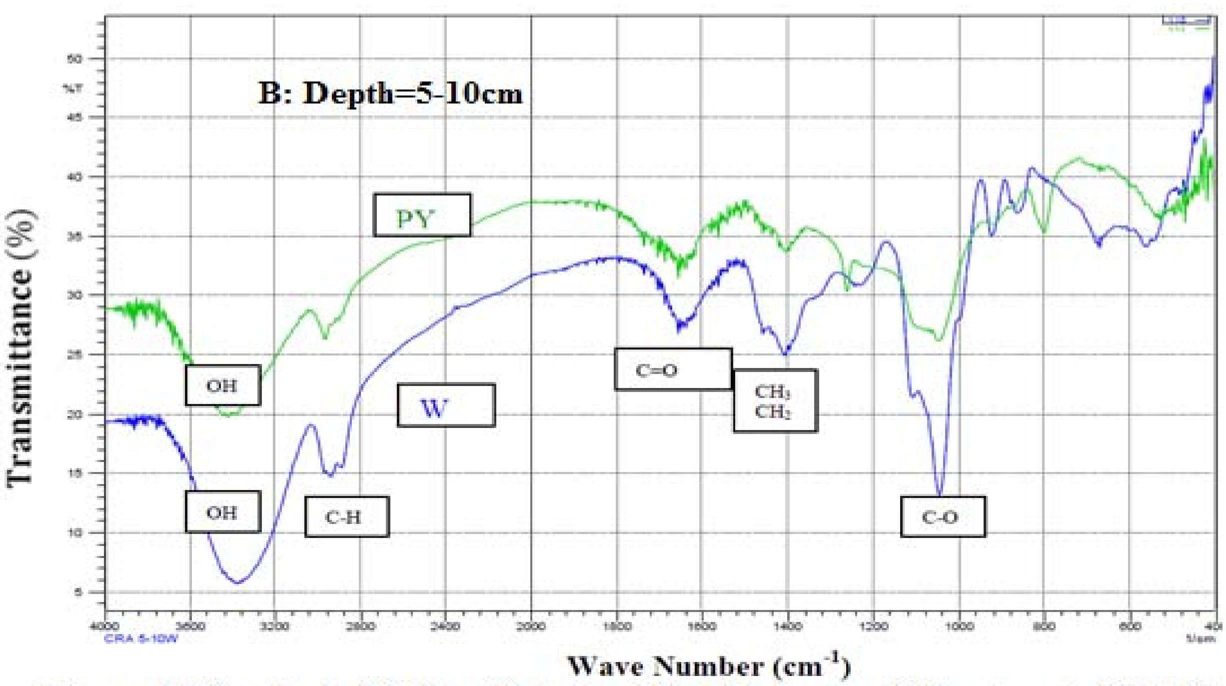


Figure 4.1 Spectral of Cullars Rotation "No N + Legume" Treatment, (Plot A)

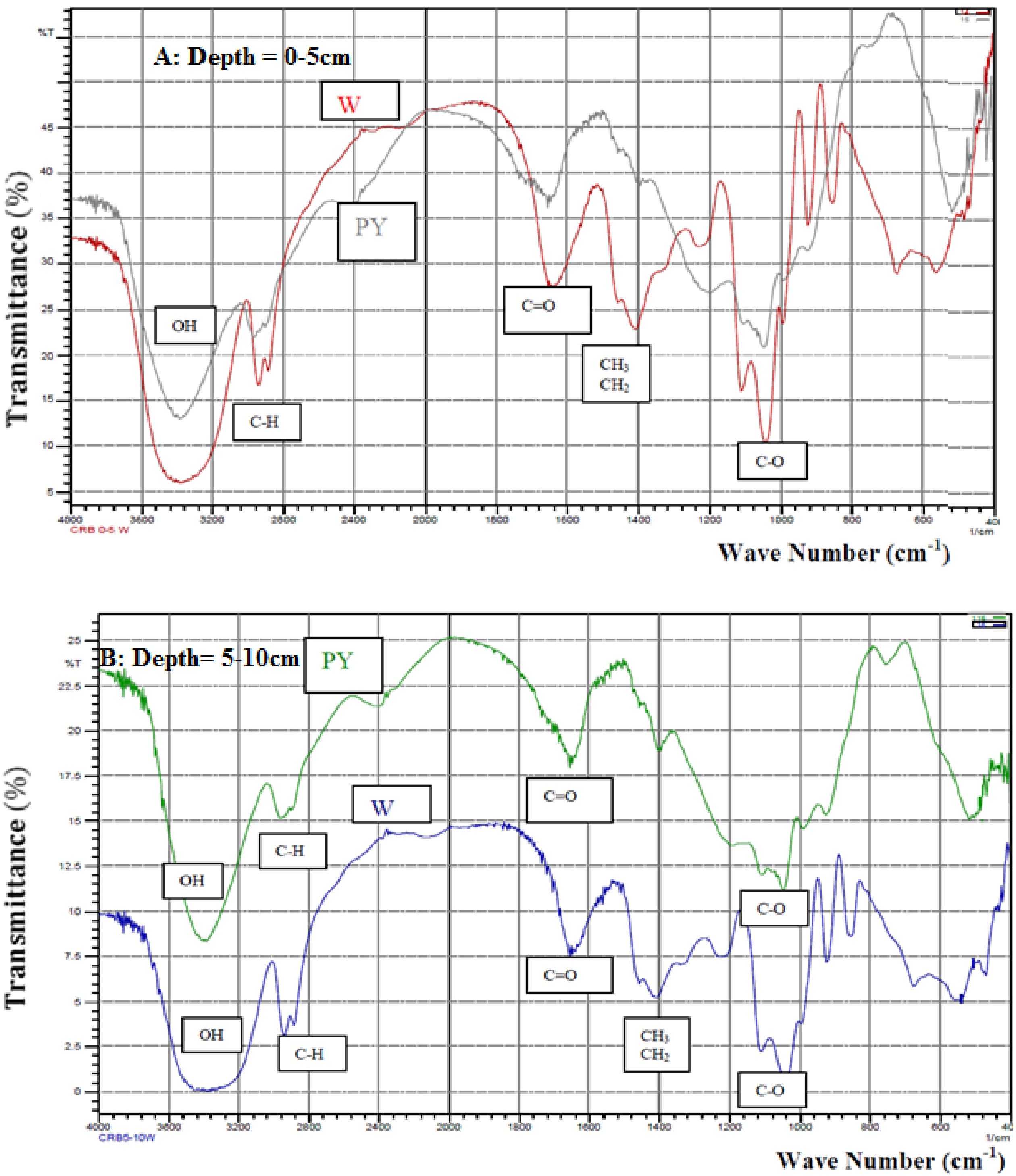


Figure 4.2 Spectral of Cullars Rotation "No N + Legume" Treatment (Plot B)

