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Biochar From Agricultural Byproducts For Improved Soil Quality And Carbon Sequestration

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Biochar From Agricultural Byproducts For Improved Soil Quality and Carbon Sequestration

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North Carolina A&T State University

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in partial fulfillment of the requirements for the degree of
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This is to certify that the Doctoral Dissertation of

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has met the dissertation requirements of
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2012

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Biographical Sketch

Djaafar Rehrah was born on November 27, 1971, in Akbou, Algeria. He received the Bachelor and Master of Science degree in Animal Science from National Institute of Agronomy (Algiers-Algeria) in 1996 and the Master of Science degree in Food Science and Nutrition from North Carolina Agricultural and Technical State University in 2004.

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Nomenclature

PC	Pecan shells
PS	Peanut shells
CG	Cotton gin
SG	Switchgrass
CEC	Cation exchange capacity
GHGs	Greenhouse gases
GWP	Global warming potential
IPCC	Intergovernmental Panel on Climate Change
IUPAC	International Union of Pure and Applied Chemistry
UNFCCC	United Nations Framework Convention on Climate Change
WMO	World Meteorological Organization
UNEP	United Nations Environment Programme
USDA-ARS	United States Department of Agriculture-Agricultural Research Service
ASTM	American Society for Testing and Materials
OM	Organic matter
WHC	Water holding capacity
DOC	Dissolved organic carbon
NC	North Carolina
SOC	Soil organic carbon
SOM	Soil organic matter
N	Nitrogen
BET	Brunauer, Emmet, and Teller

EC	Electrical conductivity
Gt C /yr	Giga tone carbon per year
Tg	Teragram
C/N ratio	Carbon to Nitrogen ratio
P	Phosphorus
K	Potassium
S	Sulfur
Cu	Copper
Zn	Zinc
Ca	Calcium
Mg	Magnesium
Mn	Manganese
B	Boron
Na	Sodium
Cr	Chromium
Cd	Cadmium
Pb	Lead
$W_{\text{air dry}}$	Air dry Weight
$W_{\text{oven dry}}$	Oven dry Weight
wt	Weight
w/w	Weight by weight
w/v	Weight by volume
Cs	Surface charge per weight of adsorbent

U_b	The difference in NaOH uptake between the titrated sample and the titrated blank
R_b	The ratio of base volume in the original slurry to the filtrate volume
M_c	The weight of carbon in grams
ppm	Part per million
T0	Time zero or day one
TCN	Total Carbon and Nitrogen
ICP	Inductively Coupled Plasma Spectrophotometer
B_{pH}	Mehlich soil-buffer pH reading for an individual soil sample
meq/100g	Milliequivalents per 100 grams
DI water	Deionized Water
TC	Total Carbon
NOxN	Total Nitrite and Nitrate
PCon0	Piedmont soil control
Soil(Con)	Soil control
SGB(Con)	Switchgrass biochar control
SGR(Con)	Switchgrass raw material control
SGB+Soil	Switchgrass biochar plus soil
SGR+Soil	Switchgrass raw material plus soil
CGB(Con)	Cotton gin biochar control
CGR(Con)	Cotton gin raw material control
CGB+Soil	Cotton gin biochar plus soil
CGR+Soil	Cotton gin raw material plus soil

Abstract

Soil carbon sequestration has emerged as an innovative approach that may offer a low-risk and an efficient way to mitigate climate change and replenish soil fertility. In various agricultural production systems, byproducts are produced in significant amounts from crop residues such as pecan shells (PC), peanut shells (PS), and cotton gin (CG) that can be used to produce biochar and applied to agricultural soil first to sequester C and second to enhance plant growth by supplying and retaining nutrients, improving soil physical and biological properties. The objectives of this study were to (a) produce biochars from different byproducts (PC, PS, CG, and switchgrass) at different pyrolysis temperatures and times, and determine their physico-chemical properties, (b) apply the biochars to the coastal plains and Piedmont regions soils and determine their effects on the soil characteristics (bulk density, water holding capacity, aggregate stability, pH, CEC, and macro and micronutrients content) and leaching of nutrients, (c) perform a greenhouse testing of the best biochars and compare treated and untreated soils in terms of plant growth using lettuce as a crop, and (d) determine the effect of the best biochars on the GHGs emission (CO_2 and NH_4) during a 10 weeks soil incubation study. Higher pyrolysis temperatures resulted in lower biochar recovery, greater surface areas, higher pH, minimal total surface charge, and higher ash contents. Soil properties were significantly improved after biochar addition. No significant increase in the crop biomass, while, a net decrease in GHGs was observed following the biochar addition to soil. Biochars produced from different feedstocks and under different pyrolysis conditions influenced soil physical and chemical properties in different ways; consequently these may be designed to selectively improve soil chemical and physical properties by altering feedstocks and pyrolysis conditions. The addition of biochar to soil did not significantly improve the crop growth, but significantly reduced the emission of GHGs from soil.

CHAPTER 1

Introduction

High levels of greenhouse gases (GHGs) emissions due to human activities lead to disturbances in the energy balance of the earth system. As a consequence, changes in climate occur. The main drivers of this changes are carbon dioxide (CO_2) emissions – 77%, primarily from fossil fuel use and excessive land-use; methane (CH_4) emissions – 14% – attributed to agriculture and fossil fuel use; and nitrous oxide (N_2O) emissions – 9%, mainly from agriculture (IPCC, 2007). Furthermore, these activities such as fossil fuel use and land degradation greatly alter most important biogeochemical cycles, such as the C and N cycles, leading to the reinforcement of the land degradation-climate change cycle. Land-use change and excessive pressure on agricultural land are responsible for land degradation, resulting in soil productivity loss and roughly one third of global greenhouse gas (GHG) emissions (IPCC, 2007).

In several agricultural production systems, byproducts are produced in significant amounts from crop residues such as Nut-shells, peanut shells, cotton gin, and corn cubs. Many of the agricultural residues can be used to produce biochar for use in agricultural soil both to sequester C (improve soil structure, nutrient retention, and pH) and to increase the production potential of crops (Glaser, Lehmann, & Zech, 2002; Lehmann & Rondon, 2006). In many cases, these waste materials have little or no economic value and their disposal incurs costs. For instance, today large amounts (more than 50% of total available agricultural residues in the U.S.; Walsh, Burton, Hyland, & Robinson, 1999) can be acquired for less than $30 per ton of biomass.

Conversion of low value and underutilized agricultural by-products and high volume/low cost industrial crops is ecologically and economically attractive given the fact that energy is produced at the same time as biochar is produced equivalent to the amount that can be achieved by direct charring. Some crop residues such as nut shells (e.g., groundnut, hazelnut, macadamia nut, walnut, chestnut, coconut) but also bagasse from sugar cane processing, olive or tobacco waste are suitable and are in some locations available in large quantities.

Land application of biochar is not a new concept. For example, certain dark earths in the Amazon Basin (so-called Amazonian Dark Earths or “terra preta”) have received large amounts of charred materials, the residues from biomass burning (Sombroek, Ruvio, Fearside, Glaser, & Lehmann, 2003). These applications were most likely the result of both habitation activities and deliberate soil application by Amerindian populations before the arrival of Europeans (Erickson, 2003).

The application of biochar to soil is proposed as a novel approach to establish a significant, long-term, sink for atmospheric carbon dioxide in terrestrial ecosystems. The production of biochar and its application to soil can deliver immediate benefits through improved soil fertility and increased crop production (Ketterings, 1999). The value of biochar for soil improvement is probably partly related to the huge surface area of its particles and their many micropores, which provide a microhabitat for beneficial soil microorganisms and enable moisture retention and nutrients adsorption (Lehmann & Joseph, 2009; Sohi, Lopez-Capel, Krull, & Bol, 2009).

Conversion of biomass C to biochar C leads to sequestration of about 50% of the initial C compared to the low amounts retained after burning (3%) and biological decomposition (<10–20% after 5–10 years), therefore yielding more stable soil C than burning or direct land application of biomass (Lehmann, Gaunt, & Rondon, 2006). In addition to reducing greenhouse gas emissions, biochar applications to soil have the potential to decrease environmental pollution. Like biochars, black C in soil efficiently adsorbs ammonia (NH_3) (Iyobe, Asada, Kawata, & Oikawa, 2004) and prevent groundwater pollution.

Diverting only 1% of C released through biomass respiration would prevent about 10% of current global GHG emissions (Lehmann et al., 2006). By avoiding GHGs emissions and sequestering C, biochar application in soil could be considered a mitigation pathway. In a well-managed system, biochar could be a key component for a doubly green revolution (sustainable food production and land degradation prevention); it could also be one of the best practical ways to counter global warming and it might be an effective way to rehabilitate degraded land and counter pollution of streams and groundwater (Barrow, 2012).

1.1. Rationale

A combination of needs constitute the rationale for the proposed work; (a) soil pH, CEC, OM, water holding capacity, and aggregate stability are among the most important characteristics of soil fertility which affects plant growth in numerous ways. In addition southeastern Soils of the U.S. are characterized by low CEC, OM, water holding capacity, aggregate stability, a weak and instable structure, and pH which inhibit soil microbial activity and the availability of nutrients for the plant. New methods to address these problems have the potential to enhance NC agriculture (e.g. biochar application), (b) at the same time, major and underutilized agricultural by-products in the U.S. generate billions of pounds of waste materials each year. These waste streams have to be disposed of, often costing producers.

Therefore, new value-added approaches are needed to address the disposal of these by-products (economic and environmental) and ideally provide other economic and environmental benefits. New use of agricultural byproducts in soil improvement could help alleviate the problem of waste disposal and reduce related costs, (3) there is considerable interest in finding reliable methods of sequestering carbon in agricultural soils to both help solving the soil problems discussed above and contribute to carbon storage.

The conversion of these underutilized agricultural byproducts into carbonaceous materials may provide cost effective ways to improve soil quality while allowing long term sequestration of carbon in the soil. The latter may have additional environmental benefits such as global warming mitigation as stated above.

This research effort aims to produce agricultural byproducts-based biochars that are suitable to enhance the soil quality, improve plant growth, and help decrease GHGs emissions. A series of experiments were carried out to test the following hypotheses: (a) that optimized agricultural byproducts-based carbons will enhance soil fertility parameters by increasing nutrients and water retention capacity of the soil, therefore allowing better plant growth, (b) biochar sequestration in the soil will prevent the pollution of underground water by stopping fertilizers and pesticides leaching due to their high adsorption capacity and internal surface area that act as a filter, and (c) biochar produced at high temperature that has higher surface area and pH will improve the aggregate stability and buffer pH of the sandy soils known for their low pH.

The specific objectives of this study were to: (a) produce biochars from different byproducts (pecan shell, peanut shell, cotton gin) and switchgrass (a high volume and low cost crop) at different pyrolysis temperatures and times, and determine their physico-chemical and surface properties; (b) apply the biochars to the coastal plains and piedmont regions soils and determine their effects on soil characteristics (bulk density, water holding capacity, aggregate stability, pH, CEC, and macro and micronutrients content) and leaching of nutrients; (c) determine the best performing biochars using optimization and screening procedures based on their suitability in specific soil amendment needs; (d) perform a greenhouse testing of the best Carbons and compare treated and untreated soils in terms of plant growth; and (e) determine the effect of the best performing biochars on the emission of GHGs (CO_2 and NH_4) during a 10-week soil incubation study.

CHAPTER 2

Literature Review

2.1. Types of Soil in North Carolina

The soils of North Carolina are many and varied, and classified as coastal plain, piedmont, and mountain soils. Some are suited to a wide range of crops, while others are notably limited in this respect. Late in the 19th century, as the realization grew that soil is a complex system, the influence of soil-forming factors became more evident. These factors are parent material (rocks), climate (temperature and rainfall), organisms (mainly vegetation), relief (topography or slope), and time (age of soil) (Lee, 1955). Thus, the soil is the product of certain environmental factors acting upon geologic material. The influence of these factors is interdependent and, in effect, a combined but by no means exert an equal control on soil formation making it difficult to discuss each separately (Sohl & Owens, 1991).

North Carolina may be divided into two distinct regions on the basis of geology. The eastern part consist of unconsolidated rock material (sands and clays) called the Coastal Plain (Sohl & Owens, 1991). The western part is composed of consolidated rocks, known as the Appalachian Highlands with two provinces (Piedmont Plateau and the Blue Ridge). These two regions differ from each other not only in geologic materials and age, but also in their elevation above sea level, relief, climate, native vegetation, and, as a result, in soils (Lee, 1955).

2.1.1. Coastal plain soils. The Coastal Plain occupies 44.7% of the land of the state. It is a relatively smooth plain ranging in elevation from sea level along the coastal portions to generally less than 300 feet where it borders the piedmont. Nearly all the materials of the Coastal Plain region are laid down in horizontal or gently sloping beds. In general, the soils of the northern half contain a moderately high portion (> 55%) of very fine sand, silt, and clay combined and those of the southern half have moderately low portion (< 40%) of very fine sand, silt, and clay combined (Sohl & Owens, 1991). The differences in geologic parent materials as influenced by relief are the basis for the classification of soils in the Coastal Plain into units. These units are the lower (Tidewater) on the east, the middle, and the upper coastal plain (Lee, 1955).

2.1.2. Piedmont soils. The Piedmont Plateau which occupies 38.8% of the state is a much more elevated area than the Coastal Plain with an average elevation ranging from 500-900 feet. As the uplift progressed the various streams crossing the plateau cut deeper and deeper into the valleys and extend their tributaries throughout the region. This resulted in the development of rolling to hilly relief, and the rather excessive drainage of the region (Lee, 1955).

2.1.3. Mountains soils. The mountain region occupies only 16.5% of the state. It is bounded on the east by the Blue Ridge and on the west by the Unaka Mountains. The average elevation of the typically mountainous portions is about 3,200 to 4,000 feet (Lee, 1955). The character of geologic materials in the piedmont and mountains provinces has exerted a greater influence on soil formation than has that of the coastal plain materials. But when certain materials in the mountains are compared to similar materials in the piedmont, the influence of climate on soil formation becomes quite apparent.

Certain soils series are found only in association with particular rock groups. To some extent, therefore, the classification of Piedmont and Mountains soils into series may be based upon the classification of the geologic materials. Soils developed over Triassic formations have sandy surface soils and highly variable subsoils ranging from sandy clay loams to clays found mainly in Granville, Mayodan, and White store series (Lee, 1955).

According to Lee (1955), in the basic crystalline diorite and related rock group are the counties of Clifton, Davidson, Iredell, Lloyd, and Mecklenburg soil series which have loam to clay loam surface soils and clay subsoils. Quartzite and shale have given rise to the Habersham, Fletcher, Matney, and Ramsey soils. Among the soil series developed over the mica schists are Piedmont soils with sandy loam surface materials and clay loam to clay subsoils which are known as the Louisa, Surry, Madison, and Grover; and mountains soils dominantly silty throughout and carrying much fine mica which are known as the Fannin, Watauga, Talladega, and Chandler (Lee, 1955; Soller, 1988).

The most important direct influence of climate on soils is the alteration of parent material. This works largely through temperature changes, moisture, and vegetation. In North Carolina because of warm temperature with moderately high rainfall, most of the soils of the Coastal Plain, Piedmont, and Lower Mountains are relatively deep and well oxidized. They resemble soils to the south and belong to the Red-Yellow Podzolic Great Soil Group because of climatic differences, similar parent materials have given rise to red soils in the Piedmont, to reddish-brown soils in the lower Mountains, and to brown or gray-brown soils in the higher Mountains (Lee, 1955). The rainfall and the warm temperature have resulted in considerable leaching of soils. Oxidation or decomposition of organic matter has been rapid in most places, and there has been little accumulation of organic matter under trees.

2.2. Description of Soil Properties

Soil forming factors are responsible for the series of layers common to soils. The layers are approximately parallel to the earth’s surface and are called soil horizons. The soil profile is a vertical section of the soil from the surface downward to the parent material, and includes all horizons. A distinctive feature of many soils is color.

Generally somewhat less noticeable features are (a) texture, which refers to the proportion of sand, silt, and clay composing the soil; (b) structure, which refers to the arrangement of primary soil particles into aggregates; and (c) consistence, which refers to the degree of cohesion of the soil and resistance opposed to forces tending to deform or rupture the aggregates (Lee, 1955). Important, but not observable features of North Carolina soils are their reaction or degree of acidity or alkalinity, and the cation exchange capacity (CEC).

2.2.1. Soil horizons. A field examination of soils reveals that generally they have several more or less clearly defined layers. Usually there are three major layers in a well-developed soil. These commonly are called surface soil, subsoil, and underlying material or soil parent material. For convenience and uniformity, several soil horizons are named by giving them letter designations. The letter A denotes the surface soil, B the subsoil, and C the parental material. The surface layer termed A00, consists of leaves, twigs, and other plant remains, generally of the past year. The partially decomposed and usually matted plant remains below A00 comprise the A0 horizon (Lee, 1955).

The A horizon usually consists of a mineral surface layer which contains some organic materials, and one or two subsurface layers. It has simple structure forms which are single grain or granular. The topmost mineral soil layer is A1 which is darker than the other layers due to the presence of organic matter with greatest biological activity. The subsurface horizon, or A2, generally light in color that has lost materials such as clay minerals, iron, and aluminum by leaching, and is a layer of eluviations. In many soils there is a layer transitional from the surface soil to the subsoil, but more like the surface called A3 horizon (Lee, 1955).

The B horizon may be considered the layer of accumulation, an illuvial horizon. In well drained soils the B horizon usually has a concentration of clay, iron, or aluminum with little or no organic material. In most soils some structure forms are present. Also, the colors are more pronounced than those of the horizons above or below. Here are two or three subdivisions, of which the B1 represents a transition from the A to B, but is more like B than A. The B2 is the subhorizon of maximum accumulation of clay minerals and iron, and it shows the strongest development of structure, which is more or less blocky in most North Carolina soils. The layer transitional to C is the B3 and is more like B than C (Lee, 1955).

The C horizon is a layer of unconsolidated material supposedly similar in chemical, mineralogical, and physical properties to the material from which some or much of the B and A horizons have developed. In North Carolina the C layer under Piedmont and Mountain upland soils is commonly called “rotten rock”. In the Coastal Plain the C material somewhat closely resembles the subsoil, but often is different. The lowest layer or D is not a horizon since it cannot be considered any part of soil profile. Usually it is the “hard rock” of the Piedmont and the Mountains. In the Coastal Plain it may be loose sand, gravel, firm clay, or mixtures of two or all of these in varying proportions (Lee, 1955).

2.2.2. Soil color. Soil color is the most noticeable feature of the soil. It is a significant and very useful characteristic for soil identification or for soil evaluation for agriculture. They are due chiefly to the content of organic matter, to iron compounds, or to quartz. The extreme color range in NC is from black (Hyde loam, which is very organic matter) to white (St. Lucie sand, which is nearly devoid of organic matter and almost entirely quartz). All surface soil colors are not due to variations in organic matter content. However, in the soils of the coastal plain region organic matter is one of the most materials influencing the color of surface soils (Soller, 1988). It exerts much of the influence on the color of the surface soils in the mountain region, but little on the Piedmont soils (Lee, 1955).

The range in color of the subsoils is from dark to gray due to iron in the ferrous form to white due to quartz. The depth in a soil to which black or gray extend depends upon the nature and distribution of the organic matter and, indirectly, upon the degree of soil drainage, texture, and structure. Dark gray in the subsoils indicates poor drainage in soils of N C. Red and reddish-brown soil colors are due to the presence of well oxidized iron compounds (Lee, 1955).

2.2.3. Soil texture. The term soil texture refers to the relative proportions of the various size groups of the particles composing a soil. Practically all soils are made up of three size groups of individual grains-sand, silt, and clay. Sand gives soil a gritty feel, and it may be separated into several grades according to its coarseness or fineness. Clay is composed of extremely fine particles. In NC soils clay tends to make them sticky when wet, and hard and cloddy when dry. Silt is intermediate in size between sand and clay particles. It gives the soil a very smooth feel when moist, and is floury when dry. The proportions of sand, silt, and clay in soils vary widely, but one size particle usually dominates a soil as sandy loam, clay loam, or silt loam (Lee, 1955).

The soil texture is of major importance in evaluating soil behavior, in soil classification, and in management of soil. It determines the soil types within the soil series of the surface soil, although texture of the subsoils is an important series consideration. It determines also its physical character, and its chemical properties to a large degree (Lee, 1955).

Texture exerts a major influence on the plant growth and soil management. Soils with coarse texture are rapidly permeable, and have low adsorptive properties for water and plant nutrients. On the contrary, soils with fine texture are slowly permeable and highly adsorptive. The texture of the surface horizon may be modified very quickly and severely as by poor management which results in erosion losses (Lee, 1955).