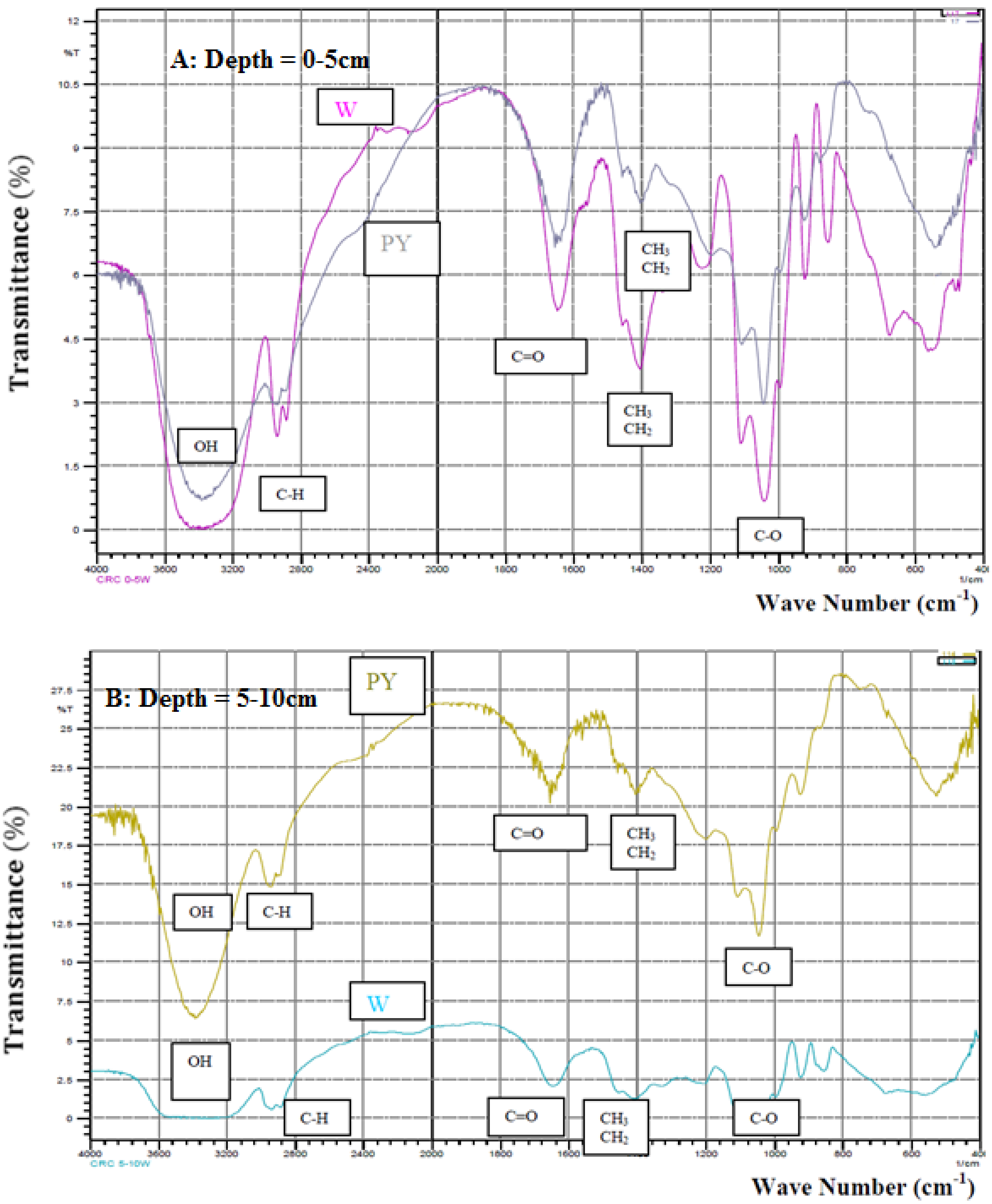


Figure 4.3 Spectral Cullars " Nothing" Treatment, (Plot C)