In North Carolina broad geographic areas may be defined on the basis of soil texture. Among these areas, parent material appears to be the principal factor responsible for the difference in texture. However, for the Mountain region, as compared to the entire Piedmont, the cooler climate of the higher elevations, and the younger soils, probably are responsible for some differences in texture. Soil formation in the Mountains has proceeded more slowly, and textural grades are not as distinct as in the Piedmont. These broad texture areas are partly responsible for the differences in the types of farming throughout the state.

Soil textural classes may be listed in general terms as follows: (a) coarse-textured soils (Sands, Loamy sands, and Sandy loams), (b) medium-textured soils (Fine sandy loam, Very fine sandy loam, Loam, Silt loam, and Silt), and (c) fine-textured soils (Clay loam, Sandy clay loam, Silty clay loam, Sandy clay, Silty clay, and Clay; Lee, 1955).

2.2.4. Soil structure. Soil structure refers to the arrangement of soil particles. Sand, silt, and clay seldom occur as separate units in the soil; rather, they combine into aggregates held together by small binding forces of clay and organic matter. The size and form of aggregation is known as the structure of the soil. Soil structure is one of the more important physical characteristics of soil, yet perhaps the least understood. Plant growth is strongly influenced by soil structure. Soil structure affects plant growth in many ways (Lee, 1955).

Soil structure affects movement of water, air, and roots through the soil. A granular structure provides an ideal environment for plant roots, and is helpful for establishing plants from seeds or transplants. The larger pores between the granular aggregates are continuous, and roots may penetrate them with ease. Roots grow most rapidly in a very friable soil, but their water and nutrients uptake may be limited due to an inadequate contact with soil solid and liquid phases. In hard soil, this contact is more intimate resulting in a strongly inhibited root growth and a poor foraging ability, therefore the plant may eventually become short of water or nutrients.

However, many soils, even if hard, contain continuous macropores that provide niches for the roots to grow (Lee, 1955).

Soil structure not only affects the ability of roots to grow but also their ability to supply the leaves with water and nutrients. In adverse conditions, it also induces the slow of shoot growth using hormonal signals, even if the water and nutrients are available (Passioura, 1991). Soil structure influences soil water movement and retention, erosion, crusting, nutrient recycling, root penetration, and crop yield (Stirzaker, Passioura, & Wilms, 1996).

There are four type of soil structure (a) blocklike, (b) spheroidal, (c) platy, and (d) prismlike. All four structure types occur in North Carolina, where the blocklike types are the more common in subsoils and the spheroidal in surface soils. Prismatic and blocky structures most often occur as the result of shrinking and cracking of clay loams and clay soil layers (called horizons) upon drying (drought). Thus, the roots may have a limited access to a significant portion of the water and nutrients in these soils. To determine whether a soil has a good structure, aggregate stability is used as an indicator (Six, Paustian, Elliott, & Combrink, 2000). Soil aggregation plays a very important in soil stability and productivity which is improved by the presence of organic matter. Aggregation is mediated by soil organic carbon (SOC), biota, ionic bridging, clay, and carbonates (Bronick & Lal, 2005).

The SOC acts as a binding agent and as a nucleus in the formation of aggregates. Biota and their organic products contribute to the development of soil structure; which in turn exert a significant control over SOC dynamics. The SOC residence time and decomposition rate are considered as key factors that reinforce the soil aggregation stability. Crystalline and amorphous metal oxides, hydroxides, and clay are important aggregants in soils where metal ions form bridges between mineral and organo-mineral particles. Clay acts as soil particles binding agent and influencing SOC decomposition and turnover. Long term stability of aggregates is often related to the presence of recalcitrant C compounds and metal ions (Bronick & Lal, 2005). The decline in soil structure is increasingly seen as a form of soil degradation (Chan, Zwieten, Meszaros, Dowine, & Joseph, 2007) and is often related to land use and soil/crop management practices.

The effectiveness of soil organic carbon in forming stable aggregates is partly related to its decomposition rate, which in turn is influenced by its physical and chemical protection from biotic and abiotic degradation (Bronick & Lal, 2005).

There are several mechanisms of aggregation. Aggregates are formed in stages, with different bonding mechanisms dominating at each stage (Tisdall & Oades, 1982). The process of building structure is quite slow unless more and more compound polysaccharides are left in the soil matrix as well as cellulose and lignin materials. Roots and hyphae will link particles together all the while realigning them and releasing organic compounds that hold particles together. This can be a process with a positive impact on soil C sequestration. Long lasting carbon compounds from degenerating roots and fungi hyphae are slow to accumulate from fine rooted crops such as small grains. The precipitation of hydroxides, phosphates and carbonates can enhance aggregates formation (Bronick & Lal, 2005).

Tisdall and Oades (1982) have put together a model that better describes how soils aggregate. First, amorphous organics attach to the clay particles, and then microbial debris encrusts those particles so they can bind together. This occurs with other primary soil particles (sand, silt & clay) forming micro-sized aggregates. Next step, roots and fungi hyphae bind the micro-sized aggregates to larger forms. The varied charged cations of aluminum, iron, calcium and magnesium bridge the clays with electronic bonds and organic matter continuing to stabilize soil aggregates (Edwards & Bremner, 1967).

Microaggregates (< 250 µm) are formed from organic molecules (OM) attached to clay (Cl) and polyvalent cations (P) to form compound particles (Cl–P–OM), which are joined with other particles (Cl–P–OM) to form macroaggregates $[(\mathrm{Cl–P–OM})_x]_y$ (Tisdall, 1996; Edwards & Bremner, 1967). Alternatively, macroaggregates can form around particulate organic matter (POM). As POM is decomposed and microbial exudates are released, the macroaggregate becomes more stable, the C:N ratio decreases, and microaggregates are formed (Figure. 2.1) containing more recalcitrant SOC pool (Plante & McGill, 2002). The rate and stability of aggregation generally increases with SOC, clay surface area, and CEC.

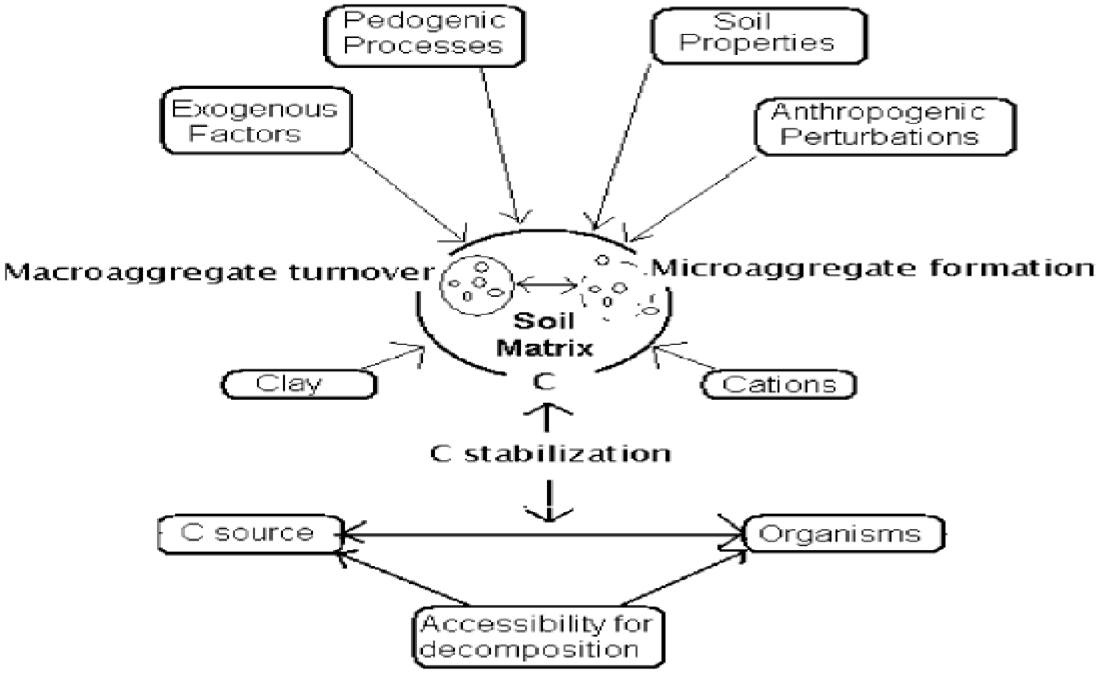

Figure 2.1. Factors affecting soil aggregation.

In soils low in SOC or clay concentration, aggregation may be dominated by cations, while the role of cations in aggregation may be minimal in soils with high SOC or clay concentration. Soil pH significantly influences aggregation formation and stability; Large aggregates form in soils of high pH and high carbonate concentration (Boix-Fayos, Calvo-Cases, & Imeson, 2001).

Lime is commonly used to increase soil pH resulting in higher microbial activity, improved crop yields, and contributing to higher SOM and better aggregation stability (Haynes & Naidu, 1998). High carbonate concentration enhances SOC protection, probably because of decreased SOC mineralization and increased Ca^{2+}. The chemical properties of SOC determine their charge and complexation capacities and influence decomposition rates which have direct effects on aggregation (Schulten & Leinweber, 2000).

2.2.5. Soil consistence. It refers to the relative mutual attraction of the particles in the whole soil mass and to their resistance to deformation or rupture. Consistence deals with the strength and nature of the forces of attraction within the soil mass. Soil drainage is dependent to a considerable degree on soil consistence. A soil which is plastic when wet is difficult to till, and generally slow to drain. Consistence terms apply to three soil moisture conditions-dry, moist, and wet. Under average or moist field conditions in North Carolina most soil materials tend to break into smaller particles rather into powder. They are not sticky or plastic when wet, they show some deformation before rupture, and there is an absence of brittleness. Yet the material will cohere again when pressed together (Lee, 1955).

2.2.6. Soil drainage. Soil drainage refers to the removal of excess water from the soil through runoff and by internal movement or percolation. Evaporation and transpiration are contributing factors to total soil water loss. When drained, a soil is free of saturation or partial saturation with gravitational water. It is also an indication of the frequency and length of the periods the soil pores are partially air filled. The drainage conditions of a soil are due to the existing combination of flow over the soil surface runoff (flow) and flow through the soil profile-internal drainage (Lee, 1955).

Permeability and internal drainage are terms often used interchangeable; each refers to the movement of water through the soil profile. Soil permeability refers to the quality or factor of the soil enabling it to transmit water or air. It can be measured in terms of flow rate of water through a unit cross-section of saturated soil in unit time, under specified temperature and hydraulic conditions. Internal soil drainage is that quality of a soil that permits the downward flow of excess water through it. The water rate of movement, externally or internally, is affected by the texture, structure, and consistence of both surface soil and subsoil, by the properties of the layers underlying the profile, vegetation covering, the slope, and by the height of the ground water table (Lee, 1955).

2.2.7. Soil pH. The pH value of a soil is influenced by the kinds of parent materials from which the soil was formed. Soils developed from basic rocks generally have higher pH values than those formed from acid rocks. Rainfall also affects soil pH. The movement of water through the soil leaches basic nutrients such as calcium and magnesium from the soil which are replaced by acidic elements such as aluminum and iron. For this reason, soils formed under high rainfall conditions are more acidic than those formed under arid conditions (Lee, 1955).

A pH level of around 6.3-6.8 is also the optimum range preferred by most soil bacteria. Under conditions in which rainfall exceeds evapo-transpiration, during most of the year, the basic soil cations (Ca, Mg, and K) are gradually depleted and replaced with cations held in colloidal soil reserves, leading to soil acidity. Clay soils often contain iron and aluminum hydroxides, which affect the retention and availability of fertilizer cations and anions in acidic soils. Soil acidification may also occur by addition of hydrogen, due to decomposition of organic matter, acid-forming fertilizers, and exchange of basic cations for H^+ by the roots. Strongly acidic soils often have poor incorporation of the organic surface layer with the underlying mineral layer (Lee, 1955).

Alkaline soils are clay soils with a relatively high exchangeable sodium percentage, relatively high pH (> 9), poor soil structure and low infiltration. Often they have a hard calcareous layer at 0.5 to 1 m. depth. They are difficult to use for agricultural production. Due to the low infiltration capacity, rain water stagnates on the soil easily and, in dry periods, irrigation is hardly possible. Agriculture is limited to crops tolerant to surface water-logging (e.g. rice, grasses) and the productivity is low. Soil alkalinity is associated with the presence of sodium carbonates (Na_2CO_3) in the soil, either as a result of natural weathering of the soil particles or brought in by irrigation and/or flood water (Lee, 1955).

Alkalinity problems are more pronounced in clay soils than in loamy, silty or sandy soils. The clay soils containing montmorillonite or smectite (swelling clays) are more subject to alkalinity problems than illite or kaolinitic soils (Lee, 1955). The reason is that the former types of clay have larger specific surface areas (i.e. the surface area of the soil particles divided by their volume) and higher cation exchange capacity (CEC). In North Carolina, the soils of the coastal plain are more acidic than those of the Mountains or Piedmont, and Piedmont soils are less acidic than Mountain soils (Lee, 1955).

2.2.8. Soil cation exchange capacity. The cation exchange capacity (CEC) is defined as the capacity of a soil for ion exchange of positively charged ions (cations) between the soil and the soil solution. it is used as a measure of fertility, nutrient retention capacity, and the capacity to protect groundwater from cation contamination. The quantity of positively charged ions that a clay mineral or similar material can accommodate on its negatively charged surface is expressed as milliequivalent (meq) per 100 g (Lee, 1955).

2.3. Approaches to Improving Soil Properties/Fertility

Soil quality is of fundamental importance for agricultural production, and soil fertility management is increasingly becoming a central issue in the decisions on food security, poverty reduction and of environment management. The soil is one of the key factors affecting plant growth. The major functions of the soil are to provide plants with nutrients, water and oxygen. Soil properties affected by soil degradation are nutrient content, water holding capacity, topsoil depth, acidity, salinity, porosity, and soil biomass. Soil degradation has serious economic consequences such as higher food prices and flux to urban areas (Reuler & Prins, 1993).

Integrated Nutrient Management is a way of combating nutrient depletion. It is an approach to soil fertility management that combines organic and mineral methods of soil fertilization with physical and biological measures for soil and water conservation. It is based on the following principles: (a) maximize use of organic materials (compost, manure, crop residues). Soil organic matter plays a critical role in maintaining the fertility of the soil by increasing water holding capacity, reducing surface crusting, increasing cation exchange capacity and acting as a buffer against pH changes in the soil, (b) judicious use of inorganic fertilizer: Inorganic fertilizers have an immediate effect, and the release of nutrients is often well synchronized with plant growth. Uptake of nutrients from fertilizer is more efficient than from organic sources of fertilizer. Recovery of nitrogen (N) from leguminous plants incorporated into the soil is 10-30%, while the recovery of fertilizer N is 20 to 50% (Sanchez et al. 1997), and (c) minimize losses of plant nutrients especially from erosion.

The choice of tillage methods, crop rotation, ensuring permanent cover for the soil and no disturbance of the top soil layer have been found to affect soil erosion through effects on soil aggregation, water infiltration, water holding capacity of the soil, and surface characteristics of the soil.

2.4. Use of Biochar for Soil Amendment

2.4.1. Biochar production. The process used to produce biochar is called carbonization which is the pyrolysis or thermal decomposition process to remove most of the non-carbon elements (hydrogen, oxygen, traces of sulfur and nitrogen) from a carbonaceous material in gaseous form in the absence of air and without the addition of chemical agents. This enriches the carbon content, creates an initial porosity and aromatization in the resulting char (Smisek & Cerny, 1970). The free valences of released carbons are satisfied to group them into organized crystallographic formations known as elementary graphitic crystallites.

The mutual arrangement of these crystallites is irregular, so that free interstices remain between them and, apparently, as the result of deposition and decomposition of tarry substances, these become filled or blocked by disorganized carbon (Wigmans, 1989). The biochar characteristics are dependent mainly on the pyrolysis conditions. During the pyrolysis process, both hydrogen and oxygen contents of biochar decrease as the temperature is increased. The decrease of H/C ratio indicates an increase in the aromaticity and carbonaceous nature of biochar.

Brunauer, Emmet, and Teller (BET) surface area and the total pore volume increase with pyrolysis temperature, and reach a maximum at about 500 °C; thereafter, the trend is a decrease with pyrolysis temperature. The rate of decrease is not as fast as that of increase. However, increasing pyrolysis temperature from 500 to 800 °C may induce shrinkage in the carbon structure, resulting in a reduction in the surface area and the pore volume (Ioannidou & Zabaniotou, 2007). The activation of biochar can be performed to enhance its adsorption capacity which further develops the porosity and creates some ordering of the structure to generate a highly porous solid as the final product.

A novel approach is to explore the value of this byproduct (biochar) when added to soil. Two aspects of biochar make it valuable for this purpose: (a) its high stability against decay, and (b) its superior ability to retain nutrients as compared to other forms of soil organic matter. Three environmental benefits arise from these properties: (a) mitigation of climate change, (b) improvement of soils, and (c) reduction of environmental pollution (Lehmann, 2007b).

Activated carbons are highly porous materials with surface areas of up to 3000 m^2/g. The surface area of a typical activated carbon is about 1000 m^2/g. These high surface areas are the result of development of mainly micro and mesopores while a little contribution is also come from macropores. According to the International Union of Pure and Applied Chemistry (IUPAC) classification, pores having the radii less than 2 nm are called micropores whereas pores having the size of radii in between 2 to 50 nm are identified as mesopores. Macropores are defined as pores having the radii size above 50 nm.

Chars and activated carbons are often termed as amorphous carbon. X-ray diffraction and electron microscopy have shown that these materials have crystalline characteristics, even though they may not show certain features, such as crystal angles and faces, usually associated with the crystalline state. The amorphous carbon consists of graphitic flat plates in which the carbon atoms are arranged in a hexagonal lattice, each atom, except those at the edge, is held by covalent linkages to three other neighboring carbon atoms. The crystallites are formed as a result of the stacking of two or more of these plate-structures with an interlayer distance of 3.6 Å (Hassler, 1974).

Almost any carbonaceous material can be converted into biochar or activated carbon (Hsisheng & Sheng-Chi, 2000; Girgis, Yunis, & Soliman, 2002), whether it is occurring naturally such as coal (e.g. lignite and all forms of coal) and lignocellulosic materials (e.g. wood, coconut shell, fruit stones, and nut kernels) or prepared synthetically such as organic synthetic polymers (e.g. synthetic resins, polyacrylonitrile, polyvinylidene chloride, waste resins, textile wastes, rubber, and dumped gangue). Bansal, Donnet, and Stoeckil (1988) summarized the principal commercial carbon feedstocks as: coal, lignite, and peat 52%; wood 35%; coconut shell 10%; and others 3%.

It has been already extensively demonstrated that the microporous properties of biochar or activated carbons depend not only on the experimental conditions of the pyrolysis process and activation steps but also preponderantly on the original nature and structure of the involved precursor. In term of weight, the main constitutive fractions of these lignocellulosic materials are the hemicellulose, the cellulose and the lignin, the thermal decomposition of which form the carbonaceous structure of the char precursor and the subsequent activated carbon (Cagnon, Py, Guillot, Stoeckli, & Chambat, 2009).

During the carbonization process of the lignocellulosic precursors, hemicellulose, cellulose and lignin decompose at different rates and within distinct temperature ranges. Due to the differences in reactivity between those three basic components during the pyrolysis step, as well as the competition of the reactions involved during their decompositions. Basically, there are two main steps for the production of activated carbon: (a) the pyrolysis of the carbonaceous raw material below 800 °C, in the absence of oxygen, and (b) the activation of the carbonized product (biochar), which is either physical or chemical. Based on the required properties of the activated carbon, the proper raw material and most importantly the activation process are utilized (Bansal et al., 1988).

Physical activation is a two-step process. It involves the pyrolysis of a carbonaceous material followed by the activation of the resulting char at high temperature in the presence of any oxidizing agents such as carbon dioxide, steam, air or their mixtures (Ioannidou & Zabaniotou, 2007). Rice husk, corn cob, oak, corn hulls, corn stover, rice straw, rice hulls, pecan shells, peanut hulls and almond shells were the raw materials studied. Carbonization temperature range between 400 and 850 °C, and sometimes reaches 1000 °C, and activation temperature range between 600 and 900 °C.