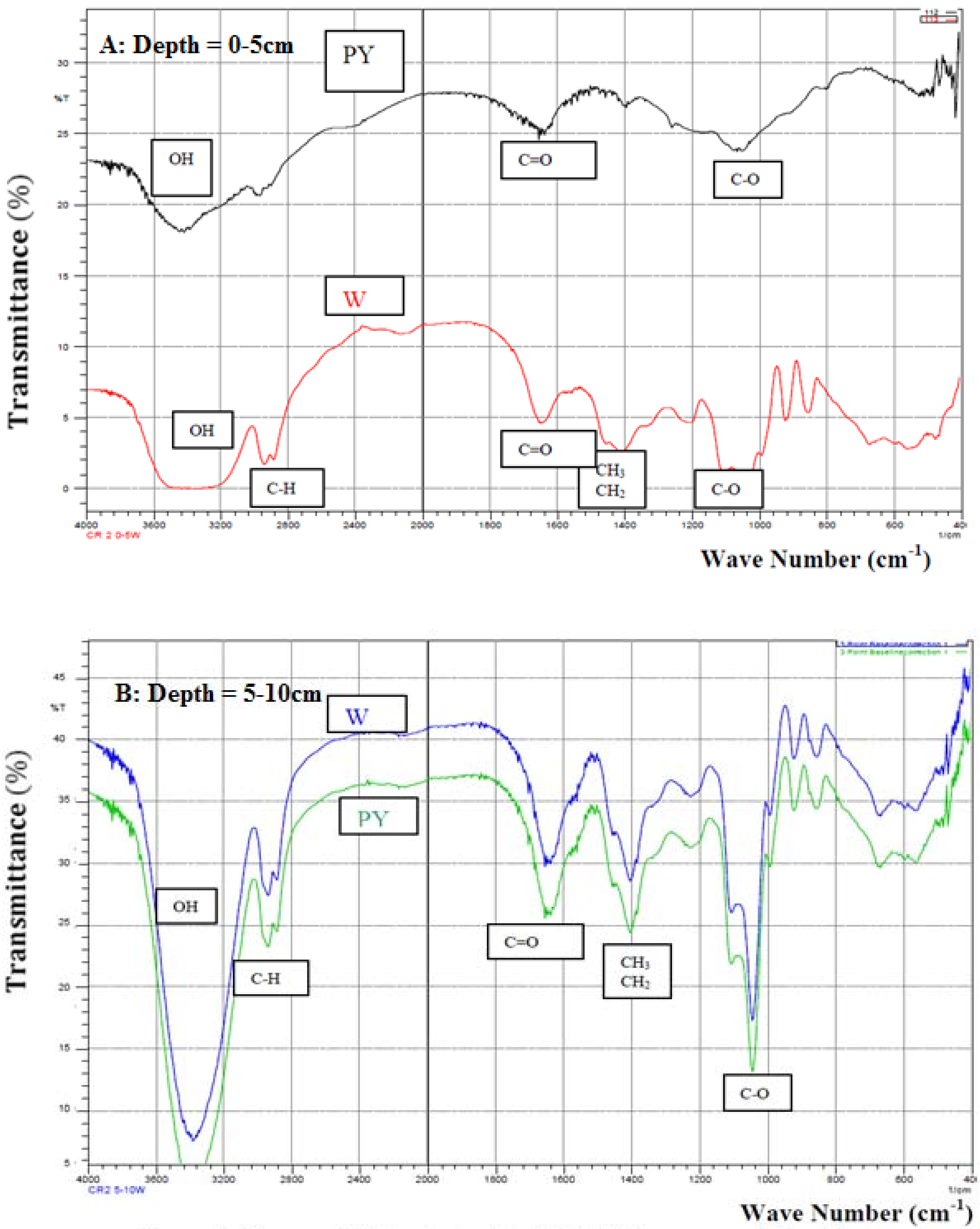
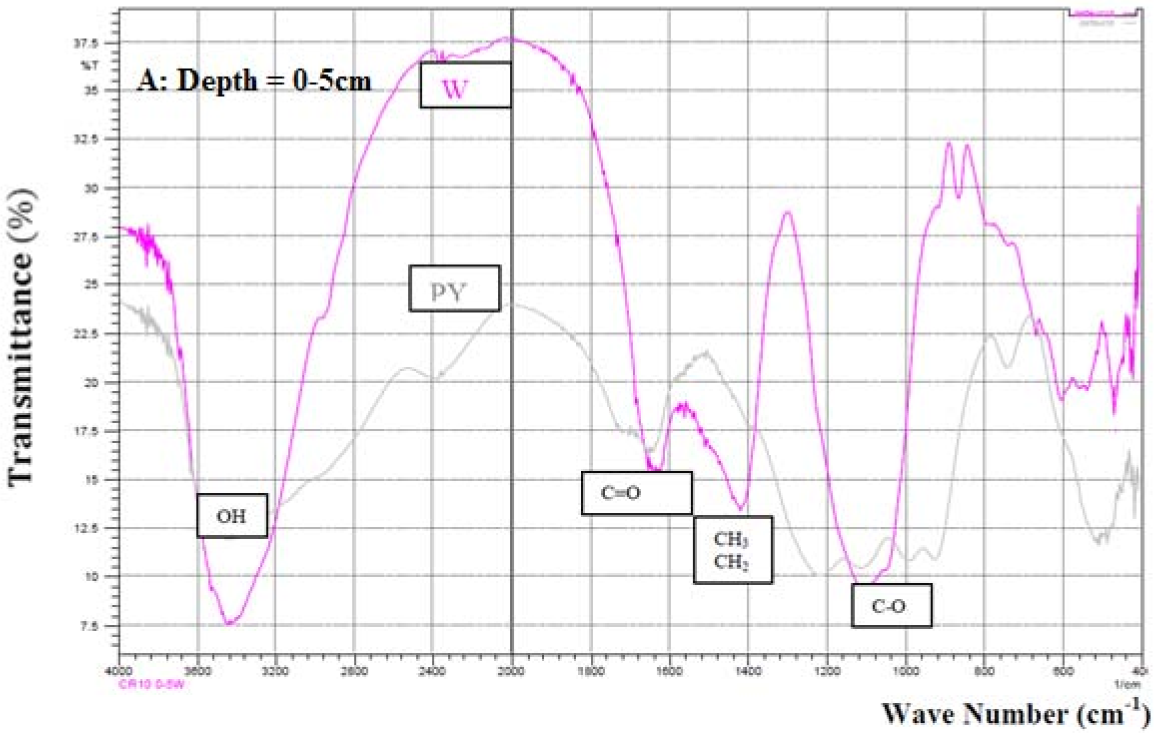


Figure 4.4 Spectral Cullars Rotation "No P" Treatment, (Plot 2)



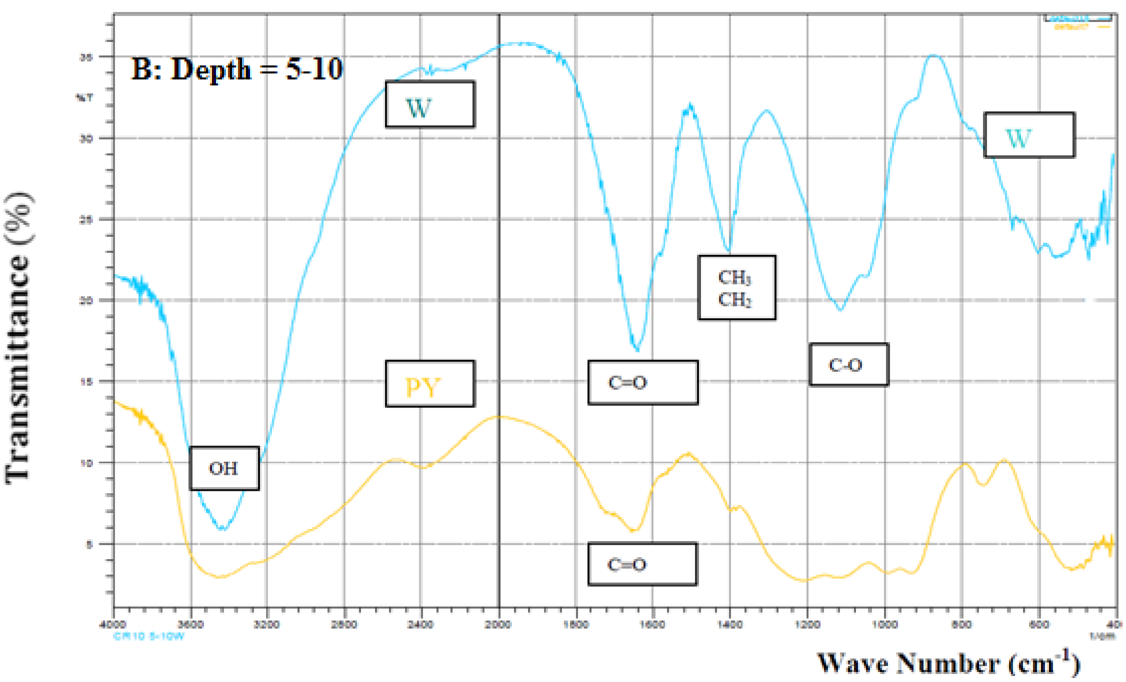


Figure 4.5 Spectral of Cullars "Complete fertilization + micronutrients" Treatment,(Plot 10)

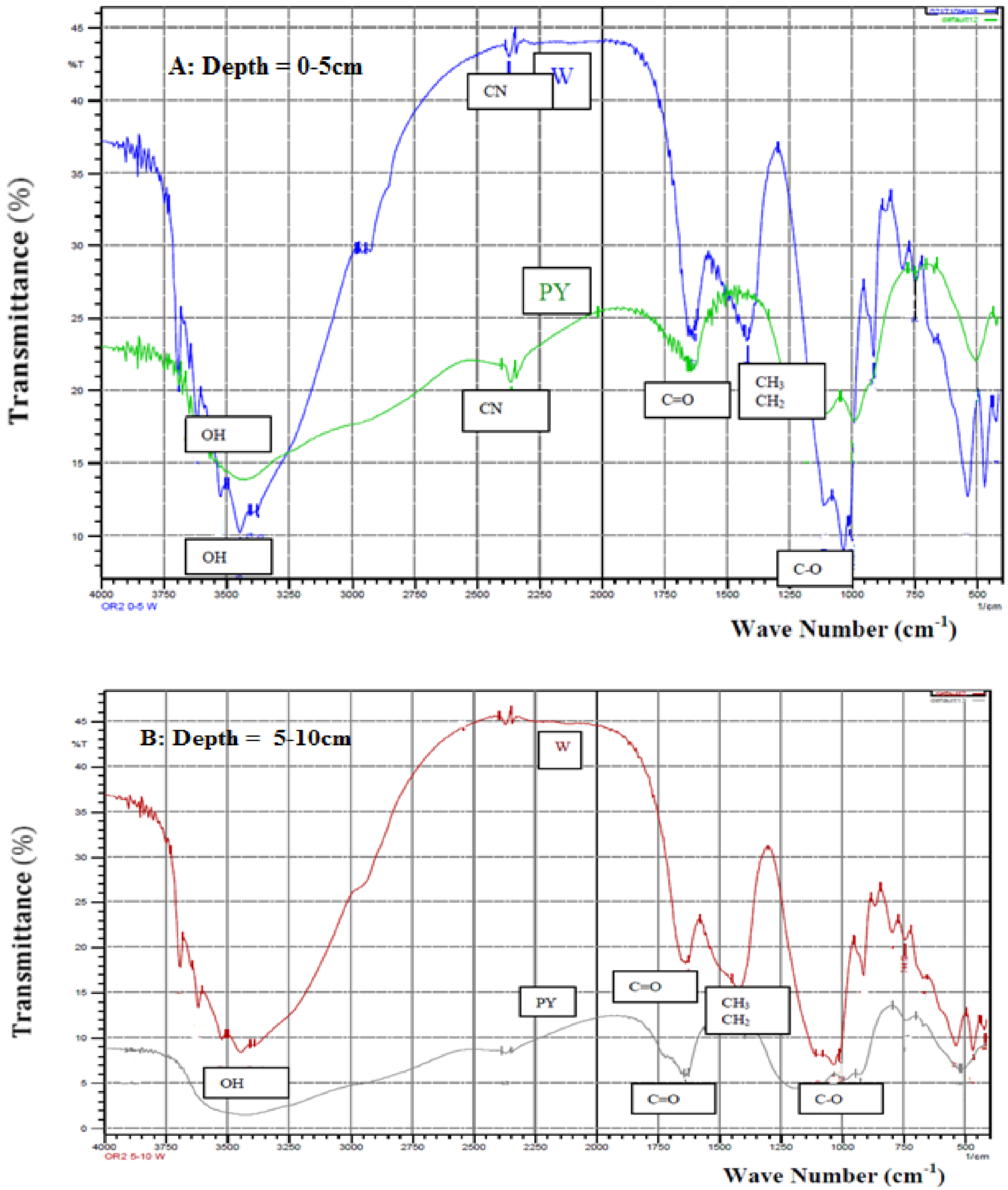


Figure 4.6 Spectral of Old Rotation "Winter Legume" Treatment, (Plot 2)