In the chemical activation process the two steps are carried out simultaneously, with the precursor being mixed with chemical activating agents, as dehydrating agents and oxidants. It offers several advantages since it is carried out in a single step, combining carbonization and activation, performed at lower temperatures and therefore resulting in the development of a better porous structure and inhibits the formation of tar. As a result, higher yield is obtained with a high bulk density, although the environmental concerns of using chemical agents for activation could develop. Chemical activation was used in most of the studies for corn cob, olive seeds, rice husks, rice straw, cassava peel, pecan shells, Macadamia nutshells, hazelnut shells, peanut hulls, apricot stones, almond shells. The most common chemical agents are $ZnCl_2$, KOH, H_3PO_4 and less K_2CO_3 (Ioannidou & Zabaniotou, 2007).

The process parameters, which have the largest influence on the products of pyrolysis, are the particle size, temperature and heating rate. Pyrolysis temperature has the most significant effect-followed by pyrolysis heating rate, the nitrogen flow rate and then finally the pyrolysis residence time. Generally, increasing pyrolysis temperature reduces yields of both biochars and activated carbons and leads to a decreased yield of solid and an increased yield of liquid and gases. As the temperature is raised, a rise in ash and fixed carbon percentage was observed along with a decrease in volatile matter. Consequently, higher temperature yields biochars of greater quality (Pütün, Ozbay, Pehlivan, Pütün, 2005).

The process conditions can be optimized to maximize the production of the pyrolytic char which are carbons of highly microporous form with both high internal surface area and porosity, and commercially the most common adsorbents used for the removal of organic compounds from air and water streams. They also often serve as catalysts and catalyst supports (Ioannidou & Zabaniotou, 2007).

2.4.2. Potential of agricultural by-products as precursors of biochar. In many agricultural production systems, byproducts are produced in significant amounts from crop residues such as nut-shells, peanut shells, cotton gin, and corn cobs. Many of the agricultural residues can be used to produce biochar and applied to agricultural soil to sequester C, improve soil fertility, and increase the production potential of crops. In many cases, these waste materials have little value and their disposal incurs costs.

Today large amounts (more than 50% of total available agricultural residues in the U.S.; Walsh et al., 1999) can be acquired for less than $30 per ton of biomass. The most suitable materials have high lignin concentration yielding the most biochar (Demirbas, 2004) such as residues from sawmills, forest residues, or nutshells. Conversion of agricultural residues into biochar is ecologically and economically attractive given the fact that energy is produced at the same time, as biochar is produced at a rate equivalent to the amount that can be achieved by direct charring. Some crop residues such as nut shells (e.g., groundnut, hazelnut, macadamia nut, walnut, chestnut, and coconut) but also bagasse from sugar cane processing, olive or tobacco waste are suitable for biochar production and are in some locations available in large quantities.

Biochar can act as a soil conditioner enhancing plant growth by supplying and, more importantly, retaining nutrients and by providing other services such as improving soil physical and biological properties (Glaser et al., 2002; Lehmann & Rondon, 2006). Land application of biochar is not a new concept. For example, certain dark earths in the Amazon Basin (so-called Amazonian Dark Earths or “terra preta”) have received large amounts of charred materials from biomass burning (Sombroek et al., 2003). These applications were most likely a result of both habitation activities and deliberate soil application by native Amerindian populations before the arrival of Europeans (Erickson, 2003).

The application of biochar (charcoal or biomass-derived black carbon) to soil is proposed as a novel approach to establish a significant, long-term sink for atmospheric carbon dioxide in terrestrial ecosystems. The production of biochar and its application to soil will deliver immediate benefits through improved soil fertility and increased crop production (Ketterings, 1999). Conversion of biomass C to biochar C leads to sequestration of about 50% of the initial C compared to the low amounts retained after burning (3%) and biological decomposition (<10–20% after 5–10 years), therefore yielding more stable soil C than burning or direct land application of biomass (Lehmann et al., 2006). The viability of such a biochar management system depends on (i) the competing uses for the biochar, and the biomass that it is produced from, (ii) on environmental constraints (Lehmann et al., 2006).

In addition to reducing greenhouse gas emissions, biochar applications to soil have the potential to decrease environmental pollution. Black C in soil similar to biochars efficiently adsorbs ammonia (NH_3) (Iyobe et al., 2004) and acts as a buffer for ammonia in soil, therefore having the potential to decrease ammonia volatilization from agricultural fields. Biological immobilization of inorganic N also aids in retaining N and in decreasing ammonia volatilization, due to the low N concentrations and high C/N ratios of biochars (Lehmann & Rondon, 2006).

In biochar pyrolysis systems, the process occurs in three steps: first, moisture and some volatiles are lost; second, unreacted residues are converted to volatiles, gasses and biochar, and third, there is a slow chemical rearrangement of the biochar (Demirbas, 2004) which shows different properties than the parent biomass materials. The differences are mainly in porosity, surface area, pore structures (micropores, mesopores, and macropores) and physicochemical properties such as composition, elemental analysis, and ash content (Haykiri-Acma, Yaman, & Kabyrak, 2005). Generally, the lower the temperature at which pyrolysis occurs, the higher the carbon recovery of the original biomass (Lehmann et al., 2006). If the feedstock is dry and the biochar yield is high, the heat produced can warm the incoming feedstock sufficiently to initiate the pyrolizing reactions to sustain the process (Antal & Gronli, 2003). The production of high yield biochar is favored when there are low temperatures and low oxygen levels inside a pyrolysis chamber.

At 400 °C or higher temperature, the biomass material is converted into fused aromatic ring biochar structures with the loss of carbon dioxide (CO_2), carbon monoxide (CO), water, and hydrogen (H_2). The released gases (CO_2 and H_2) are further converted to a useful synthetic gas (a mixture of carbon monoxide and hydrogen) used as a significant source of heat (Demirbas, 2004).

This process has the potential to be the lowest cost biomass to electrical energy conversion systems (Bridgwater & Peacocke, 2000). During pyrolysis at high temperature ~700 ˚C, lignin and cellulose compounds lose their aliphatic components along with the conversion of ring structures into condensed and single-ring aromatic structures, with carboxylic as the main groups.

2.5. Characterization of Biochar

2.5.1. Physical properties.

2.5.1.1. Bulk density. Bulk density is that of the material consisting of multiple particles and includes the macro-porosity within each particle and the inter-particle voids (Lehmann & Joseph, 2009). The density of biochar depends upon the nature of the starting material (Pandolfo, Amini-Amoli, & Killingley, 1994). Guo and Lua (1998) reported that the bulk density increased with the development of porosities from 8 to 24% at pyrolysis temperatures up to 800 ˚C. However, when the temperature was increased to 900 ˚C, the bulk density of the biochar increased and the porosity decreased due to sintering. Brown, Kercher, Nguyen, Nagle, and Ball (2006) showed that the density is dependent on the final pyrolysis temperature but independent of heating rate.

2.5.1.2. Particle size. It is essential that carbon particles are of appropriate size and structure to have a positive effect on soil structure in the short and long term. Because biochar exists as particulates, biotic or abiotic decay must be initiated on its surface. Such surface oxidation may be initiated quite rapidly (i.e. within a few months; Cheng, Lehmann, Thies, Burton, & Engelhard, 2006), but is restricted to the outer areas of a particle, even after several hundred years in soils (Lehmann, Liang, et al., 2005).

Biochar’s particulate form also clearly distinguishes it from other stable forms of organic matter, which are commonly perceived as macromolecules or macromolecular associations entrapped in fine pores, adsorbed to mineral surfaces, or occluded in aggregates. Particulate organic matter, on the other hand, is mostly unprotected by mineral association and is therefore easily mineralizable (Golchin, Oades, Skjemstad, & Clarke, 1994). Although biochar is present in particulate form, it is very recalcitrant to microbial decomposition (Schmidt & Noack, 2000).

2.5.1.3. Hardness. The hardness is a characteristic used for defining the quality of carbon as it is related to its ability to withstand wear and tear during use (Lehmann & Joseph, 2009). Agricultural wastes (almond, walnut, etc.), and fruits stones (apricot, olive pits, etc.) are of interest as biochar or activated carbon because of their high mechanical strength and hardness.

2.5.2. Surface properties.

The BET surface area of char is important because, like other physico-chemical characteristics, it may strongly affect the reactivity and combustion behavior of the biochar. The biochars from pyrolysis above 400 °C had a surface area and a high surface area formed (Pütün et al., 2005). The type of chemical agent used in the activation process has a significant effect on the carbon produced. The experimental results of Macadamia nutshells show that surface area and micropore volume of the samples produced by chemical activation with $ZnCl_2$ are much higher than those with KOH (Ahmadroup and Do, 1997). The BET surface area and total pore volume of the produced biochar after demineralization were increased nearly twice as much before demineralization.

The demineralization that resulted in an approximately twofold increase in the intensity of pore size distribution over all the ranges of pore diameter; a significant increase can be observed for pores of diameter about 2 and 30 nm. This study clearly showed that porous carbons with highly developed porosities could be prepared simply, without an activation process at high temperature, if the demineralization is performed after sufficient carbonization of precursor materials (Chang, Yun, Gyu, & Chong, 2000).

2.5.3. Chemical properties

2.5.3.1. Surface chemistry, functional groups and charges. The surface chemistry of biochars is quite rich and varied. Biochar surfaces exhibit hydrophilic, hydrophobic, acidic, and basic properties whose relative contributions to biochar reactivity depend upon the feedstock and on the thermal degradation process used to create biochar (Lehmann & Joseph, 2009). Experimental evidence shows that a range of different functional groups exist on the surfaces of biochar. Groups such as OH, NH_2, OR, or O(C=O)R are classified as electron donors, whereas (C=O)OH, (C=O)H or NO_2 groups are classified as electron acceptors. Carboxyl groups are strong Bronsted acids. Less acidic groups include phenols and carbonyls. Chromenes and pyrones are basic functional groups.

2.5.3.2. pH value. pH is defined in terms of the relative activity of hydrogen ions in solution. It is a measure of the acidity or basicity of an aqueous solution. Biochar pH values are relatively homogeneous, that is to say they are largely neutral to basic. Chan and Xu (2009) reviewed biochar pH values from a wide variety of feedstocks and found a mean of pH 8.1 in a total range of pH 6.2 – 9.6. The lower end of this range seems to be from green waste and tree bark feedstocks, with the higher end from poultry litter feedstocks.

2.5.3.3. Ash content. Ash content is the nonvolatile inorganic matter of a compound, which remains after subjecting it to a high decomposition temperature. Wood and related plants (e.g. bamboo, coconut shells) are characterized by a very low ash composition (<3%) and a very open porous structure. Other byproducts such as Animal manures and rice husks are high mineral ash residues and are not very porous (Joseph, Peacocke, Lehmann, & Munroe, 2009).

2.5.3.4. Electrical conductivity. Electrical conductivity (EC) estimates the amount of total dissolved salts or the total amount of dissolved ions in the water. Therefore, EC in leachate measures the risk of groundwater pollution by dissolved base ions, such as NH_4^+ (Lehmann & Joseph, 2009).

2.6. Adsorption Process of Biochar

2.6.1. Role of pore size. Both the size and distribution of micropores, mesopores, and macropores determine the adsorptive properties of carbon. For instance, small pore size will not trap large adsorbate molecules and large pores may not be able to retain small adsorbates, whether they are charged, polar molecules or uncharged, non-polar compounds (Ahmedna Marshall, Hesseiny, Rao, & Goktepe, 2004). Porous properties of biochar and activated carbon depend on the types of starting materials as well as the method and conditions of preparation.

Materials with a greater content of lignin (grape seeds, cherry stones) develop carbon with macroporous structure, while raw materials with a higher content of cellulose (apricot stones, almond shells) yield carbon with a predominantly microporous structure (Savova et al., 2001).

2.6.2. Role of biochar surface chemistry on the adsorption process. Many properties of carbon materials, in particular their wetting and adsorption behavior, are decisively influenced by chemisorbed oxygen. Oxygen in the surface oxides can be bound in the form of various functional groups which are similar to those known from organic chemistry (Boehm, 2002). Faust and Aly (1987) reported that when oxygen contacts carbon surfaces some sort of oxygen-carbon complex is formed.

In general, acidic oxides are predominantly formed in carbon when it is prepared under moist air at 300 to 500 °C, and basic oxides in those carbons prepared at 800 to 900 °C in air, steam, or carbon dioxide. Amphoteric properties are found in carbons prepared between 500 to 800 °C. The activated carbons prepared at low activation temperature, below 500-600 °C, adsorb

OH^- ions primarily are called L-carbons. Those activated carbons are prepared at above 500-600 °C and adsorb H^+ ions are called H-carbons.

Acid surface sites are oxygen based while basic sites are associated with the carbon itself. Both acidic and basic sites have been found on all carbon regardless of whether they are heated at high temperature in nitrogen or oxidized chemically with nitric acid or treated electrochemically (Mattson & Mark, 1971). For the most extensively oxidized sample, the number of basic sites is approximately zero, while for heat treated carbon, the number of acidic sites is very small. Surface oxides created with oxygen at elevated temperatures (or by aging) or with liquid oxidants are acidic in character and cause cation exchange properties. Acidic and basic surface sites coexist usually, but the concentration of basic sites decreases with increasing acidic character of the surface (Boehm, 2002).

Almost every type of functional group in organic chemistry has been suggested to be present on activated carbons surface. The ones suggested most often acidic functional groups are: carboxyl, phenolic-hydroxyl, and quinone-type carbonyl groups (Figure 2.2) while other suggested groups are ether, peroxide and ester groups in the forms of normal lactones and fluorescein-like lactones, carboxylic acid anhydrides and the cyclic peroxide (Figure 2.2). On the other hand, proposed basic surface groups include chromene and pyrone.

Typical identification reactions of organic chemistry were employed by Boehm (2002) to characterize oxygen chemisorbed on carbon as comprising four types of acidic surface groups: (a) a strongly acidic carboxyl group which is neutralized by $NaHCO_3$, Na_2CO_3, NaOH, and $NaOC_2H_5$, (b) a more weakly acidic carbonyl group which is neutralized by Na_2CO_3 or stronger bases such as NaOH and $NaOC_2H_5$; but not by $NaHCO_3$, (c) a phenolic hydroxyl group which is neutralized by NaOH and $NaOC_2H_5$, and (d) a carbonyl group which is neutralized by $NaOC_2H_5$ only. The type and number of surface groups on carbon (biochar and activated carbon) will influence the extent and rate at which organic and inorganic compounds/species are adsorbed.

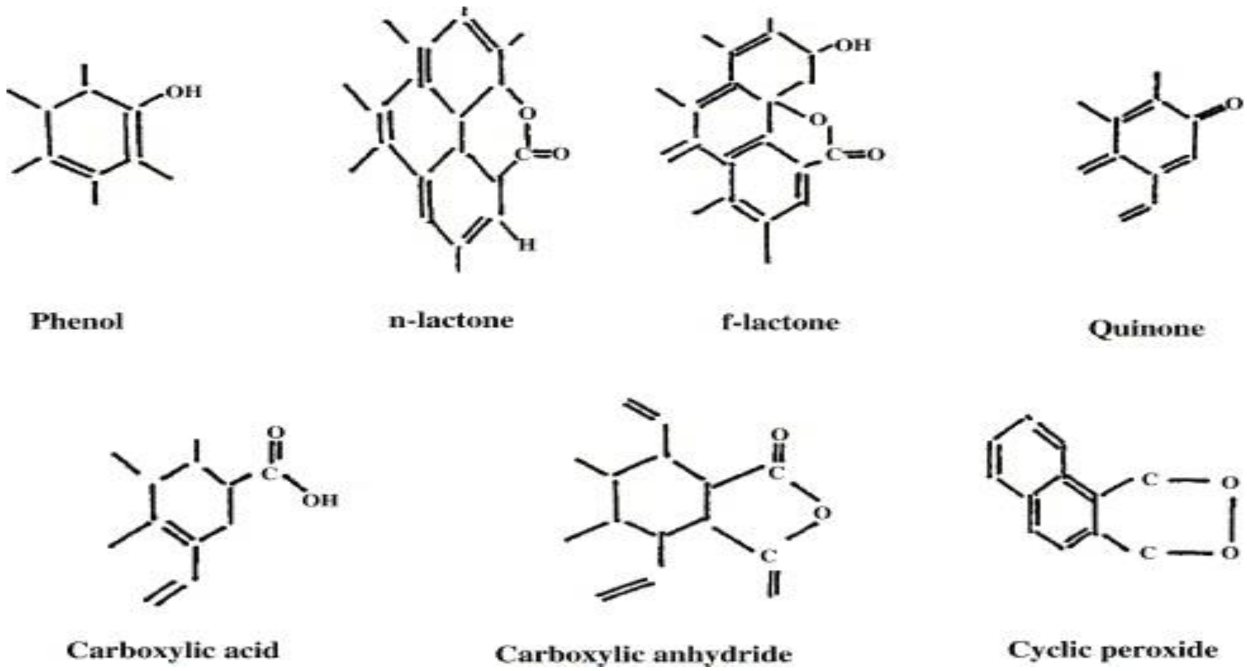

Figure 2.2. Structures of functional groups.

2.7. Environmental Applications of Biochar

A clear direct relationship was observed between change in the earth’s temperature and the atmospheric concentration of greenhouse gases over the last 1000 years indicating a strong correlation between the two parameters. The projected climate change results in an estimated increase in the earth’s temperature of 1–6 °C, depending on the models. An increase in sea level would be a direct consequence of high temperatures, for example, of 0.1–0.9 m which may cause the flooding of large regions in the world (Centi, Perathoner, & Rak, 2003).

The management of the climate change effects and minimization of dependence on fossil fuel sources has been the major focus of most of the industrial countries with a strong need to develop sustainable energy sources therefore strategic, environmental and energy policy decisions need to be taken in order to overcome this issue (Bridgewater, 1996). An agreement was signed during a meeting that took place in December 1997 at Kyoto by the parties to the United Nations Framework Convention on Climate Change (UNFCCC), popularly known as the Kyoto Protocol, to reduce collectively their greenhouse gas (GHG) emissions to at least 5% below 1990 levels over the period 2008–2012 (Ahammad, Clements, & Ye, 2001).

The main source of CO_2 emissions in the developed countries is private vehicle transportation. The second most important source is the municipal solid waste landfill facility of the cities. The remaining sources under consideration are: electricity, natural gas, incineration, and liquefied petroleum gases.

The anthropogenic emissions includes greenhouse gases (GHGs) from fossil fuel combustion (i.e., burning of fossil fuels such as coal, oil, natural gas and petroleum products) and ones due to mining, agricultural and cement production arise from both production and consumption processes. The three major GHGs, namely, carbon dioxide, methane and nitrous oxide are classified on the basis of their global warming potential (GWP) and expressed in CO_2-equivalent unit (Conrad, 1999). Methane emission is smaller compared to CO_2, but its Global Warming Potential is 25 times higher (WMO/UNEP, 1990).

The increased atmospheric emissions of greenhouse gases due to some of the industrial activities such as Fossil fuel combustion, landfills, and incinerators are causing concern to the international community. Obviously, to reduce the possibility of increasing the greenhouse effect, it is necessary to limit the emissions of the gases that produce it (De la Chesnaye, Harvey, Kruger, & Laitner, 2001). Biomass can be categorized into three different groups; agricultural wastes, energy crops and refuses and considered the third largest primary energy resource in the world, after coal and oil (McKendry, 2001, 2002) Therefore, they can provide partial or total substitution of fossil fuels due to their abundance and low cost (Fowler et al., 2009).

Energy crops are considered CO_2-neutral when they are harvested in a sustainable way and can be converted to heat, electricity or even biofuel. Nevertheless, energy crops do raise the environmental and social concerns, such as sustainable land use, soil desertification, increase of food prices, table water contamination due to fertilizers use and loss of biodiversity (Zabaniotou, Kantarelis, Skoulou, & Charziavgoustis, 2010).

In contrast, biomass and crop residues can be recycled into the soil with or without composting or stabilization processes of the organic C. Thus, the development of biochar production as a useful biotechnology in transforming organic waste into suitable agricultural products has been favored, and their application or addition to soil can contribute to (a) mitigate climate change by sequestering carbon for long time periods, (b) soil fertility and plant growth by increasing nutrient availability, changing pH, water holding capacity, and soil structure (Pankhurst et al., 2005), and (c) lower greenhouse gases emissions.

A very efficient and low-risk approach has been developed lately to both help mitigate climate change and increase soil fertility. The concept, originated from ancient soil management practiced by ancient Amerindian populations before the arrival of Europeans, and to the development of complex civilizations in the Amazon region that were able to carbonize the accumulated biomass and produce a rich Terra Preta with a half-life of thousands of years (Kleiner, 2009; UNEP, 2009), involves the production of biochar from agricultural waste by pyrolysis in the absence of oxygen at low temperature, and then mixes it with soil, which prevents CO_2 from reaching the atmosphere and decreasing the concentration of atmospheric CO_2 by plant photosynthesis (Bruun, El-Zahery, & Jensen, 2009; Gaunt & Lehmann, 2008;

McHenry, 2009). In addition, the slow degradation of biochar in the soil enhances soil fertility by increasing water holding capacity, and cation exchange capacity (Bruun et al., 2009).