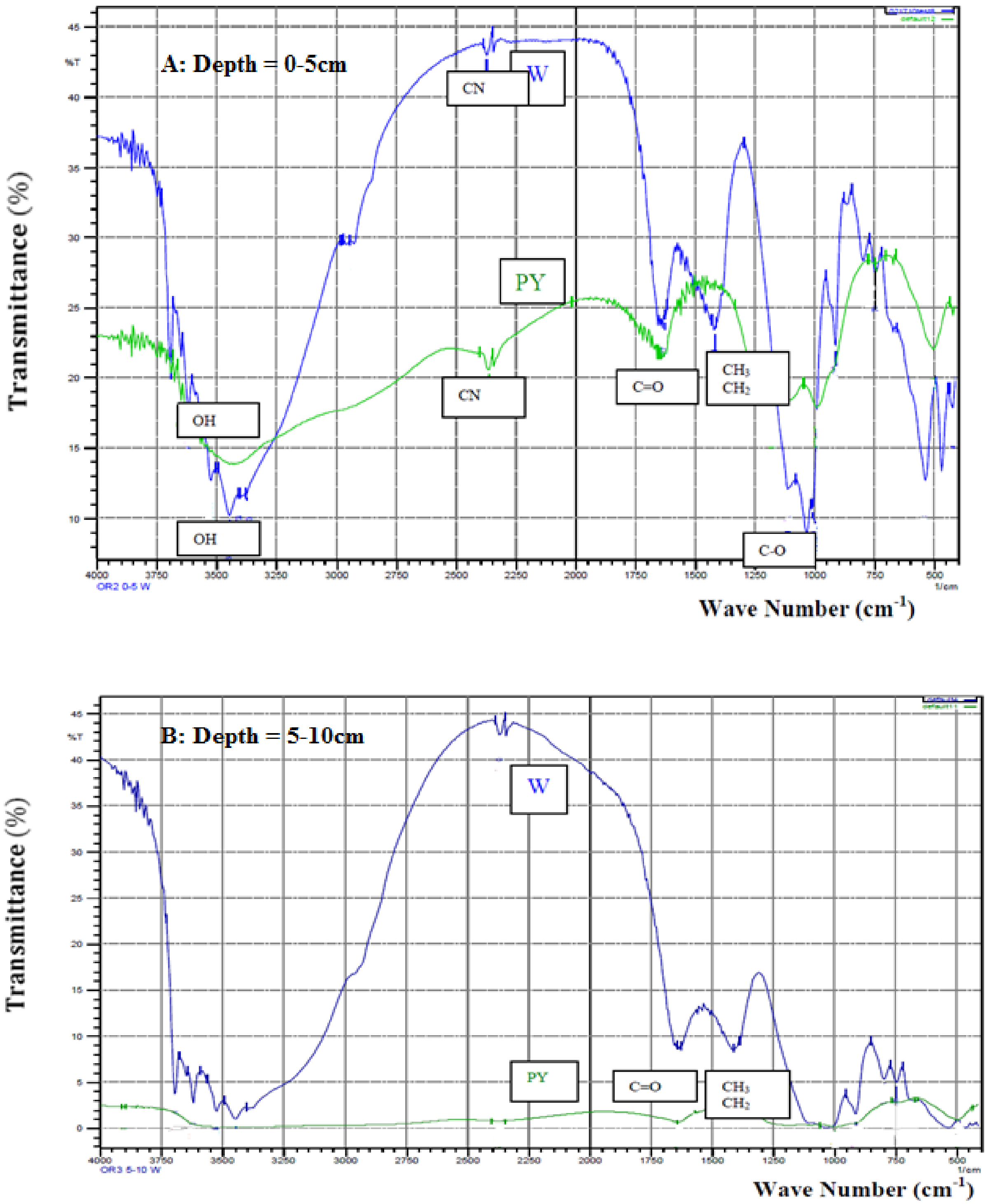
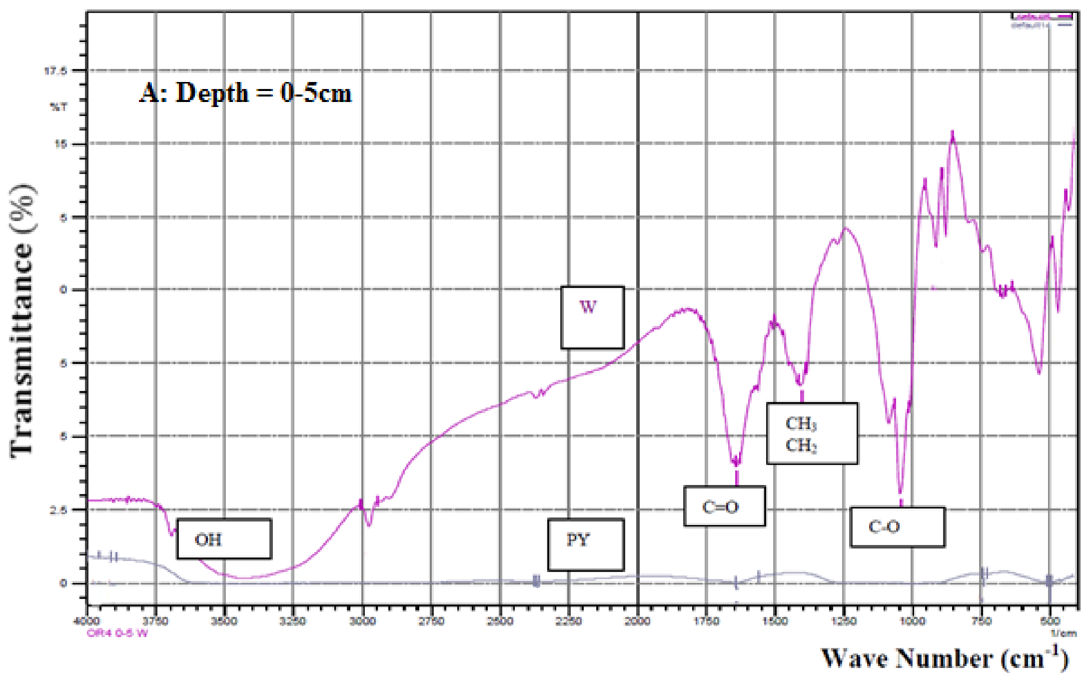


Figure 4.7 Spectral of Old Rotation "Winter Legume" Treatment (Plot 3)



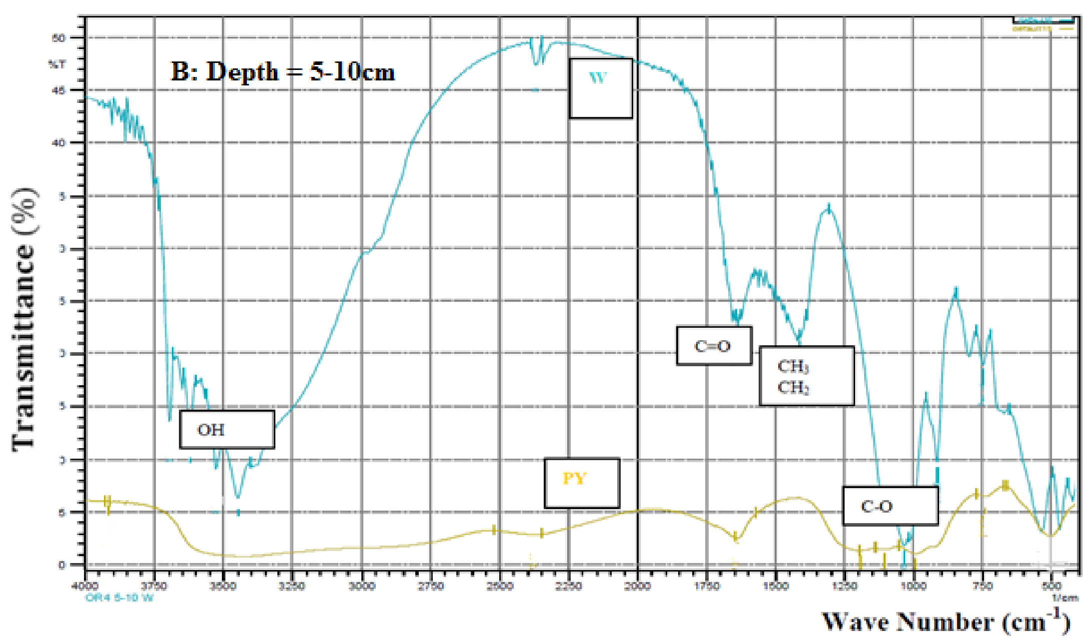
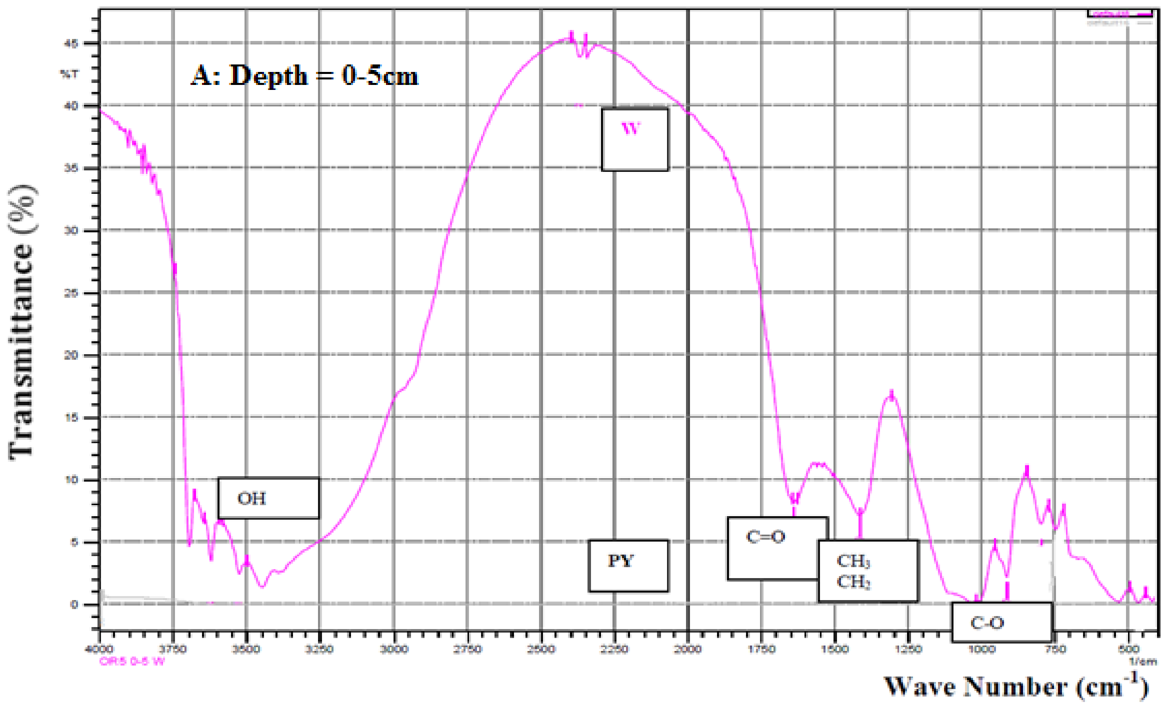


Figure 4.8 Spectral of Old Rotation "2-year rotation /+ Legume" Treatment, (Plot 4)



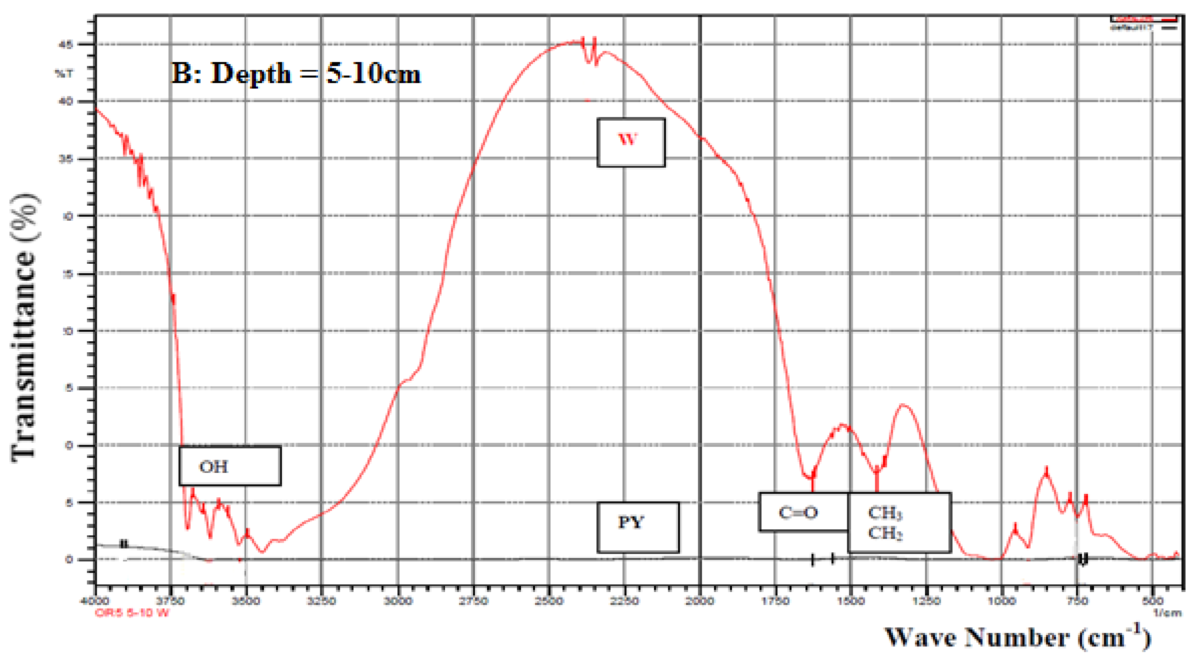


Figure 4.9 Spectral of Old Rotation "2-year rotation /+ Legume /+ N" Treatment (Plot 5)