2.7.1. Biochar for long-term carbon sequestration. To better understand the optimal benefits of biochar sequestration it is important to distinguish between how CO_2 is released and captured through the lifecycle of plant growth, a process that is considered carbon ‘neutral’, and the biochar approach which has a ‘negative’ net effect. Through the process of photosynthesis, Earth’s terrestrial plants absorb approximately 60.6 billion tons of carbon every year. A similar amount of carbon is then released back into the atmosphere through respiration (Lehmann et al., 2006).

On the other hand, biochar sequestration, by comparison, is carbon negative as it results in a long-term withdrawal of CO_2 from the atmosphere by diverting a portion of the carbon out of the photosynthesis cycle and into a much slower, stable, and resistant state of mineralized carbon. The immediate CO_2 emission from syngas released by pyrolysis would, within a few months, be exceeded by the CO_2 emitted in decomposition if the same material had been added to soil directly (Lehmann, Lan, et al., 2005). Also, although there is a CO_2 emission associated with provision of heat for the pyrolysis process, the calculations of Gaunt and Lehmann (2008) indicate that it is relatively small; in an example where pyrolysis consumed 40% of the carbon in the feedstock (in producing syngas), the CO_2 resulting from provision of process heat for biochar production would equate to only a further 10% (Gaunt & Lehmann, 2008).

The net saving is, therefore, considerable over a period of one to five decades. Even though, there is a high initial loss of CO_2 within the first few years, the effects of biochar on other soil processes, such as moisture, may offset this increase by preventing N_2O and CH_4 release (Pekrun, Kaul, & Claupein, 2003).

According to a study which examined the viability of 17 carbon management and geo-engineering options, biochar has the potential to sequester nearly 400 billion tons of carbon over the 21st century, reducing atmospheric CO_2 concentrations by 37 parts per million (Lenton & Vaughan, 2009). Although these numbers are high, even sequestration of 20 billion tons by 2030 could have a significant decrease on atmospheric GHGs concentrations. Thus biochar could be an essential element of systems management necessary for meeting the climate change challenge (Kleiner, 2009; Lehmann, 2007a). Furthermore, Lehmann et al. (2006) undertook a global analysis of biochar sequestration potential and reported that by 2100, biochar sequestration could amount to 5.5 – 9.5 Gt C/yr if renewable energy demand was met through pyrolysis, which exceeds current emissions from fossil fuels (5.4 Gt C/yr).

2.7.2. Biochar for soil improvement. Methods used to apply biochar into agricultural soils depend on the biochar physical properties and its intended function. Biochar produced under 400 °C has a low surface area and may not be useful as an agricultural soil improver (Lehmann, 2007b). The type of biomass feedstock and pyrolysis conditions will also affect the amount and type of substances produced.

The cation exchange capacity (CEC) of biochar depends on the temperature at which it is produced, the potential CEC (standardized for pH 7) increasing with temperature. Also, pH and surface area of fresh biochar increase with production temperature, as carbon yield decreases. Many positive effects of biochar applications on soil were reported on the biological processes such as biological fixation of atmospheric nitrogen by common beans was found to be enhanced by the addition of biochar to a highly weathered savanna soil, most likely through the mechanism of greater micronutrient availability (Rondon, Lehmann, Ramírez, & Hurtado, 2007). Higher bacterial growth rates with biochar were explained by better attachment and possibly physical protection of microorganisms within the pore structure (Pietikäinen, Kiikkilä, & Fritze, 2000).

When applied to soil, biochar may reduce off-site pollution in two ways: first, by retaining nutrients such as nitrogen and phosphorus in the soil, and lowering the amount of soil nutrients leached into groundwater or eroded into surface waters. Secondly, biochar would reduce pollution by improving nutrient retention in the topsoil, thereby reducing the amount of fertilizer needed to grow a crop. Reduced leaching has been demonstrated in greenhouse studies (Lehmann, Da Silva, et al., 2003) and can be expected from adsorption behavior.

Application of biochar into soil may affect the soil water retention; some field results indicate a positive impact. Glaser et al. (2002) reported that Amazonian charcoal-rich anthrosols had field water retention capacity 18% higher than surrounding soil without the charcoal. The possible mechanisms by which coal-derived humic acids improve soil physical properties are the formation of organo-mineral complexes by functional groups of the humic acids. The hydrophobic polyaromatic backbone reduces the entry of water into the aggregate pores leading to an increased aggregate stability and water availability (Glaser et al., 2002).

Tyron (1948) investigated the effect of biochar addition on available moisture in brown podzolic forest soils (in Connecticut, USA) of three different textures—sandy, loamy, and clayey. In this study, it was found that biochar increased the available moisture in sandy soil, had no effect in loamy soil and decreased the available moisture in clayey soil. This suggests that biochar addition may be ill-suited to soils that have high clay content. Conversely, the increase in available moisture observed in sandy soils may make biochar a useful tool in the reversal of desertification. Further research will be required to determine just which soils may be suited to biochar amendment with regard to the effect on their water retention properties (Woolf, 2008).

The presence of biochar in soil mixture can influence texture, structure, porosity and consistency through changing the bulk surface area, pore size distribution, particle size distribution, density and packing. These factors can have a direct impact on plant growth, because the penetration depth and availability of air and water within the root zone is determined largely by the physical makeup of soil horizons. The influence of biochar on soil physical properties will affect soil's response to water, aggregation, workability, shrink-swell dynamics and permeability. Biochar specific surfaces, being generally higher than sand and comparable to or higher than clay, therefore will cause a net increase in the total soil specific surface when added as an amendment (Downie, Crosky, & Munroe, 2009).

Given the fact that biochar has a very porous nature that improves soil aggregation (Liang et al., 2006) its application to soil should improve soil aeration. Further, improved water holding capacity and reduced tensile strength (Chan et al., 2007) have also been demonstrated. Improved aeration will be partly due to increases in macroporosity with resulting higher air-filled porosity and improved supply of oxygen to soil under a wide range of soil water conditions. However, the extent of changes will depend on the porosity characteristics of different biochar types and application rates. Pore size distribution of biochar depends on anatomical structure of parent feedstock and process conditions during pyrolysis such as charring temperature and activation (Zwieten et al., 2009).

Piccolo, Pietramellara, and Mbagwu (1996) carried out experiments in laboratory conditions and found significant improvements in aggregate stability and water holding capacity of Mediterranean soils when added with coal-derived humic substances. Biochar has a greater ability than other soil organic matter to adsorb cations due to its greater surface area, greater negative surface charge and greater charge density (Liang et al., 2006). This makes it potentially more capable of retaining nutrients and providing these to growing plants. The cation exchange capacity of freshly produced biochar is relatively low and only aged biochar shows high cation retention as in Amazonian Dark Earths (Liang et al., 2006). In contrast to other organic matter in soil, biochar also appears to be able to strongly adsorb phosphate, even though it is an anion (Lehmann, Lan, et al., 2005).

Application of biochar to soil may also reduce off-site pollution by, firstly, retaining nutrients such as nitrogen and phosphorus in the soil and lowering the amount of soil nutrients leached into groundwater or eroded into surface water. Secondly, biochar would reduce pollution by improving nutrient retention in the topsoil, thereby reducing the amount of fertilizer needed to grow a crop. Reduced leaching has been demonstrated in greenhouse studies by Lehmann, Da Silva, et al. (2003).

The total nutrient content of biochar is typically high but this is not necessarily a true reflection of the proportion that can be made available for plant uptake. The available form of the nutrient is the important form for uptake by plants. Chan and Xu (2009) stated that very limited data is available in the literature on available nutrient contents of biochar. He also reported that mineral N is very low (< 2 mg/ kg) and available P is highly variable (15 – 11 600 mg/ kg). The supply of available K in biochar is typically high and an increased K uptake as a result of biochar application has been frequently reported (Lehmann, Da Silva, et al., 2003; Chan et al., 2007). The reported range of available K by Chan and Xu (2009) is 1 – 58 g/ kg depending on the precursor.

C/N (carbon to nitrogen) ratio is usually used as an indicator of the ability of organic substrates to mineralize and release inorganic N when applied to soils. The C/N ratios of biochar varies widely from 7-400, with a mean of 61 (Chan & Xu, 2009). Sullivan and Miller (2001) suggested that composts with C/N ratios above 25 to 30 immobilize inorganic N. Based on these values, given their very high C/N ratios; most types of biochar are expected to cause N immobilization and thereby possibly induce N deficiency of plants when applied to soils alone. However, there is a degree of uncertainty if the same criterion is directly applicable to biochar (Chan & Xu, 2009). C/N ratios of Terra Preta soils are usually higher than the adjacent Ferralsol, but they tend to have higher available N (Lehmann, Kern, et al., 2003).

For biochar produced from sewage sludge, despite its relatively high total N content of 6.4%, a laboratory incubation study with soil at 25 °C and field capacity indicated that negligible amounts of mineral N were detectable even after 56 days (Pritchard, 2003). This indicated that N in sewage sludge biochar was in forms that are very resistant to decomposition and mineralization. Likewise, laboratory incubation studies indicated that the availability of P in the biochar is only 13% of total P, much lower than those of the biosolid and dry pellet biosolid (30-40%) (Pritchard, 2003).

The most important condition affecting nutrient composition and availability of biochar is the production temperature. Other important factors including heating rate and particle size of the feedstocks may also be important. Up to 50% of N, K and S are commonly lost from biochar when temperatures exceed 500 °C. Furthermore, there is evidence suggesting that the remaining nutrient elements tend to become less available with further increases in temperature. For P, while total losses are minimal, available forms of P are also greatly reduced at higher temperature.

Very little is known about the half-life of biochar for two reasons: first, the recalcitrance of biochar greatly depends on a multitude of factors, including the type of biomass used for pyrolysis, the production conditions, soil properties, and climate (Lehmann et al., 2006). Some biochars may decompose relatively rapidly in soils, while others persist for millennia.

even though there is a lack in understanding the rates of subsequent demineralization through chemical breakdown, farmers are moving ahead with the use of biochar because of its ability to reinvigorate degraded soils by retaining nutrients for plant uptake and soil fertility and limiting the infiltration of chemical fertilizers and pesticides (Gaunt & Lehmann, 2008; Bruun et al., 2009).

2.7.3. Biochar for reduction of emissions of non- CO_2 GHGs from soil. The soil is both a significant source and a sink for the greenhouses gases CO_2, methane (CH_4), and nitrous oxide (N_2O). Small reductions in the N_2O and CH_4 emissions could potentially provide significant benefits for the environment since their global warming potential is 298 and 25 times greater, respectively, than the CO_2 (Forster et al., 2007). Biochar addition to soil has a significant effect on the carbon and nitrogen transformation and retention processes in the soil which could play a significant role in mitigating soil emissions of the two significant non- CO_2 GHG's (N_2O and CH_4). Around 8% of the global emissions are anthropogenic sources of N_2O.

In 2004, agriculture was responsible of 42% of the GHGs emissions (Denman et al., 2007). The main sources of the nitrogen that can lead to N_2O emissions are N fertilizers, biological N fixation by associative, free-living, and mutualistic bacteria, organic N and the excreta of grazing animals (Dalal, Wang, Robertson, & Parton, 2003). In 2004, CH_4 constituted around 14% of global GHGs emissions. Denman et al. (2007) reported that globally soils had consumed 30 Tg CH_4/yr during 2000 and 2004, equivalent to 5% of the annual load of CH_4 to the atmosphere. The CH_4 uptake capacity of soil varies with land use, management practices, and soil conditions (Liebig et al., 2005; Schutz, Seiler, & Conrad, 1990). Large emissions of CH_4 are common where anaerobic conditions coupled with warm temperatures and the presence of soluble carbon (Dalal, Allen, Livesley, & Richards, 2008).

Several studies have been reported in the literature confirming that biochar addition to the soil reduces N_2O emissions and CH_4 uptake from soil which can be a big contribution to the mitigation of the GHG emissions (Rondon et al., 2006; Yanai, Toyota, & Okazaki, 2007). Yanai et al. (2007) reported that adding biochar to a soil re-wetted to 73% water-filled pore space in laboratory chambers a decrease in N_2O from 105 µg/m^2 to 11 µg/m^2 over a seven day incubation.

In another experiment where biochar is used up to 10% showed a maximum emission rate of 2620 µg N_2O-N/m^2/hr in the control soil, while the maximum emission rate in biochar-amended soil was 383 µg N_2O-N/m^2 /hr. in laboratory incubation studies conducted by Rondon et al. (2006) using glass jar (5 liters) with air-tight lids filled with 1.5 kg dry weight equivalent soil. Low and high temperature biochars derived from both green waste and poultry litter were applied at an equivalent of 10 t dry biochar/ha. Results showed that the soil amended with poultry litter biochar emitted almost no N_2O during the incubation, while low-temperature green waste biochar increased N_2O emissions by over 100% that of the control.

Evidence of reducing CH_4 emissions was also reported. Rondon et al. (2006) has demonstrated that addition of wood-derived biochar (20 t/ha) to a non-fertile tropical soil increased the annual methane sinks in the soil by around 200 mg CH4/m^2 compared to the control.

2.8. Biochar Research Initiatives

To date there are a limited number of examples of large scale publicly funded research initiatives that assess the use and optimization of biochar for use in soil. In the UK the Engineering and Physical Sciences Research Council supports two established projects, one building capacity in technology for fast pyrolysis (as part of a wider bio-energy initiative, SUPERGEN) and testing by-products in soil, and the other developing Carbon Sequestration and Capture technology. In New Zealand the Massey University has a Biochar Research Initiative. Brazil has funded second and third tier levels within 'macro-programs' defined by the research organization, EMBRAPA. These will extend field experimentation to create new terra preta (Sohi et al., 2009).

The US has created the Farm Bill that supports 'biochar research development and demonstration' which seeks to enhance agricultural energy programs (Anon, 2007). Biochar was specifically mentioned in the Garnaut Climate Change Review in Australia (Garnaut, 2008) and has been raised in Environment Select Committee discussions in the UK. The only full-scale field trials using biochar from slow pyrolysis energy plants are being conducted in NY (Cornell University), USA.

2.9. Economic Viability of Biochar

The determination of the economic value of sequestered carbon depend on several factors such as energy supplies and demand, the supply and demand for low emissions technologies, the availability of alternative carbon sequestration technologies and global policy responses to climate change. The growing price of waste disposal is likely to make the production and application of biochar for electricity and waste management economically viable. Carbon offsets will have a greater role once biochar is certified under the Clean Development Mechanism (CDM) of the Kyoto Protocol. Uncertainty over market interventions may risk the investment in energy facilities that are able to produce biochar (Sohi et al., 2009).

At the Power-Gen Renewable Energy and Fuels meeting in Las Vegas 2006, Lehmann and colleagues presented calculations showing that biochar sequestration could be economically attractive when the value of CO_2 emissions, currently trading at $4/t on the Chicago Climate Exchange, reaches $37/t (Renner, 2007).

Given the current trajectory of global greenhouse gas emissions, the price of emissions as a tradable commodity will be increasingly important. There will be a corresponding increase in value of the residual energy in biochar as fossil energy prices rise. The price of bio-energy may also be enhanced by Government subsides designed to improve energy security and promote environmental goals. In many industrialized countries the opportunity cost associated with using biochar in soil is artificially enhanced by renewable energy subsidies (Sohi et al., 2009).

2.10. Research Gaps and Future Challenges in Biochar Field

Given that biochar technology is in its early stages of development, there are many concerns about the applicability of the technology. Among these issues we have feedstock availability, biochar handling, and biochar system deployment, which are slowing the realization and application of this technology. The availability of enough data on the effect of biochar additions on trace gas emission (NO_2 and NH_4) is also another concern, but has a potentially great impact on the net benefit of biochar application. Modeling of the linked carbon and nitrogen cycles in soil with and without application of biochar is an essential factor in understanding the fundamental mechanisms and the impact on soil-based emissions of greenhouse gases (Sohi et al., 2009).

Some research priorities have been identified based on the research results of Sohi et al. (2009) which include: (a) determination of the relationship between the biochar properties and qualities and its manufacture for a better optimization for soil use; (b) model the impact of alternate bio-energy systems on the carbon cycle at the global scale, and in the context of national targets, in order to support policy decisions and devise suitable market instruments; (c) research is needed to provide a fundamental, mechanistic understanding of how biochar provides its unique functional characteristics, probably embodied in models, and would include its interactions with other living and nonliving components of soil; and (d) globally coordinated research activity across a range of countries and climates is necessary if the global applicability of knowledge gained is to be rigorously assessed.

According to Sohi et al. (2009) two types of carbon modeling are required: static spreadsheet models to compare alternative scenarios for their relative carbon-equivalent gain, and mechanistic soil simulation models that capture information from short term experiments to predict longer-term impacts on soil function. In addition, socio-economic models that incorporate a spatial dimension are required to assess the workability of particular scenarios, and set a global system that enables optimal biochar products to be selected for application in a particular location and system.

CHAPTER 3

Materials and Methods

3.1. Carbon Production and Characterization

3.1.1. Preparation of biochar. Four agricultural byproducts (Pecan shells, Peanut shells, cotton gins) and forage crop (switch grass) were used to produce biochar. Pecan shells were obtained from Carolina Grains, Lumberton, North Carolina, and Peanut shells from Golden Peanuts Company (Alpharetta, GA, USA). Cotton gin and switchgrass were obtained from the USDA-ARS Coastal Plain Research Center, Florence, South Carolina, where cotton, soybeans, and switchgrass were grown for research purposes.

The four precursors were dried overnight at 90 °C using a Laboratory oven (Fisher Scientific, USA). The peanut and pecan shells were used without any further treatment; however the cotton gin and switchgrass were cut into pieces of four inch long before pyrolysis. A Lindberg box programmable furnace equipped with a retort (model 5116HR; Lindberg, Watertown, WI) was used in pyrolysis (Figure 3.1). The furnace was purged using nitrogen gas prior to initiation of pyrolysis to prevent carbon losses due to oxidation. Production of biochar involved the testing of various pyrolysis temperatures, and times.

An incomplete 4 x 3 x 3 factorial design was used in this study. Four different agricultural precursors were used, three feedstocks (cotton gin, peanut, pecan shells, and switchgrass) , 3 different temperatures (300, 500, and 750 °C) and 3 different pyrolysis residence time (8, 16, and 24 h for 300 °C), (4, 8, and 12h for 500 °C), and (1, 2, and 3h for 750 °C) were used in the production of biochars. Prepared feedstocks were pyrolyzed under nitrogen gas using a Lindberg box programmable furnace equipped with a retort (model 5116HR; Lindberg, Watertown, WI) at 3 different temperatures (300, 500, and 750 °C) and different pyrolysis residence time (8, 16, and 24 h), (4, 8, and 12h), and (1, 2, and 3h), respectively as shown in Table 3.1.

Figure 3.1. Lindberg furnace.

Table 3.1

Biochar production conditions

Pyrolysis Temperature (C°)	**Pyrolysis Time (hours)**		
300	8	16	24
500	4	8	12
750	1	2	3

3.1.2. Measurement of carbon properties.

3.1.2.1. Physicochemical properties. Physical (bulk density, surface area, moisture) and chemical (ash, pH, surface charge, and electrical conductivity) properties were determined according to the procedures of Ahmedna, Marshall, and Rao (2000) and Toles, Marshall, Johns, Wartelle, and McAloon (2000).