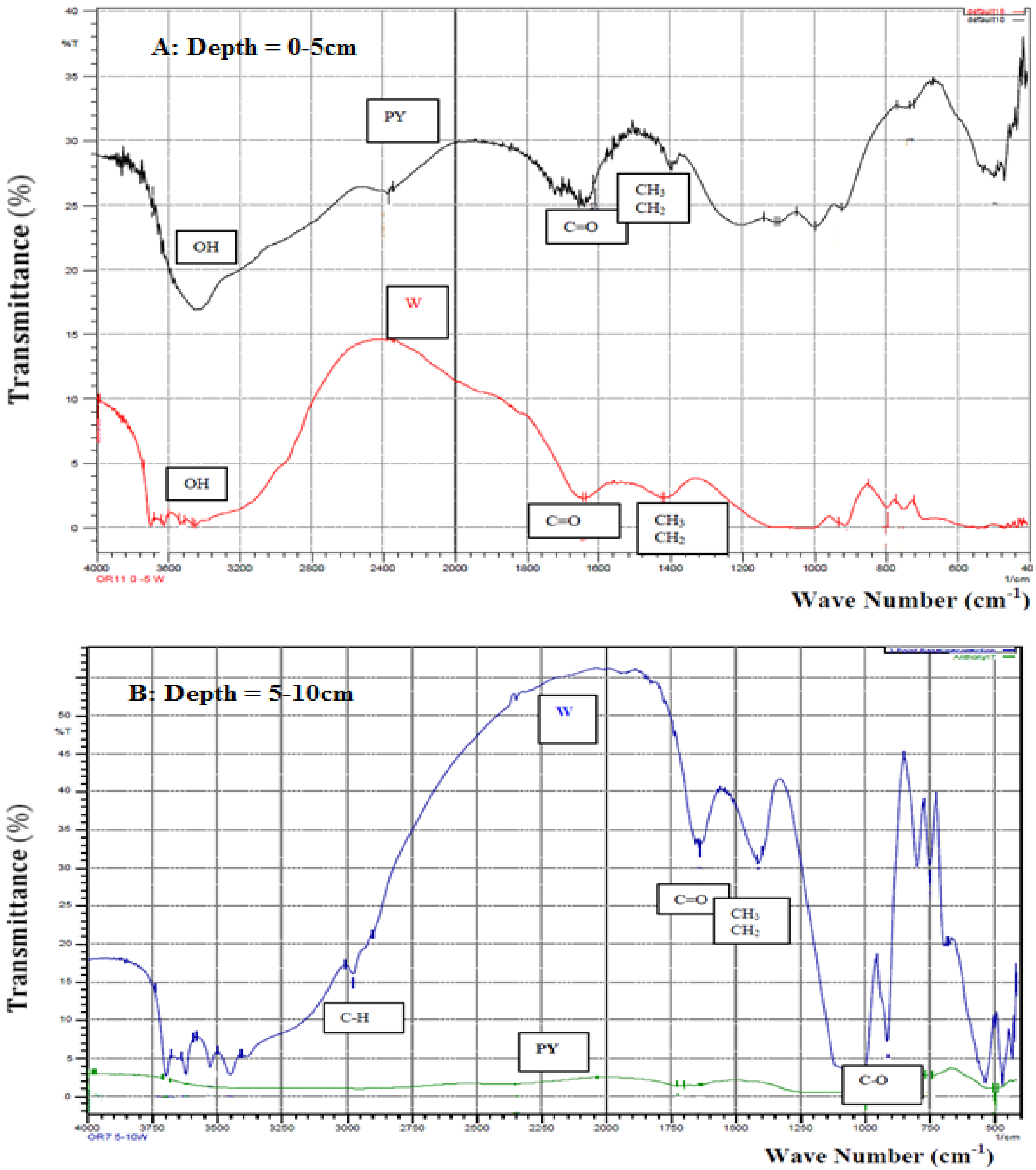


Figure 4.10 Spectral of Old Rotation "2-year rotation /+ Legume" Treatment (Plot 7)

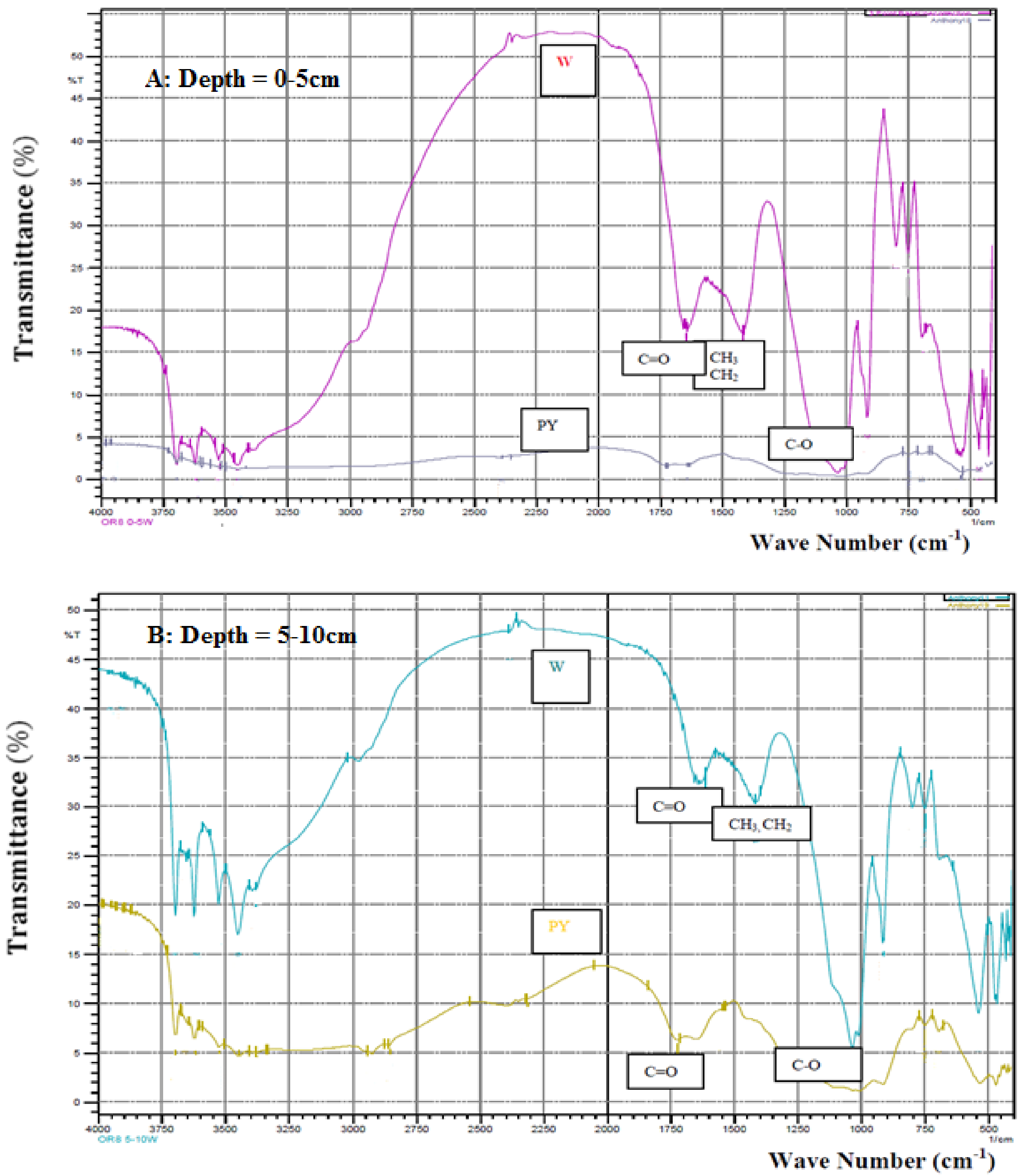


Figure 4.11 Spectral of Old Rotation "Winter Legume" Treatment (Plot 8)