3.1.2.1.1. Moisture content. Moisture content of biochar was determined using the standard ASTM method, with minor modification, using a vacuum oven (Standard Test Method for Chemical Analysis of Wood Charcoal, 2001). A two-gram biochar sample was dried at 98-100 ˚C in a drying oven for 24 hours. The initial weight of the measuring dishes was recorded. The weight (W) difference between the samples before and after the drying was recorded. The moisture was then calculated as follow:

$$\text{Moisture (\%)} = (\text{Wair dry} - \text{Woven dry}) / \text{W sample} * 100 \qquad \text{(Eq 1)}$$

3.1.2.1.2. Bulk density. Bulk density was determined using the method of Ahmedna et al. (2000). A 25 mL cylinder was filled to a specified volume with 10–30 mesh biochar that had been oven dried at 80 °C overnight. The pre-weighted cylinder was tapped for at least 1–2 min to compact the carbon and weighed (Bansode, Losso, Marshall, Rao, & Portier, 2003). The bulk density was then calculated by the following formula:

$$\text{Bulk density (g/mL)} = [\text{wt of dry material (g)/vol of packed dry material (mL)}] \qquad \text{(Eq 2)}$$

3.1.2.1.3. Ash content. Approximately 2 g of biochar was placed into pre-weighed ceramic crucibles. Crucibles and their contents were dried overnight at 80 °C and reweighed to obtain the dry carbon weight. The samples were heated in a Laboratory Muffle Furnace (Fisher Scientific, USA) at 760 °C for at least 6 h. The crucibles were cooled in a desiccator, and the remaining solids (ash) were weighed (Bansode et al., 2003). The percent ash was calculated as follows:

$$\% \text{ ash} = [\text{remaining solids wt (g)/ original carbon wt (g)}] \times 100 \qquad \text{(Eq 3)}$$

3.1.2.1.4. pH measurement. The pH measurements of biochar were conducted using the method described by Ahmedna et al. (2000). The method for pH measurement consists of preparing 1% (wt/wt) suspension of biochar in deionized water. The suspensions were heated to approximately 90 °C and stirred for 20 min. The suspensions were then allowed to cool to room temperature, and the pH was measured with a Corning pH 10 portable pH meter (Acton, MA). The pH meter was initially calibrated with pH 4 and pH 7 buffers. If the pH was found to be above pH 7, the pH meter was recalibrated with pH 7 and pH 10 buffer solutions (Bansode et al., 2003).

3.1.2.1.5. Electrical conductivity. A 1% (w/w) solution of biochar in water was stirred at room temperature for 20 min (Ahmedna, Johns, Clarke, Marshall, & Rao, 1997) and electrical conductivity was measured using a TDS/Conductivity meter (Oakton Instruments, Vernon Hills, Il) with values given in MicroSiemens (µS).

3.1.2.1.6. BET surface area. A Quantachrome Nova 2200 (Boynton Beach, FL) surface area analyzer (Figure 3.2) was used to determine the surface area of test carbon based on nitrogen adsorption at 77 K. Between 0.2 and 0.25 g of biochar that was previously degassed overnight (for at least 8 hours) was placed into the evacuated sample chamber of the surface area analyzer. The Nova 2200 was equipped with automated software for acquisition of BET surface area and pore size distribution based on monolayer adsorption of nitrogen. The BET (Brunauer, Emmett and Teller) equation was used by the software to calculate the specific surface area of the test carbon. The Barrett, Joyner and Halenda (BJH) model was used by the software to compute pore sizes from equilibrium gas pressures. Micro, meso, and macropore volumes were also calculated using the BJH model and pore surface areas were calculated using t-plots (Johns, Marshall, & Toles, 1999, Bansode et al., 2003; Toles, Marshall, & Johns, 1997).

Figure 3.2. Surface area analyzer nova 2200.

3.1.2.1.7. Biochar surface charge. The total negative surface charge was measured on duplicate samples based on the Boehm (1994) method. One-tenth N solutions of sodium bicarbonate, sodium carbonate, sodium hydroxide and sodium ethoxide were prepared along with a 0.1N solution of HCl. Fifty mL of each base were placed in a 250 mL Erlenmeyer flask. An amount of 0.5 g of biochar was introduced into each flask with a Teflon stirring bar. A blank (base with no biochar) was run in parallel with the biochar samples. Flasks containing 1% (w/v) carbon slurries along with the blanks were sealed and continuously stirred for 24 h. At the end of 24 h, carbon was separated from the solution using 0.45 µm filters. Ten (10) mL of the filtrate were pipetted into a 50 mL beaker and 15 mL of 0.1N HCl were added to the filtrate. Excess HCl was subsequently determined by titration with 0.1N NaOH.

Titrations were carried out using an 836 Titrando Autotitrator (Metrohm USA Inc., Riverview, Florida) equipped with a 50 mL burette and a Corning pH Meter probe. The titrant volume was automatically controlled at 0.3 pH unit increments. This option allowed good control of the volume of titrant around inflexion points of the titration curves, where pH change is most rapid, thereby ensuring accurate detection of the inflexion points. The volume of NaOH necessary to reach the equivalent point was recorded for the blank and the carbon samples (Boehm, 1994). The difference in volume of NaOH consumed by the blank and by the carbon sample was calculated and converted to a titratable negative surface charge with results expressed as mmol H^+ equivalent neutralized by standard base per gram of biochar, from the following equation:

$$C_s = U_b * R_b * N / M_c, \qquad \text{(Eq 4)}$$

in which C_s is the surface charge per weight of adsorbent in mmol H^+ eq/g, U_b is the difference in NaOH uptake between the titrated sample and the titrated blank, R_b is the ratio of base volume in the original slurry to the filtrate volume used in titration, N is the normality of HCL, and M_c is the weight of carbon in grams.

3.2. Soil and Biochar Incubation

3.2.1. Norfolk and Mecklenburg soils collection and analysis. Bulk sample of a Norfolk and Mecklenburg soils from the Ap horizon (0-15 cm deep) were collected from a USDA-ARS field station in Florence, South Carolina and from NC A&T University farm, North Carolina, respectively. The soils were air dried, 2-mm sieved, and stored for use in the incubation experiments. The Ap horizon of the Norfolk soil is a loamy sand with a particle size distribution of 730, 250, and 20 g/kg, respectively of sand, silt, and clay, classified as fine-loamy, Kaoliuitic, thermic Typic Kandiudult (Novak, Busscher, et al., 2009). The A&T university farm soil is a Mecklenburg soil, classified as a fine, mixed, thermic Ultic Hapludalfs soil.

3.2.2. Biochar-soil incubation. Two different soils (Norfolk and Mecklenburg), and four biochar application rates (0, 0.5, 1, 2%) produced from four different precursors (Cotton gin, Switchgrass, Pecan and Peanut shells) at three different temperature (300, 500, and 750 °C) and different pyrolysis residence time (8, 16, and 24 h), (4, 8, and 12h), and (1, 2, and 3h) by temperature, respectively, were used in this incubation. Since the number of treatments required to conduct full factorial was unrealistically large (>300) and hard to manage, Box-Behnken experimental design (Table 3.2) was used to decrease the number of treatments to a manageable level (136 treatments) with four replications at the center. The soil and biochar incubation experiment was conducted in open-top greenhouse pots that measured 8.5 cm (i.d.) by 13 cm tall. Pot drainage holes were sealed using a nylon mesh fabric.

Samples of 0.25-mm sieved carbons were mixed with sufficient quantities of 2-mm sieved dried soil samples to yield 0, 0.5, 1, and 2% (wt/wt) carbon in soil mixtures or treatments. Water was added to obtain a soil-moisture content of ~ 10% and 12% (wt/wt) for the Norfolk and Piedmont soil, respectively which are typical moisture content at field capacity (Novak, Busscher, et al., 2009). Wetting water contained Atrazine, Copper, and Zinc concentrations of 1.5 Quarts/Acre, 400 ppm, and 400 ppm in water solution, respectively. The moist carbon treated soils were then gently tamped down by hand to obtain a bulk density of 1.2-1.3 g/cm leaving a headspace of 2 to 3 cm above the soil for adding water. The pots were then incubated in the laboratory for up to 150 days at 10% and 12% soil moisture. The laboratory room temperature and percent relative humidity, respectively, ranged between 18 to 29 ºC and 35 to 75% during the incubation period.

Table 3.2

Box-Behnken design

Pyrolysis Temperature	**Pyrolysis Time**	**Biochar Rate**
300	1	1
750	2	0.5
750	1	1
750	2	2
500	3	0.5
300	3	1
500	1	0.5
500	1	2
300	2	0.5
300	2	2
750	3	1
500	3	2
500	2	1
500	2	1
500	2	1

Soils with and without biochar (referred to as T0), were arbitrarily allowed to incubate for 1-2 h, and then were air-dried for between 2 to 3 days. Afterwards, all samples were sent to the Clemson University Soil Test laboratory for standard nutrient analysis. Over a period of four months, all pots were leached monthly with 1.2 pore volumes of deionized water; the leachate was collected over a 30 hours period and later weighed. The mass of leachate recovered was subtracted from the total volume of water added and the difference was attributed to water retained by each treatment. The percentage of water retained by each pot was then calculated. The soil bulk density was measured one to two times weekly to monitor the changes overtime.

3.2.3. Soil fertility parameters analysis. After the 5 months incubation, the different soil treatments were air-dried, crushed and screened through a 10 mesh screen. A portion was sent to the Clemson university soil lab for fertility analysis (pH, EC, CEC, Exchangeable Acidity, macro & micronutrients content) according to the procedure mentioned below. The remaining sample was used to measure aggregate stability, total carbon and nitrogen (TCN), and heavy metals content.

3.2.3.1. Macro and micronutrients analysis. The measurements of soil samples were conducted using the method described by Isaac (1983) and Donohue (1992). Mehlich 1 Extracting Solution (0.05 N HCl + 0.025 N H_2S0_4) was prepared by mixing 77 mL concentrated HCl and 13 mL concentrated H_2S0_4. Deionized water was added to bring the total volume to 18 liters.

After drying, soil samples were crushed and screened through a 10 mesh stainless steel screen. Five g of soil was weighed then twenty milliliters of Mehlich 1 extracting solution was added by automatic pipette to each sample to displace and dissolve the plant nutrients which are held on to the soil particles. The samples were shaken on a mechanical reciprocating shaker, adjusted to 180 oscillations per minute with a 4 cm stroke, for 5 minutes to allow it time to remove the plant nutrients from the soil.

After shaking, the samples were immediately filtered using prefolded high quality filter paper, moistened with deionized water into funnels and the collected extract were stored for nutrient analysis (P, K, Ca, Mg, Na, Zn, Mn, Cu, and B) using inductively coupled plasma spectrophotometer (ICP) where the solution is pumped through tubing into very hot plasma (ranging from 12,000 to 23,000 degrees Fahrenheit) and analyzed for the amount of phosphorus, potassium, calcium, magnesium, zinc, copper, manganese, boron, and sodium (Donohue, 1992; Issac, 1983).

3.2.3.2. Soil pH measurement. The pH measurements of soil were conducted using the method described by Isaac (1983) and Donohue (1992). Soil pH was determined on all samples using a 1:1 (weight: volume) soil to water ratio. After transferring 15 g of soil to cups, 15 mL of deionized water was added using an automatic pipette with enough force to mix thoroughly and the mixture was allowed to stand for at least 1 hour. An AS-3000 Dual pH Analyzer (Labfit Pty Ltd., Athens, GA) was used to measure pH after calibration with pH 7.0 and pH 4.0 buffers.

3.2.3.3. Buffer pH measurement. The buffer pH measures the total exchangeable or potential acidity in the soil [as hydrogen (H^+) and aluminum (Al^{3+}) ions]. The Moore-Sikora buffer method (2008) was used for the exchangeable acidity determination. Fifteen milliliters of Moore-Sikora buffer solution at pH 8.0 were added to the soil-water slurry used for the soil pH determination. After mixing and equilibrating for 30 minutes, the buffer pH was determined using an AS-3000 Dual calibrated reference-glass electrode equipped pH meter (Labfit Pty Ltd., Athens, GA).

3.2.3.4. Cation exchange capacity measurement. Cation exchange capacity (CEC) is the maximum quantity of total cations, of any class, that a soil is capable of holding, at a given pH value, for exchange with the soil solution. CEC is used as a measure of fertility, nutrient retention capacity, and the capacity to protect groundwater from cation contamination. It is expressed as milli-equivalent of hydrogen per 100 g (meq H^+/100g), or centimol per kg (cmol/kg). In other words it is a measure of exchangeable bases and soil acidity at some specific soil pH. CEC was calculated by summing Mehlich I exchangeable bases (Ca, Mg, K, and Na) and acidity from the Moore-Sikora buffer (Sikora & Moore, 2008).

Estimated Soil CEC = Acidity + Ca + Mg + K (in the units of meq/100 g soil or cmol/kg) (Eq 5)

$$\text{Acidity (meq/100 g of soil)} = 37.94 - (5.928 \times B_{pH}), \quad \text{(Eq 6)}$$

where B_{pH} = Mehlich soil-buffer pH reading for an individual soil sample.

3.2.3.5. Aggregate stability measurement. Dry Sieving method was used to determine if any aggregate particles were formed during the incubation period (Novak, Busscher, et al., 2009). The method consists mainly of sieve shaking the soil samples for a short period of time using a sieve shaker that has different sieves size. Dry fragment separation is done with a vibratory or oscillatory movements imposed on a nest of flat sieves. At the end of the incubation period, soils were removed from pots and 100 g sub samples were taken for aggregate analysis. A nest of sieves with openings 2 mm, 1 mm, 0.5 mm and 0.25 mm and shaking the nest with an Octagon Digital Sieve Shaker (Endecotts, Inc., London) that ran at a rate of 60 Hz with amplitude of ~3 mm for 1 min using the procedure of Sainju, Terrill, Gelaye, and Singh (2003).

3.2.3.6. Heavy metals content. The soil heavy metals content was determined using standard EPA (EPA SW 846 Method 3050B, 1989) method with minor modifications (Kimbrough & Wakakuwa, 1989). Between 0.1and 0.3 g of dried soil was added to 7.5 mL citric acid and 2.5 mL of HCL, mixed and digested for approximately 30 min in a microwave digestion system. Digested samples were filtered with a 0.45 µm filter, then diluted with DI water to 50 mL, and analyzed for Cu, Zn, Cr, Cd, and Pb using ICP (Agilent 710 Series ICP-OES spectrophotometer, Agilent Technologies, Santa Clara, CA, USA). A series of multi-elements standards across a range of concentrations near the expected concentration of analyte in the unknown solutions were prepared using 1,000 µg/mL stock solutions in 4% HNO_3. Samples containing elements exceeding the working range were diluted and reanalyzed.

3.2.3.7. Total carbon and nitrogen. The total C and total combustible nitrogen (TCN) contents were determined using a LECO TruSpec CN analyzer (LECO Corp., St Joseph, Ml) as described by Novak, Busscher, et al. (2009). A 0.5 g soil sample was weighed in aluminum dish, and then transferred to a hot chamber where the sample was combusted. TCN analyzer was equipped with automated software for acquisition and computation of total carbon and nitrogen percentage.

3.2.4. Soil leaching and leachates analysis. On days 30, 60, 90, and 120, each pot was leached with deionized water; the leachate was collected, weighed, and filtered using a 0.45 µm membrane. The leachate was analyzed for dissolved organic carbon (DOC) concentrations using a Shimadzu TOC-Vcs (Shimadzu Corp., Columbia. MD), and the Atrazine content was determined using GC-MS. The micro and macro elements such as: Ca, Cu, Fe, K, Mg, Mn, Na, P, S, Cr, Ni, Cd, and Pb concentrations were analyzed with ICP (Agilent 710 Series ICP-OES spectrophotometer, Agilent Technologies, Santa Clara, CA, USA). The leachate pH and electrical conductivity (EC) were measured using a standard pH and a conductivity meter.

3.2.4.1. Dissolved organic carbon determination. Dissolved organic carbon (DOC) was determined according to method described by Novak, Busscher, et al. (2009) using a TOC-VCPH/CPN analyzer (Shimadzu, Tokyo). Sample leachates were introduced into the combustion tubes, which were filled with an oxidation catalyst and heated to 680 °C. The samples were burned in the combustion tube and as a result the total carbon in the samples was converted to carbon dioxide. When the CO_2 is detected by the cell of a non-dispersive infrared (NDIR) gas analyzer, which outputs an analog detection signal that forms a peak; the peak area is measured by the TOC-Control V software. The peak area is proportional to the total carbon concentration of the sample, which can be determined by analyzing the samples to obtain the peak area and total carbon concentration calculated using the calibration curve.

3.2.4.2. Electrical conductivity and pH measurements. The leachate pH and electrical conductivity (EC) were measured using a standard pH and a conductivity meter as described by Novak, Busscher, et al. (2009). Ten milliliters leachate solution was used for the pH and EC determination. After stirring and equilibrating for 5 minutes, the pH and EC were determined using a calibrated reference-glass electrode equipped pH or EC meter.

3.2.4.3. Elemental and heavy metals analysis. The filtered leachates were analyzed for Al, Ca, Cu, Cr, Cd, K, Mg, Mn, Ni, S, P, Na, Zn, and Pb concentrations with ICP (Agilent 710 Series ICP-OES spectrophotometer, Agilent Technologies, Santa Clara, CA, USA) which consists of a high temperature discharge generated by flowing a conductive gas (argon) through a magnetic field induced by a coil that surrounds the tubes carrying the gas. The intensity of the energy emitted at a certain wavelength is proportional to the amount (concentration) of that element in the analyzed sample. The ICP detection limit for this suite of 15 elements was a conservative 0.05 mg/ L.

3.2.4.4. Atrazine content analysis.

3.2.4.4.1. Atrazine purification and concentration (liquid-liquid extraction). A fourteen mL volume of leachate sample was pipetted into a 15 mL polypropylene centrifuge tube. About one mL chloroform (HPLC grade) was added and the mixture was shaken using a rotary shaker for 30 minutes, then centrifuged at 2000g for 15 minutes. The chloroform layer (lower phase) was aspirated and passed through sodium sulfate to remove the water from chloroform into GC vials, the chloroform layer was then dried under nitrogen, until complete evaporation of the solvent. The remaining sample was re-dissolved in 100 µL of chloroform which was transferred to GC vials with 250 µL glass insert. The vials were rinsed one more time with 50 µL chloroform and transferred to the insert. After the vials were clumped tightly; the samples were ready for analysis using GC-MS.

3.2.4.4.2. GC/MS parameters for atrazine Analysis. Agilent gas chromatograph GC 7890A with 7683B auto-injector (Santa Clara, California) was used. The initial oven temperature was 100 °C for 5 minutes, then 10 °C / minute to 300 °C with no holding time. A splitless 4 µL injection volume was analyzed with an inlet temperature of 250 °C. The column used was 30 m, 250 µm inner diameter Agilent HP5-MS with film thickness of 0.25 µm. There was a 4 minute solvent delay. The helium flow was 1.2 mL/min with a run time of 25 minutes. The retention time of atrazine was 13.86 minutes.

The mass spectrometer used was Agilent 5975C triple axis detector using 280 °C transfer line with 230 °C and 150 °C source and quad temperatures, respectively. Instrument was tuned using auto-tune for each batch of samples analyzed, with scan and single ion simultaneous monitoring employed. The gain factor used was 15.00. The scan parameters were a low mass of 100 to a high mass of 220, threshold set at 150. For single ion monitoring, masses were set at 200 and 215 with dwell time of 100 for each mass.

3.3. Screening Procedures of Carbons based on Effect on Soil Properties

After the 150 days biochars-soil incubation was completed, cluster and principal components analysis were conducted using SAS 9.2 software (SAS Institute Inc., Cary, NC, USA), to select the best biochars based on a set of the most important soil parameters for the plant growth (pH, CEC, EC, TC, bulk density, water holding capacity, aggregate stability, leachate C/N ratio, DOC, atrazine content, micro and macronutrients). The best biochars were then used in the GHG (CO_2 and CH_4) emission experiment and the plant growth using lettuce as a crop.

3.4. Field Testing of the Best Biochars

After the selection of the best carbon and concentration using statistical models, the next step was the field testing, which was mainly the addition of the best carbon concentrations based on lab soil incubation tests to the Piedmont soil (Table 3.3). A crop plant, Lettuce, was cultivated on treated and untreated soils. After a three weeks germination period, the seedlings were transplanted to bigger pots containing 8 lbs of Mecklenburg soil each. The pots were randomly positioned on benches in a greenhouse setup. For each biochar, the experiment included four replicate pots for each application rate (Table 3.3).

Table 3.3

Greenhouse experiment (crop growth)

Type of Precursor	**Cotton Gin**	**Switchgrass**
Treatments application Rate	0%, 1%, 2%	
Replications	4	
Type of Crop	Lettuce	
Total number of Treatments	10	10
Total	20	

The drainage holes of the pots were fitted with fiberglass window mesh to prevent soil loss from irrigation, but pots were otherwise allowed to drain freely. Each pot was given an identical dose of starter fertilizer via fertigation. The recommended treatment for a lettuce crop was 100-150-150 lbs/acre ($N-P_2O_5-K_2O$), respectively. The control pots, which did not receive biochar, received the same amount of fertilizer and were replicated four times. The pots were watered two to three times per week. The lettuce plants were harvested 53 days after planting, and then the crop growth parameters were measured during and after the harvest as described below.

3.4.1. Soil and carbon preparation. The biochar and soil samples used were prepared exactly as described above in the biochars preparation, soils collection, and analysis sections (sections 3.1.1 and 3.2.1).

3.4.2. Plant growth parameters measurements.

3.4.2.1. Plant height. Height is a variable of fundamental importance when measuring the plant growth. It is defined as the vertical distance from the base of the plant to the uppermost point (tip) (Akbudak, Tezcan, Akbudak, & Seniz, 2006). The plant height was measured using a 20 cm ruler from the base of the plant to the top in triplicates during the harvest day.

3.4.2.2. Number of leaves per plant. This parameter was determined by counting the leaves in the plants forming each replicate, and the average values were obtained for different treatments (Akbudak et al., 2006). The counting of the leaves numbers for each plant was performed manually after the plant weight measurement.

3.4.2.3. Fresh weight of shoots and roots. The process of measuring the fresh weight is as follow: the plants were removed from the soil, the loose soil was washed off, and then they were gently blotted with soft paper towel to remove any free surface moisture. The samples were immediately weighed to prevent water loss that can lead to inaccurate data (Elahi, Mridha, & Aminuzzaman, 2010).

3.4.2.4. Dry weight of shoots and roots. Since plants have high composition of water, using the dry weight as a measure of plant growth tends to be more reliable. The plants were removed from the soil, the loose soil was washed off, and then they were gently blotted with soft paper towel to remove any free surface moisture. The plants were dried using a Laboratory oven

(Fisher Scientific, USA) at 100 °C for 48 hours. They were cooled in a dry environment then weighed (Elahi et al., 2010).

3.4.3. Soil fertility parameters analysis. After the plant harvest, soil samples were collected and sent to North Carolina soil testing lab (Raleigh) for analysis of available nutrients (micro and macronutrients), pH, CEC, and compared to soil control characteristics.

3.5. GHGs Emission Incubation

3.5.1. Soil and carbon preparation. The biochar and soil samples used were prepared exactly as described in the preparation of biochar and Norfolk and Mecklenburg soils collection and analysis sections (sections 3.1.1 and 3.2.1).

3.5.2. Experimental design. Incubation experiments were conducted to measure GHGs production in sterilized 250 ml glass vials (Wheaton Glass, Millville, NJ) and sealed with red butyl rubber septa (Grace, Deerfield, IL) containing Mecklenburg soil mixed with and without biochar produced from 2 different agricultural byproducts (cotton gin and switchgrass) and compared with the raw material from which these two biochars were produced to see if there is any greenhouse gases emission reduction between the carbon and corresponding raw feedstock in treated soil during the incubation period. Untreated soil (with no added biochar or feedstock) or raw materials with no soil were used as references. Triplicate incubations were established for each treatment as outlined in Table 3.4.

The incubations were carried out at 20% moisture (wt/wt) and 2% biochar application rate. Biochar control incubations were conducted to assess the production of GHG solely from the biochar (with water additions). The incubations of biochar alone will allow the correction of the soil + biochar incubations for the impact of the biochar, assuming that the biochar behavior is similar in both incubations.

Table 3.4

GHGs emission experiment

Treatments	Cotton Gin	Switch grass
[Biochar control – No soil added]	11	11
[Soil control – No biochar added]	11	
[Soil + Biochar Treatments]	11	11
[Soil + Raw Material Treatments]	11	11
Replications of treatments	3	3
Soil Weight /Bottle	10 g	10 g
Biochar Application Rate	2%	2%
Moisture Content of soil	20%	20%
Total Treatments	231	

3.5.3. Gas analysis. Periodic gas samples were performed from the incubations for GHGs analysis. Sampling frequency was twice per week for the first two weeks and then weekly thereafter. Portable device analyzer (CheckPoint O_2/CO_2 Analyzer, PBI-Dansensor America Inc., Glen Rock, NJ) connected to a syringe was used to quantify gas production (CO_2, NH_4) over a 10 weeks incubation period. The syringe needle was inserted through the rubber septa and approximately 5 ml gas samples were withdrawn.

CHAPTER 4

Results and Discussion

4.1. Physicochemical Characteristics of Biochars

4.1.1. Biochar yield. The physicochemical characteristics of biochars as affected by precursors and pyrolysis temperature are shown in Figures 4.1 through 4.6 and their elemental analysis is shown in Table 4.1. For all precursors used, more biochar was recovered at the lower pyrolysis temperatures due to minimal condensation of aliphatic compounds, and lower losses of CH_4, H_2 and CO as reported by Amonette and Joseph (2009). Below 500 ºC, the biochar yield was at least 50% (Figure 4.1) but it declined to about 30% as the pyrolysis temperature was increased to 750 ºC because of dehydration of hydroxyl groups and thermal degradation of ligno-cellulosic structures (Antal & Grønli, 2003). This is in agreement with the findings of McHenry (2009) who reported that at equal to, or greater than 400 °C, the biomass material is converted into fused aromatic ring biochar structures with the loss of carbon dioxide (CO_2), carbon monoxide (CO), water and hydrogen (H_2) and the biochars yield depends on the nature of the precursor irrespective of its hardness.

Sjöström (1993) stated that the chemical composition of the biomass feedstock has a direct impact upon the physical nature of the biochar produced. At temperatures above 120 °C, organic materials begin to undergo some thermal decomposition, losing chemically bound moisture. Hemicelluloses are degraded at 200 °C to 260 °C, cellulose at 240 °C to 350 °C, and lignin at 280 °C to 500 °C. Therefore, the proportions of these components will influence the degree of reactivity and, hence, the degree to which the physical structure is modified during processing (Downie et al., 2009). This can explain the decrease of the yield as the temperature increases and the difference between the feedstocks in our results.

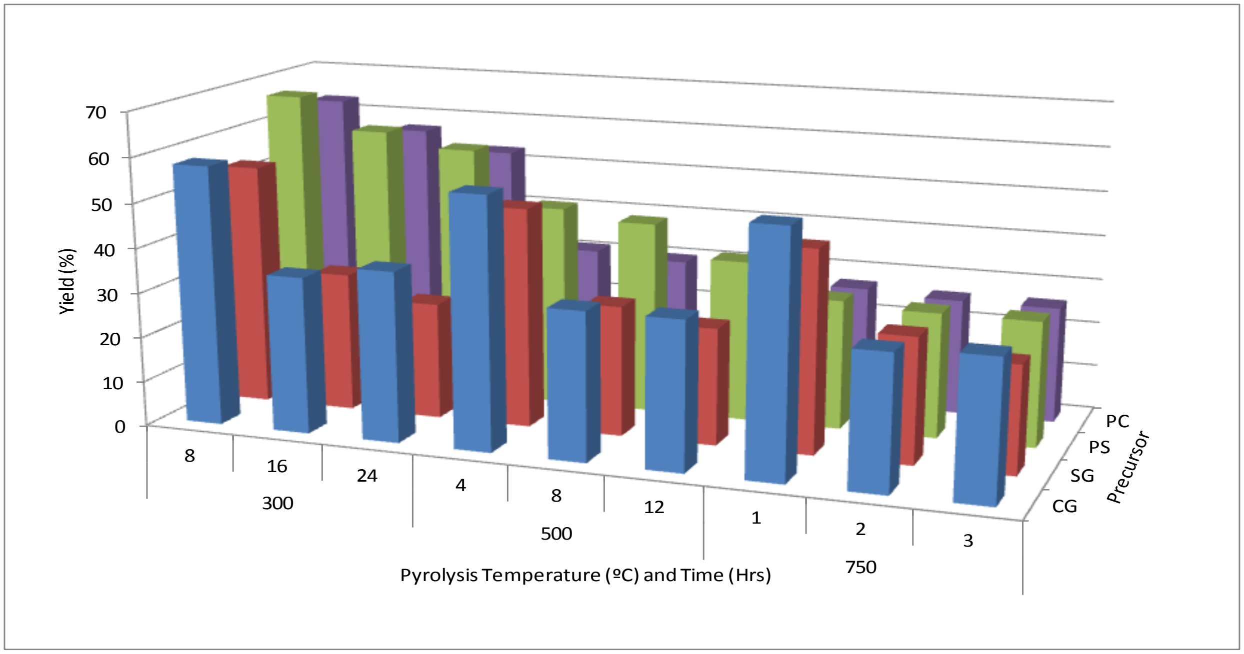

Figure 4.1. Effect of pyrolysis temperature and time on biochar yield from four precursors. Note: PS = Peanut Shells, PC = Pecan Shells, SG = Switchgrass, CG = Cotton Gin.

Shafizadeh (1982) had also reported that at high temperature between 300 °C to 600 °C tar form from cellulose composed mainly of anhydrosugars which becomes increasingly important. Therefore, the amount of biochars produced at these high temperatures, was substantially less than that at lower temperatures, which depended largely upon the relative rates of volatilization and degradation of these anhydrosugars.

4.1.2. Surface area. The pyrolysis temperature significantly increased the surface area as it increases ($p < 0.05$). Lua, Yang, and Guo (2004) demonstrated that increasing pyrolysis temperature from 250 °C to 500 °C increases the surface area due to the increasing evolution of volatiles from pistachio-nut shells, resulting in enhanced pore development in biochars.

Among the eight biochars, switchgrass-derived biochar produced at 750 ºC had the highest surface area (276 m^2/g) followed by pecan shell biochar (185 m^2/g). This can be explained by the higher lignin content of these precursors and structural modifications that occurred at higher pyrolysis temperature following the release of volatiles. The surface area for cotton gin and peanut shells biochars produced at 750 °C was much lower than the other biochars. The lower surface area exhibited by cotton gin biochar could be due to plugging of pores by the inorganic compounds from ash which is present at higher amount in cotton gin compared to other biochars (Figure 4.2) or the pores may become filled with tars (condensed volatiles) and other amorphous decomposition products, which may partially block the microporosity created (Bansal et al., 1988).

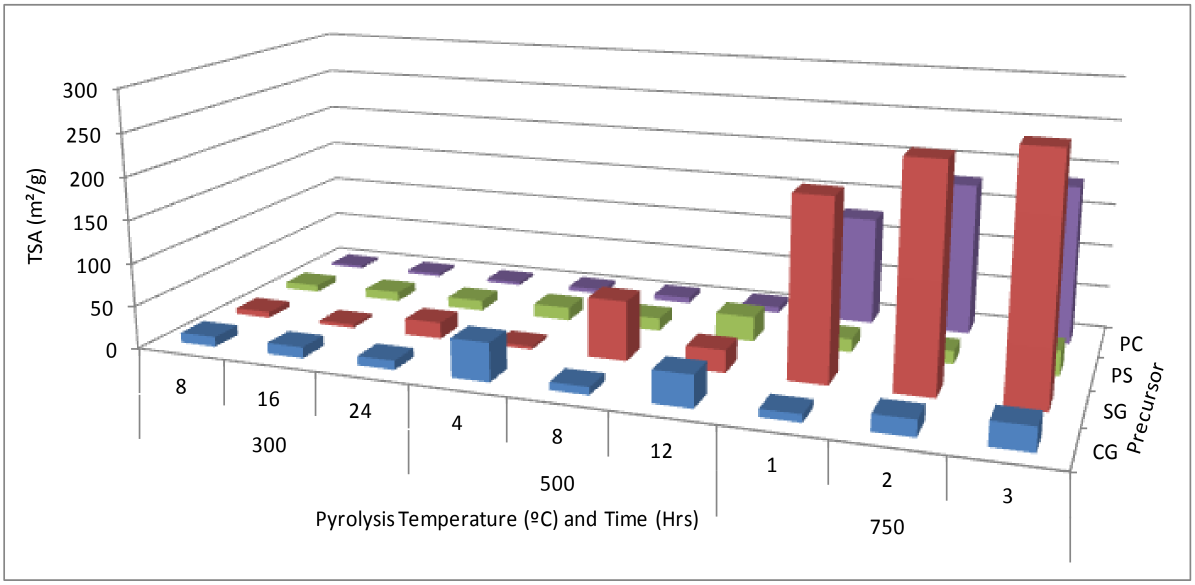

Figure 4.2. Effect of pyrolysis temperature and time on surface area of biochars from four precursors. Note: PS = Peanut Shells, PC = Pecan Shells, SG = Switchgrass, CG = Cotton Gin

Aygun, Yenisoy-Karakas, and Duman (2003) reported that even in a very low ash material, such as the hazelnut shells, the surface area was low due to some thermoplastic properties which agree with our results obtained with peanut shells. These results were also similar to those obtained by Khezami, Ould-dris, and Capart (2007), who reported that the surface area of chars never exceeded 300 m^2/g and even decreased with temperature and dropped to 27 m^2/g. It was found that cellulose plays a major role in this process as stated by Byrne and

Nagel (1997), where cellulose microfibrils dominate the mechanism of dimensional change during pyrolysis. This shrinkage is attributed to the formation of graphitic layers resulting from the aromatization process after thermal decomposition of glycosidic chains (Byrne & Nagel, 1997).

4.1.3. pH values. Generally, pH values were lower and surface areas smaller for biochars produced at the lower pyrolysis temperatures. Substantial increase in pH occurred at the higher temperatures because of the increased relative concentration of nonpyrolyzed inorganic elements in the feedstocks and the formation of basic surface oxides under high pyrolysis temperature (Novak, Lima, et al., 2009). Increase in surface area with higher pyrolysis temperatures have been linked to creation of pores and cracking in the biochars basal-structural sheets (Downie et al., 2009). Among the feedstocks, biochar produced from cotton gin had the highest pH values ranging from 8.2 to 9.8, followed by pecan shell-based biochar (Figure 4.3), probably due to their high Ca and Mg contents (Table 4.1).

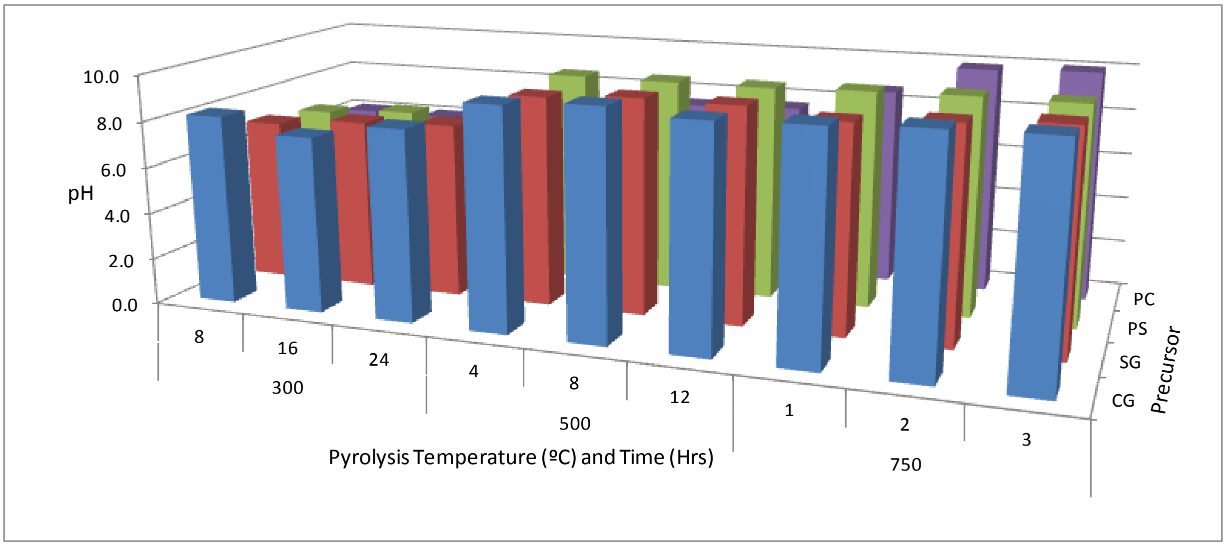

Figure 4.3. Effect of pyrolysis temperature and time on pH of biochars from four precursors. Note: PS = Peanut Shells, PC= Pecan Shells, SG = Switchgrass, CG = Cotton Gin.

The pyrolysis temperature had a significant positive effect on the pH values of biochars. pH value significantly increased as pyrolysis temperature increases from 300 °C to 750 °C passing from a value of 6 to almost 10 which is probably due to the release of the basic cations such as Ca and Mg during pyrolysis process at increasing temperatures.

4.1.4. Surface charge. The total surface charge of the biochars was significantly influenced by both feedstock and pyrolysis temperature. Biochars produced at lower temperatures had measurable total surface charge with peanut shells biochar having the highest value (3.16 meqH$^+$/g). Biochars produced between 500 and 750 °C had low or no measurable total surface charge (Figure 4.4).

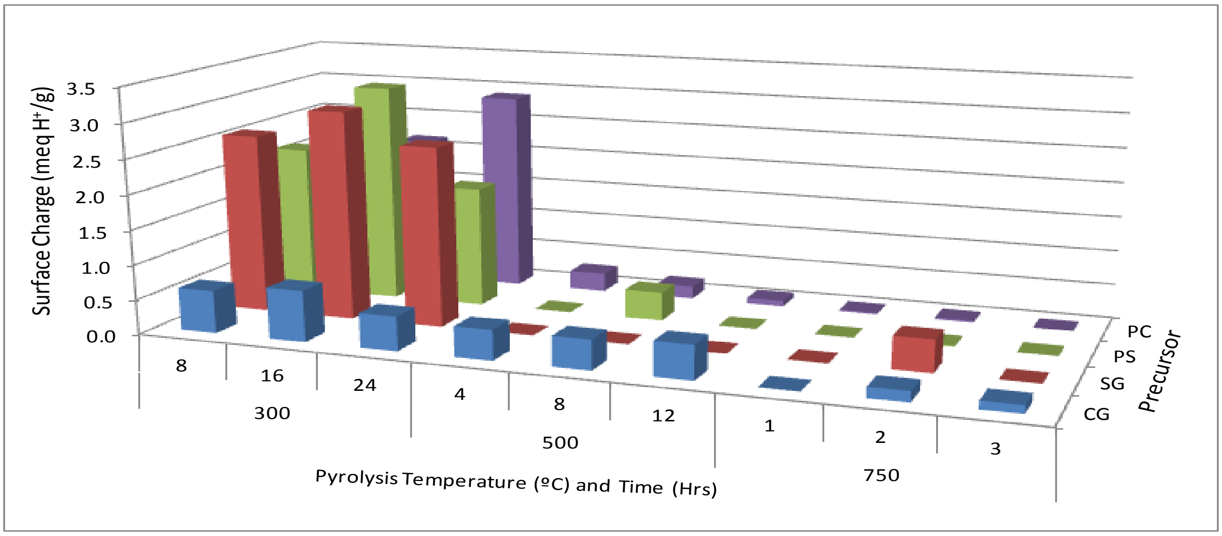

Figure 4.4. Effect of pyrolysis temperature and time on surface charge of biochars from four precursors. Note: PS = Peanut Shells, PC = Pecan Shells, SG = Switchgrass, CG = Cotton Gin.

The charring conditions were shown to influence the degree of aromaticity and, therefore, the adsorption characteristics of biochar. The degree of aromaticity increases with increasing charring temperature (Shafizadeh & Sekiguchi, 1983) and charring time (Glaser, Haumaier, Guggenberger, & Zech, 1998). The presence of alkyl aromatic units in the biochars with a variety of oxygen-containing functional groups, including hydroxyl, carboxyl, carbonyl, ether, and lactone structures are gradually lost as the pyrolysis temperature increases.

At 500 °C, the OH, C=O, and aliphatic C-H groups are largely gone, and by 750 °C, most of the aromatic C-H groups have decomposed (Novak, Lima, et al., 2009). These results suggest that, for the most part, biochars produced at higher pyrolysis temperatures could have poorer ability to increase the capacity of soil to hold cationic plant nutrients due to their low surface charge. It is possible; however, that high temperature biochars with large surface areas and aromatic character will eventually be involved in soil nutrient exchange. Cheng, Lehmann, and Engelhard (2008) reported that abiotic processes are capable of oxidizing surfaces of black carbon compounds, albeit after exposure to soil for months to years. Low temperature biochars, on the other hand, may be more readily able to increase soil nutrient retention due to their high surface charge compared to biochars produced at the high temperature.

4.1.5. Electrical conductivity. The electrical conductivity increased with pyrolysis temperature and time, with the highest EC observed in cotton gin biochar in the range 815 to 1971 µS/cm. Pecan shells showed the lowest EC among the four biochars (Figure 4.5). This difference in biochar conductivity is related to their soluble salt concentrations which are high for cotton gin and low for pecan shells (Table 4.1).

4.1.6. Ash content. The ash contents of biochars made from peanut hulls, pecan shells, and switchgrass were < 10%, while the ash content of biochar made from the cotton gin feedstock ranged from 11 to 34%. This high ash content may be partially attributed to the sand/soil contained in the cotton gin during the collection. The residual sand was difficult to cleanup during preparation for pyrolysis. For all materials, ash contents increased with pyrolysis temperature (Figure 4.6).

There is a strong positive correlation between the pH, EC, and the ash content of the biochars. The increase of ash content or EC affects positively the biochars pH as they all increase as the pyrolysis temperature increases.