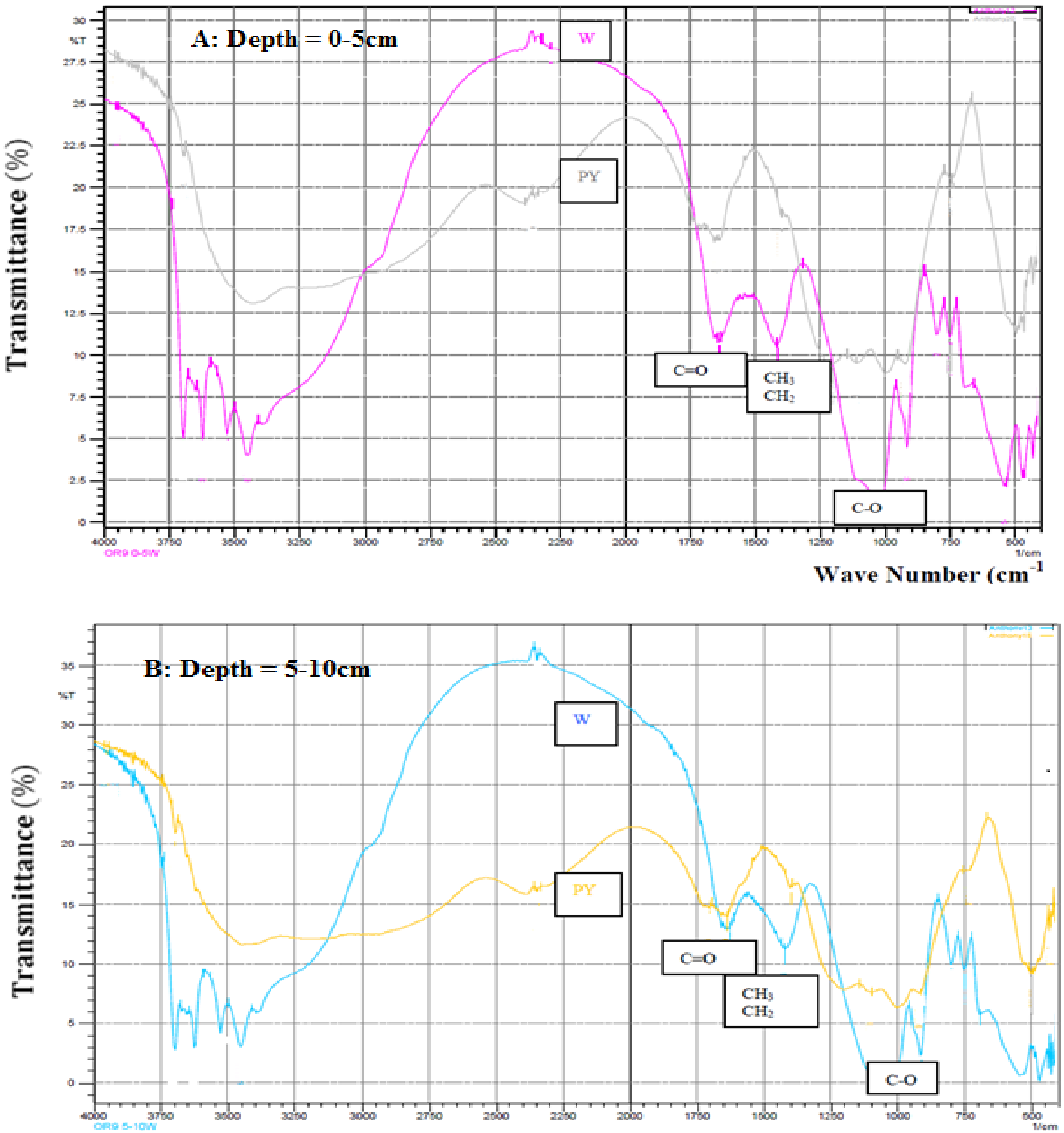


Figure 4.12
Spectral of Old Rotation "2-year rotation /+ Legume /+ N" Treatment (Plot 9)

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Chapter 5: General Summary and Conclusions

With respect to the general objectives of this study listed below:

(i) To quantify soil organic fractions into light fraction pools, heavy fraction pools by physical methods under long-term experiments.

(ii) To measure the CO_2 effluxes under different agro-ecological management and systems under long-term experiments.

(iii) To determine the major functional groups of the extracted SOM under the different agro-ecological management and systems under long-term experiments.

(iv) To establish a relationship among the above-named parameters.

The following general conclusions were drawn from these studies. With objective one, this study has shown varying factors such as fertilizer and crop rotations which are interrelated and interdependent have impacted the different fractions of SOM differently. However, it was concluded that multiple crop rotation with conducive management practices can enhance C sequestration as depicted in the absolute values of heavy fractions of carbon in both study locations. In objective two, marked seasonal variations in CO_2 effluxes were observed with summer 2008 effluxes were greater than the corresponding fall 2008 values whereas summer 2010 effluxes were greater than summer 2008 as well as fall 2008. In general, soil CO_2 effluxes were affected by crop rotation and fertilizer that are interdependent and interrelated. However, with respect to objective three, organic functional groups of higher molecular weights were conspicuously absent from the spectral graphs. Those that even showed up came out at very low percent transmittance values. Attempting to establish a relationship, it was evident that from the total and heavy fraction carbon tables, that much carbon is accumulated in these historic long-term plots after change in management from conventional tillage to strip tillage practices.

5.1 Future Studies

With the results from our studies, we will suggest the following studies to be considered for the future.

(i) There should be at least five-year periodic soil sampling of these experimental treatments,

(ii) and then physically and chemically characterize soil organic carbon and its derivatives.

(iii) Carbon dating can be done in order to reveal the true carbon fractions.

(iv) The study at the Old Rotation can be expanded to incorporate the non–irrigated treatments,

(v) whereas in the Cullars Rotation, it should be expanded to cover all the tiers concurrently.

(vi) Due to the robustness and many advantages associated with the Eddy Covariance instrumentation, it should rather be used in sampling the carbon dioxide efflux instead of LICOR instruments.