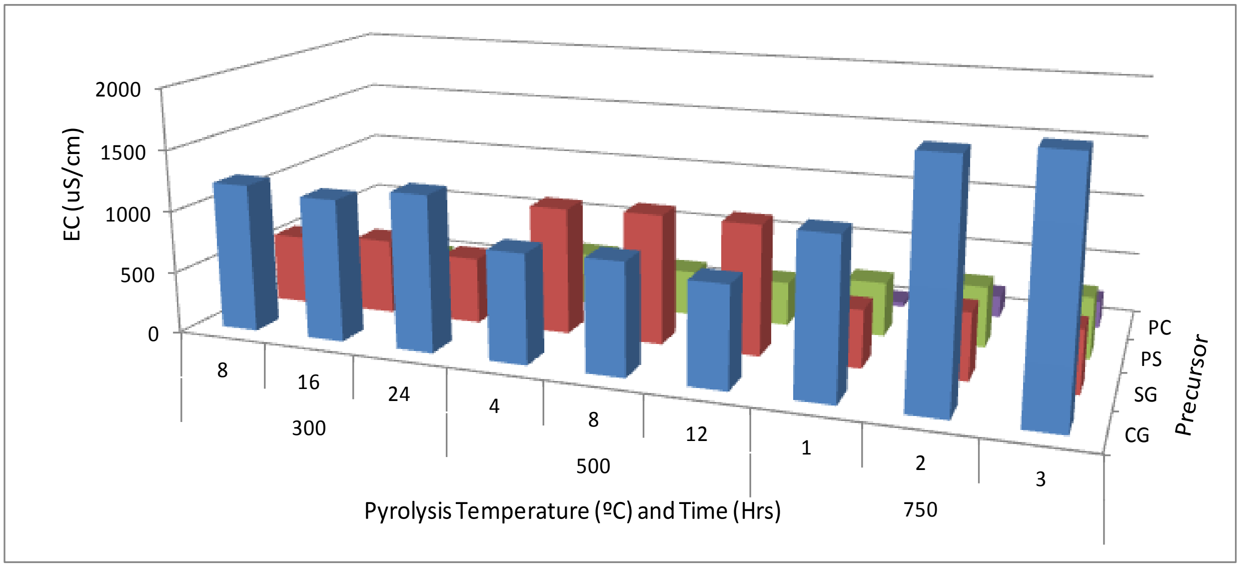

Figure 4.5. Effect of pyrolysis temperature and time on the EC of biochars from four precursors. Note: PS = Peanut Shells, PC = Pecan Shells, SG = Switchgrass, CG = Cotton Gin.

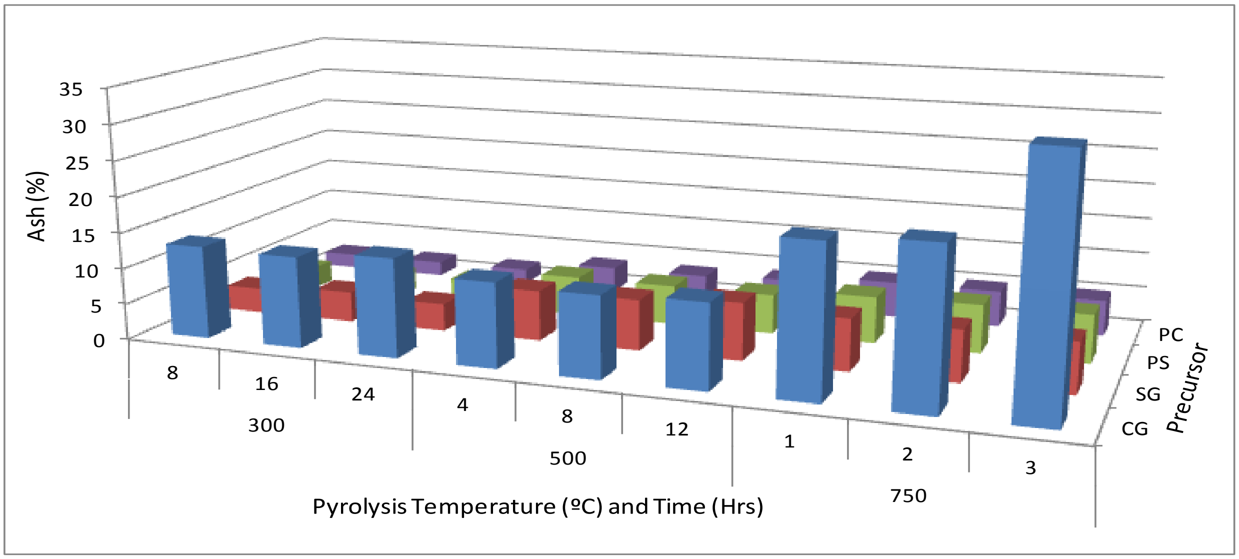

Figure 4.6. Effect of pyrolysis temperature and time on ash content of biochars from four precursors. Note: PS = Peanut Shells, PC = Pecan Shells, SG = Switchgrass, CG = Cotton Gin.

According to Demirbas (2004), the type of feedstock and conditions are important factors controlling the properties of the resulting biochar. Firstly, the chemical and structural composition of the biomass feedstock relates to the chemical and structural composition of the resulting biochars.

Secondly, the extent of the physical and chemical alterations undergone by the biomass during pyrolysis (e.g. attrition, cracking, micro-structural rearrangements) is dependent on the processing conditions (mainly temperature and residence times). Cellulose and lignin undergo thermal degradation at temperatures ranging between 240-350 °C and 280-500 °C, respectively (Demirbas, 2004).

The relative proportion of each component will, therefore, determine the extent to which the biomass structure is retained during pyrolysis, at any given temperature. For example, pyrolysis of wood-based feedstocks generates coarser and more resistant biochars with carbon contents of up to 80%, as the rigid ligninolytic nature of the source material is retained in the biochar residue (Winsley, 2007). Biomass with high lignin-cellulosic contents (e.g. pecan shells) is shown to produce the highest biochar yields, given the stability of lignin and cellulose to thermal degradation. Therefore, at comparable temperatures and residence times, lignin loss is typically less than half of cellulose loss (Demirbas, 2004). Whereas woody feedstock generally contains low proportions (< 1% by weight) of ash, biomass with high mineral contents such as grass (switchgrass), and straw residues (cotton gin) generally produce ash-rich biochars (Demirbas, 2004).

The mineral content of the feedstock is largely retained in the resulting biochar, where it concentrates due to the gradual loss of C, hydrogen (H) and oxygen (O) during processing (Demirbas, 2004; Raveendran, Ganesh, & Khilar, 1995). The mineral ash content of the feedstock can vary widely and evidence seems to suggest a relationship between that and biochar yield (Amonette & Joseph, 2009).

The elemental composition for the four different biochars is shown in Table 4.1. The different biochars show dissimilarities in terms of elemental composition. This variability can be attributed to the different feedstocks and different conditions under which the four biochars were produced. K and Mg were most concentrated in the cotton gin biochar, with biochar produced at high pyrolysis temperature having the highest Mg/K concentration followed by switchgrass. On the other hand, pecan shells showed a very high concentration of Ca compared to other biochars followed by cotton gin (Table 4.1). Unlike biochars from cotton gin and peanut shells, pecan shells and switchgrass biochars did not contain sulfur.

This high variability in inorganic nutrient content and availability is likely to affect plant and soil responses following addition of these biochars. Accordingly, it would be difficult to adopt an optimum rate of application for all biochars due to the large variability in biochars nutrient composition. Hence, optimal application rates of biochars can be accurately determined only for each soil type and plant species.

The above discussed physicochemical properties of biochars suggest that the complex and varying changes of biomass during pyrolysis affect both the composition and chemical structure of the resulting biochars with significant implications for nutrients contents and especially nutrients availability to plants. Therefore, care must be taken to identify and use the right combination of pyrolysis conditions and precursor type for the target soil and even the type of plants to be used.

Table 4.1

Total elemental analysis of biochars

Precursor	Pyrolysis temperature	Pyrolysis time	Ca	S	K	Mg	P	Fe	Zn
			--g/kg------------------------mg/kg-						
Peanut Shells	300	8	5.14	0.14	11.44	1.37	nd	nd	nd
		16	6.29	0.49	15.59	1.80	nd	nd	1.49
		24	5.80	0.26	13.38	1.51	nd	nd	nd
	500	4	10.67	1.09	26.23	2.90	nd	0.10	12.81
		8	10.28	0.97	26.25	2.72	nd	nd	5.11
		12	10.46	0.94	24.97	2.68	nd	nd	11.70
	750	1	12.09	1.10	29.46	3.09	nd	1.34	5.20
		2	12.35	1.04	28.99	3.11	nd	1.14	3.57
		3	13.25	1.18	31.13	3.30	nd	1.20	6.63
Cotton Gin	300	8	21.19	2.46	68.34	3.84	0.84	nd	nd
		16	22.00	2.65	70.55	3.90	1.27	nd	nd
		24	23.75	2.75	71.98	4.22	1.26	nd	nd
	500	4	19.17	0.66	52.66	5.94	5.06	nd	22.85
		8	17.47	0.68	50.76	6.22	5.44	nd	24.21
		12	18.36	0.53	52.44	6.29	5.97	nd	29.90
	750	1	21.01	1.14	60.22	7.42	6.96	0.18	19.67
		2	18.75	0.94	58.01	7.09	6.20	nd	18.67
		3	23.65	1.63	61.62	7.28	7.65	0.34	27.02

Table 4.1 *(cont)*

Precursor	**Pyrolysis temperature**	**Pyrolysis time**	**Ca**	**S**	**K**	**Mg**	**P**	**Fe**	**Zn**
			--g/kg					--------------------------	mg/kg-
Switch grass	300	8	3.33	nd	24.15	3.41	nd	nd	1.18
		16	3.64	nd	29.15	2.89	nd	nd	4.19
		24	3.35	nd	26.35	3.50	nd	nd	0.44
	500	4	6.61	nd	43.45	4.77	4.28	nd	12.62
		8	6.60	nd	43.18	4.65	2.25	nd	13.49
		12	7.82	nd	46.41	5.14	4.21	nd	15.16
	750	1	8.47	nd	49.84	5.67	4.21	0.18	18.19
		2	7.60	nd	47.62	5.27	2.94	0.19	15.37
		3	8.41	nd	43.42	5.59	3.15	0.26	23.68
Pecan Shells	300	8	18.14	nd	nd	0.37	nd	nd	nd
		16	19.16	nd	nd	0.38	nd	nd	nd
		24	18.48	nd	nd	0.41	nd	nd	nd
	500	4	24.62	nd	1.74	0.69	nd	nd	nd
		8	26.46	nd	2.47	0.76	nd	nd	nd
		12	28.59	nd	2.61	0.82	nd	nd	nd
	750	1	32.09	nd	5.74	0.91	nd	nd	nd
		2	33.35	nd	6.87	1.01	nd	nd	14.37
		3	31.81	nd	4.81	0.98	nd	nd	nd

4.2. Biochar Amendment and Soil Fertility

4.2.1. Mecklenburg and Norfolk soils response to biochar.

4.2.1.1. Soil pH. The application of biochars from different precursors to the Mecklenburg and Norfolk soils at different application rates has showed a significant increase in pH of treated soil compared to the soil control at day 1 and day 150 of incubation (Figure 4.7). Data in Figure 4.7 suggest that at higher pyrolysis temperature and carbon application rate, the soil pH increased significantly, particularly at 1 and 2% application rates ($p < 0.05$). This change was observed for all the precursors and at both incubation times (day 1 and day 150) at which measurement was taken. The increased soil pH is attributable to buffering effect of biochars pH. The latter also increased as the pyrolysis temperature increased.

For soil pH to change, the biochar itself or a cation in the biochar must react with the soluble monomeric Al species or displace it from exchange surfaces on clays or soil organic matter (Sparks, 1995; Novak, Lima, et al., 2009). At pH 4.43, the soil with no biochar had 42% (2.4 meq/100 g exchangeable acidity) of the total soil CEC sites occupied by $[Al(H_2O)]^2$. Additions of 0.5 and 1% biochar to the soil did not significantly modify the exchangeable acidity values, although soil pH values significantly increased.

With the addition of 2% biochar, the pH increased from 4.3 to 7.85, depending on the type of precursor and pyrolysis temperature, and exchangeable acidity was reduced by 40 to 60% (l.6 to 0.8 meq/100 g), depending on the precursor and pyrolysis temperature. Thus, biochar was an effective liming agent, neutralizing soil acidity, and reducing exchangeable acidity values of soils. However, substantial additions of biochar (2% or 40 metric tons/ ha) were required to obtain increases in pH and reductions in exchangeable acidity (Novak, Lima, et al., 2009).

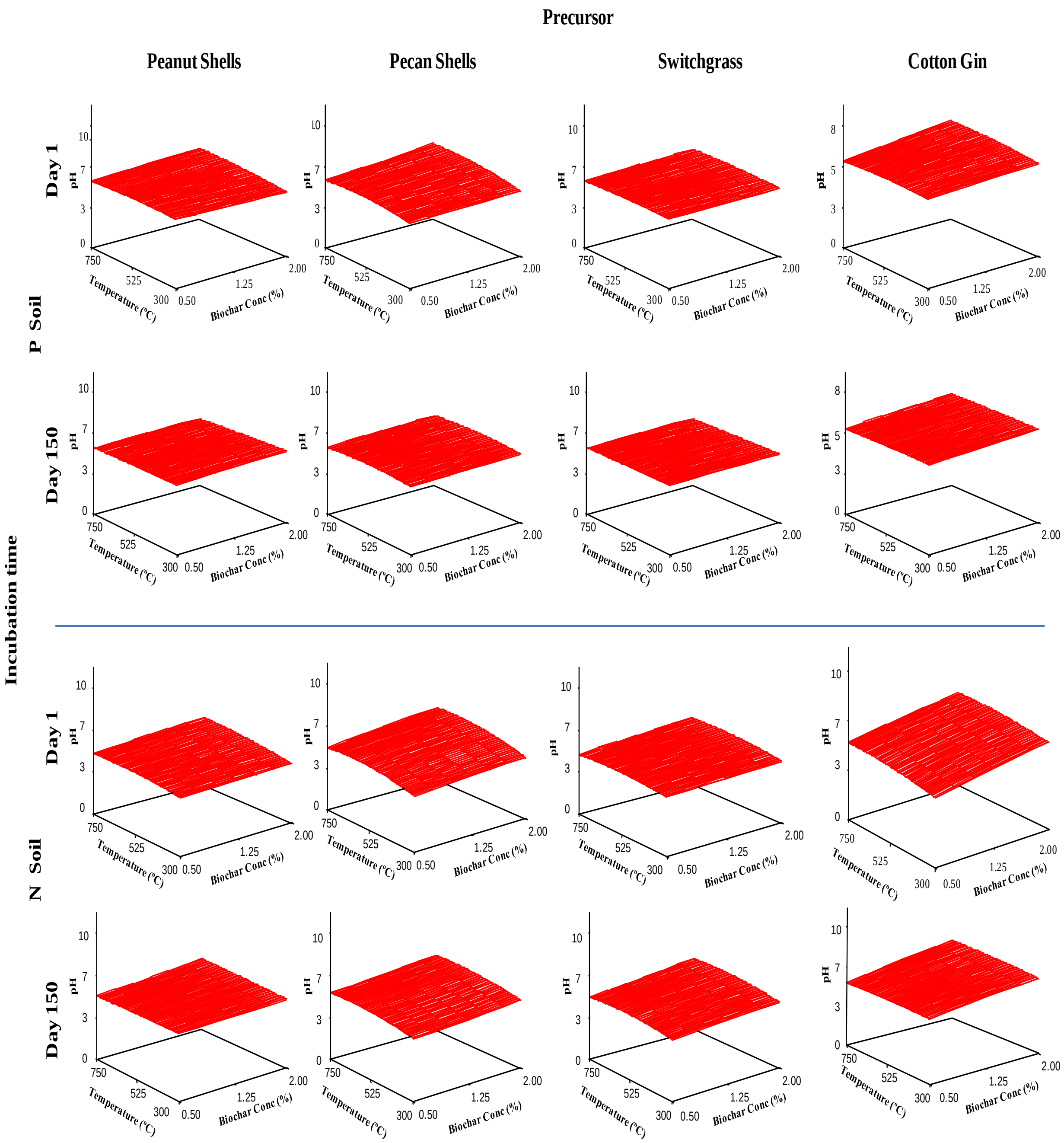

Figure 4.7. Effect of the pyrolysis temperature and carbon application rate on the pH of Mecklenburg and Norfolk soils. Note: Mecklenburg & Norfolk soils control pH at Day 1= 5.20 and 4.43, respectively. Mecklenburg & Norfolk soils control pH at Day 150 = 5.40 and 4.79, respectively.

During pyrolysis, cations (primarily K, Ca, Si, and Mg) present in the precursors form metal oxides (e.g., ash) that end up admixed with the biochar. Once in the soil environment, these oxides can react with H^{+1} and monomeric Al species, modifying soil pH and exchangeable acidity values (Novak, Lima, et al., 2009). Because biochars contained high Ca concentration ranging from 3.33 to 33.35 g/kg (Table 4.1), depending on the precursor and pyrolysis temperature with the highest values observed in pecan shells produced at 750 °C. Reaction (1) involving CaO exemplifies the liming ability of the ash associated with the biochar:

$$2\text{Al - soil} + 3\text{CaO} + 3\text{H}_2\text{O} \rightarrow 3\text{Ca - soil} + 2\text{Al(OH)}_3 \qquad (1)$$

During this reaction, Ca replaces the monomeric Al species on soil mineral or soil organic matter CEC sites. Accompanying this reaction is an increase in soil pH caused by the depletion of the readily hydrolysable monomeric Al and the formation of the more neutral $[A](OH)_3]^0$ species (Sparks, 1995; Novak, Lima, et al., 2009). This general reaction explains the decline in exchangeable acidity for the soil and the increase in solution pH and Ca on CEC sites. The pH increase and exchangeable acidity decrease were similar for day-1 and day-150 samples. This suggests that the liming effect of biochar occurred rapidly and was sustainable on equilibration.

4.2.1.2. Electrical conductivity. The application of biochars to the Mecklenburg soil at different application rates has shown a significant increase ($p < 0.05$) in EC of the soil compared to the control at the beginning of the incubation (day 1) for cotton gin and switchgrass but did not show any significant increase for peanut and pecan shells for the same period. At the end of the incubation (day 150), all of the biochars-treated soils exhibited significant increases in the soil EC. However, the soil EC at day 150 was significantly lower ($p < 0.05$) than that at day 1, which can be explained by the loss of the minerals during the monthly leaching performed during the 150 days of soil incubation.

The EC increased sharply in soils treated with switchgrass and cotton gin biochars but a slower increase was observed in soils treated with biochars derived from pecan and peanut shells for day 1 period. This could be attributed to the nature of the feedstocks used to produce biochars since pecan and peanut shells are hard material compared to the switchgrass and cotton gin which are softer and produce biochars that are easier to break down ash-rich powder releasing inorganic soluble salts such as potassium, magnesium and phosphorus into the soil.

For days 1 and 150, the soil EC increased with pyrolysis temperature and carbon application rate, for all the precursors used in this study, except for switchgrass that showed a decrease in EC for Norfolk soil as the biochars application rate increases. This can be explained by the increase of pH at high application rate that prevented the solubility of some mineral (Figure 4.8).

4.2.1.3. Cation exchange capacity. A significant increase in CEC was observed at low (300 °C) and high (750 °C) temperatures, especially at high biochars concentration (2%) in both soils (Figure 4.9). Soil CEC increase is likely due to carboxylate groups on the surfaces of the biochar itself and to exposed carboxylate groups of organic acids sorbed by the biochar, both of which contribute negative surface charge to biochar particles (Liang et al., 2006). Low pyrolysis temperature (300 °C) may have contributed to the relatively high level of surface oxidation of the biochars and hence the significant increase of the CEC in soil.

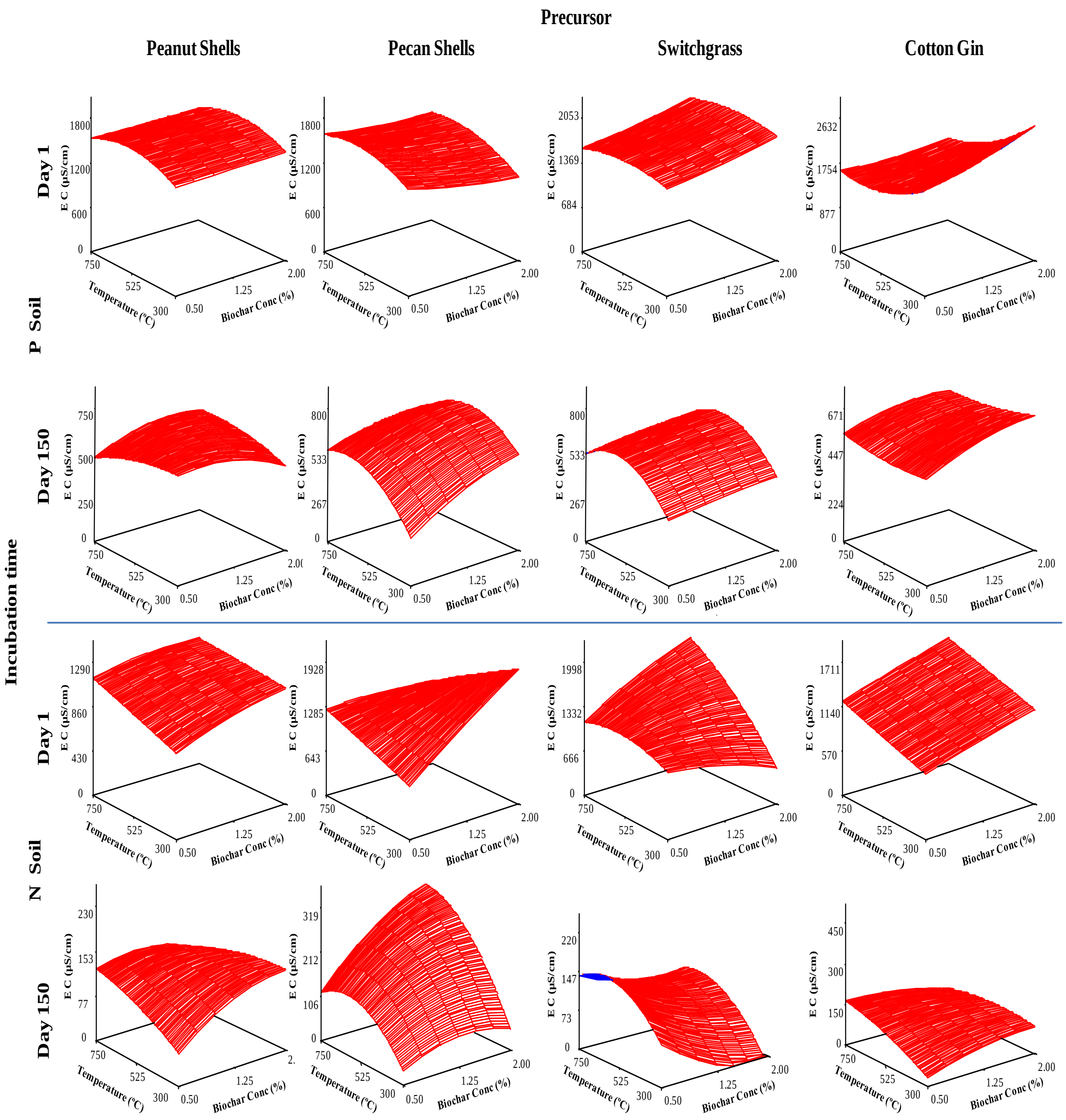

Figure 4.8. Effect of pyrolysis temperature and carbon application rate on the EC of Mecklenburg and Norfolk soils. Note: Mecklenburg & Norfolk soils control EC at Day 1= 1584 and 1038 µS/cm, respectively. Mecklenburg & Norfolk soils control EC at Day 150 = 498 and 116 µS/cm, respectively.

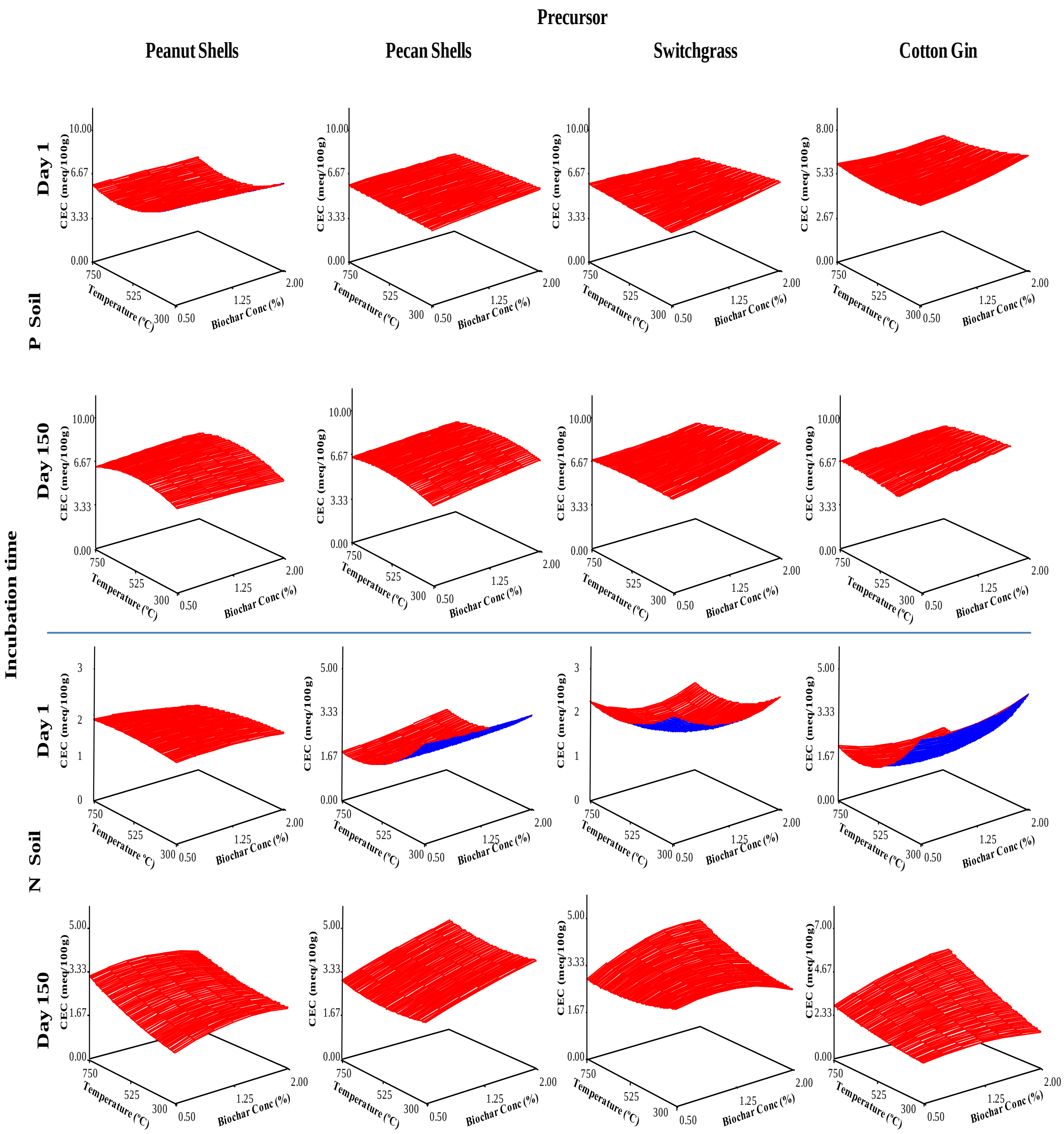

Figure 4.9. Effect of pyrolysis temperature and carbon application rate on CEC of Mecklenburg and Norfolk soils. Note: Mecklenburg & Norfolk soils control CEC at Day 1= 6.30 and 2.89 meq/100g, respectively. Mecklenburg & Norfolk soils control CEC at Day 150 = 5.73 and 1.80 meq/100g, respectively.

Higher pyrolysis temperatures generally cause greater condensation of aromatic structures and even the formation of graphitic structure. Such highly condensed aromatic C has less surface area and fewer oxidizable surface functional groups than more open (less condensed) aromatic C structures (Antal & Grønli, 2003). High-temperature biochars are also more resistant to chemical oxidation and microbial degradation and hence have a longer half-life in soil environments than soil organic matter (Laird, 2008; Novak, Lima, et al., 2009).

Surprisingly, the biochars produced at high temperature significantly increased ($p < 0.05$) both soils CEC possibly due to the high surface area and porosity of the biochars that caused this increase. On the other hand, a sharp decrease was observed in the soil CEC at the end of the incubation (day 150) compared to day 1 CEC. This decrease in day 150 CEC is probably due to the repeated soil leaching which affected the surface chemistry of the soil and biochars leading to low CEC.

4.2.1.4. Total carbon. Regardless of the type of precursor, the addition of biochars has significantly increased the Total Carbon (TC) of both soil types compared to the control soil (Figure 4.10). The total carbon increased with both the application rate and pyrolysis temperature. The biochar application rate has also a significant positive effect consistent across soils, precursors, and incubation times (day1 and day 150).

Biochar pyrolysis temperature mostly favored increased TC with variation depending on the type of precursor, soil type, and time of incubation. For instance, the effect of pyrolysis temperature on Piedmont soil TC increased from day 1 to day 150 in the case of biochar from cotton gin and pecan shells. This may be attributed to the oxidation and microbial activity processes that speeded up the process of mineralization in the soil (Verheijen, Jeffery, Bastos, van der Velde, & Diafas, 2010).

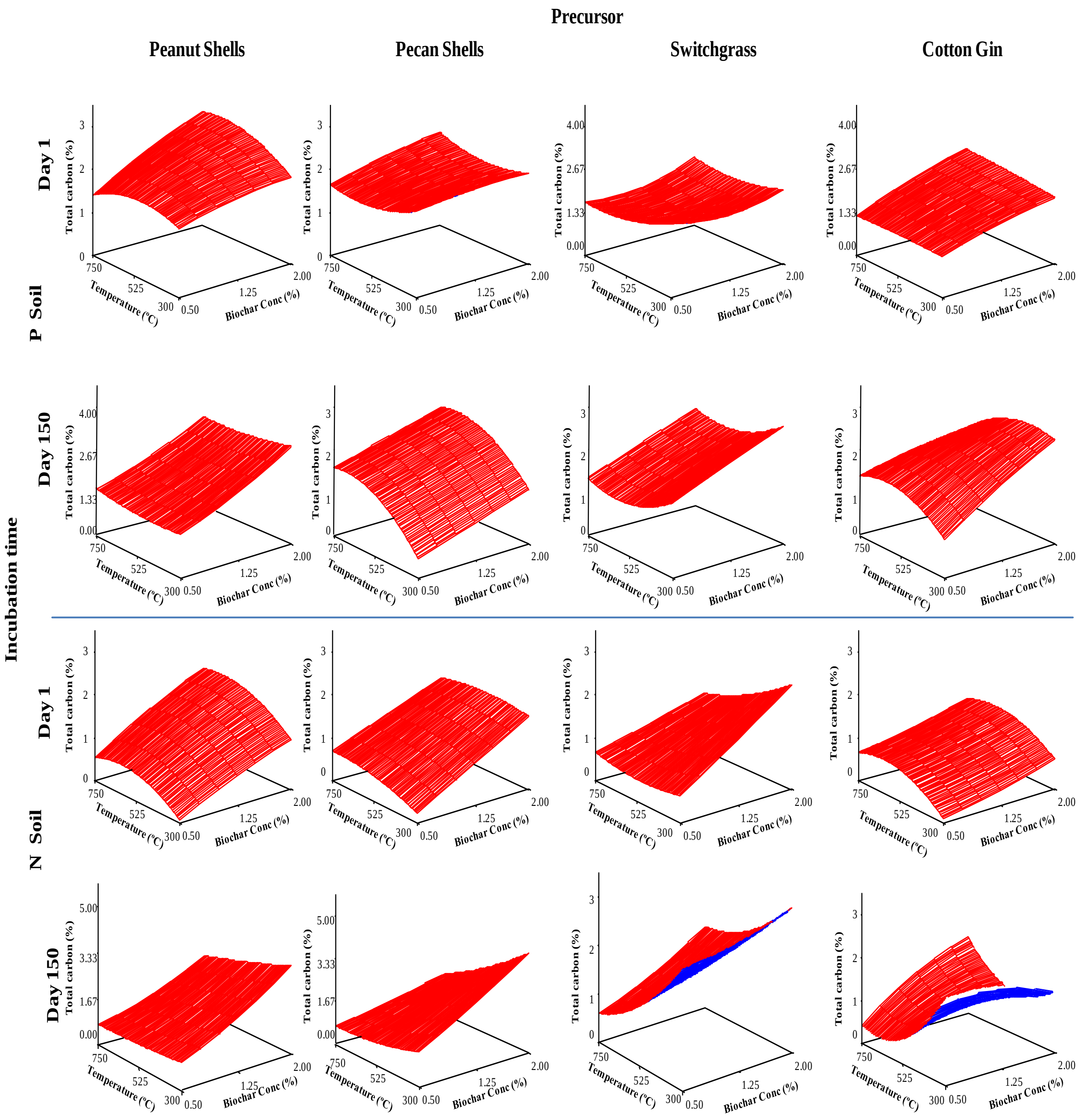

Figure 4.10. Effect of the pyrolysis temperature and carbon application rate on TC of Mecklenburg and Norfolk soils. Note: Mecklenburg & Norfolk soils control TC at Day 1= 1.06 and 0.36%, respectively. Mecklenburg & Norfolk soils control TC at Day 150 = 1.05 and 0.34%, respectively.

For the Norfolk soil, the same trend was observed across the precursors at day 1; however, a sharp decrease was observed at day 150 as the pyrolysis temperature increased in the case of switchgrass and cotton gin biochars. This is likely due to the fast mineralization of the biochars and faster loss of carbon in Norfolk soil during the leaching.

4.2.1.5. Carbon/nitrogen ratio. The biochar application rate and pyrolysis temperature showed significant effects on the carbon to nitrogen (C/N) ratio in both Mecklenburg and Norfolk soils (Figure 4.11). In both soils, C/N ratio increased as the biochar rate increases and the C/N ratio was significantly higher than the control and remained higher during 150 days of incubation time. C/N ratio is usually used as an indicator of the ability of organic substrates to mineralize and release inorganic N when applied to soils.

Nitrogen immobilization typically occurs when organic residues, possessing a C:N ratio of greater than 32:1, are added to soils (Alexander, 1977; Thompson & Troeh, 1978). The wide variation in C:N ratio, in association with its aromaticity, causes slow biochar decomposition (Lehmann, 2007b). Although biochars/soil black carbon will undergo slow chemical and microbial decomposition (Schmidt & Noack, 2000), the rate of decomposition is so slow that even large additions of biochar to soil will probably not significantly immobilize N (Novak, Busscher, et al., 2009). Similar results were reported by Novak, Lima, et al. (2009) using pecan shells biochar produced at 700 °C in a soil incubation experiment with different application rates.

It was also observed that the C/N ratio significantly decreased over time probably due to the mineralization process and the effect of monthly leaching during the incubation period. Chan and Xu (2009) reported that the C/N ratios of biochar varies widely from 7-400, with a mean of 61. Sullivan and Miller (2001) suggested that composts with C/N ratios above 25 to 30 immobilize inorganic N.

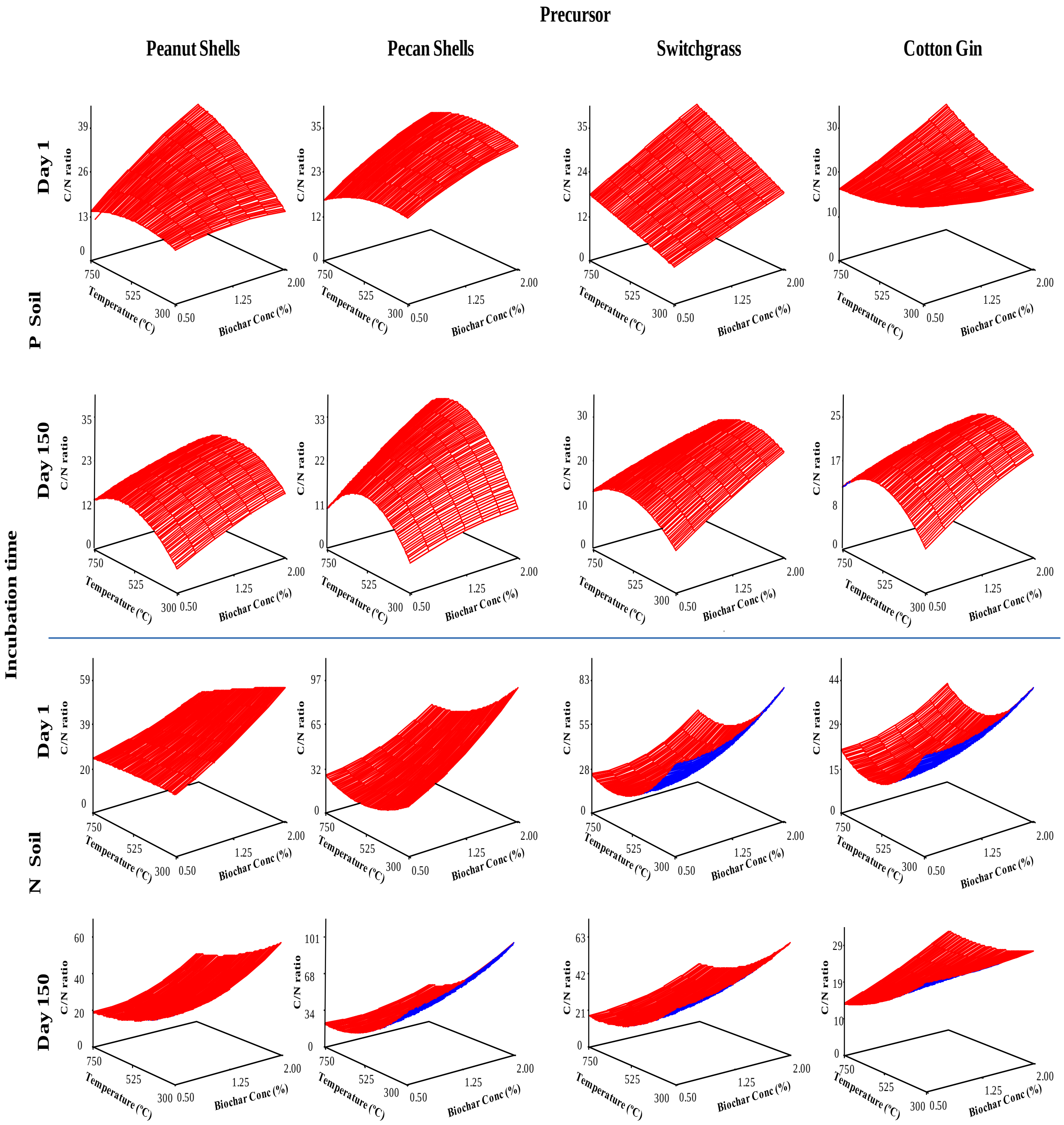

Figure 4.11. Effect of the pyrolysis temperature and carbon application rate on C/N ratio in Mecklenburg and Norfolk soils. Note: Mecklenburg & Norfolk soils control C/N at Day 1= 12.50 and 10.01, respectively. Mecklenburg & Norfolk soils control C/N at Day 150 = 9.20 and 9.08, respectively.

Based on these values, given their very high C/N ratios, most types of biochar are expected to cause N immobilization and thereby possibly induce N deficiency in plants when applied to soils alone. However, Lehmann, Da Silva, et al. (2003) stated that the C/N ratios of Terra Preta soils are usually higher than the adjacent Ferralsol, but they tend to have higher available N.

4.2.1.6. Aggregate stability. Overall, the biochar application rate has a positive effect on the aggregate stability (Figure 4.12). This is due to the ability of the carbon to interact with the soil and bind with its molecules to form aggregates which help the aeration of the soil and store water for the plants. The combined effect of the biochars application rate and pyrolysis temperature has significantly increased the aggregate stability in both soils, with more pronounced increase in aggregate stability in the treated Norfolk soil. The Norfolk soil composition is mainly sand and is known to have very low aggregates compared to Mecklenburg soil which contains more clay contributing to the formation of more aggregates. Therefore the addition of organic matter to the Norfolk soil is expected to significantly increase the aggregates. Hence, the effect of biochar on soil aggregation was more visible in Norfolk soil than in Mecklenburg soil.

Addition of 2% biochars has significantly increased the aggregate stability of both soils, with no significant differences associated with biochar precursors. This can be explained by the accumulation of organic matter that was favored by the binding of organic carbon compounds to soil mineral through cation bridging and formation of microaggregates that would then bind together with additional persistent organic matter compounds to form larger aggregates (Busscher, Novak, Caesar-TonThat, & Sojka, 2007).

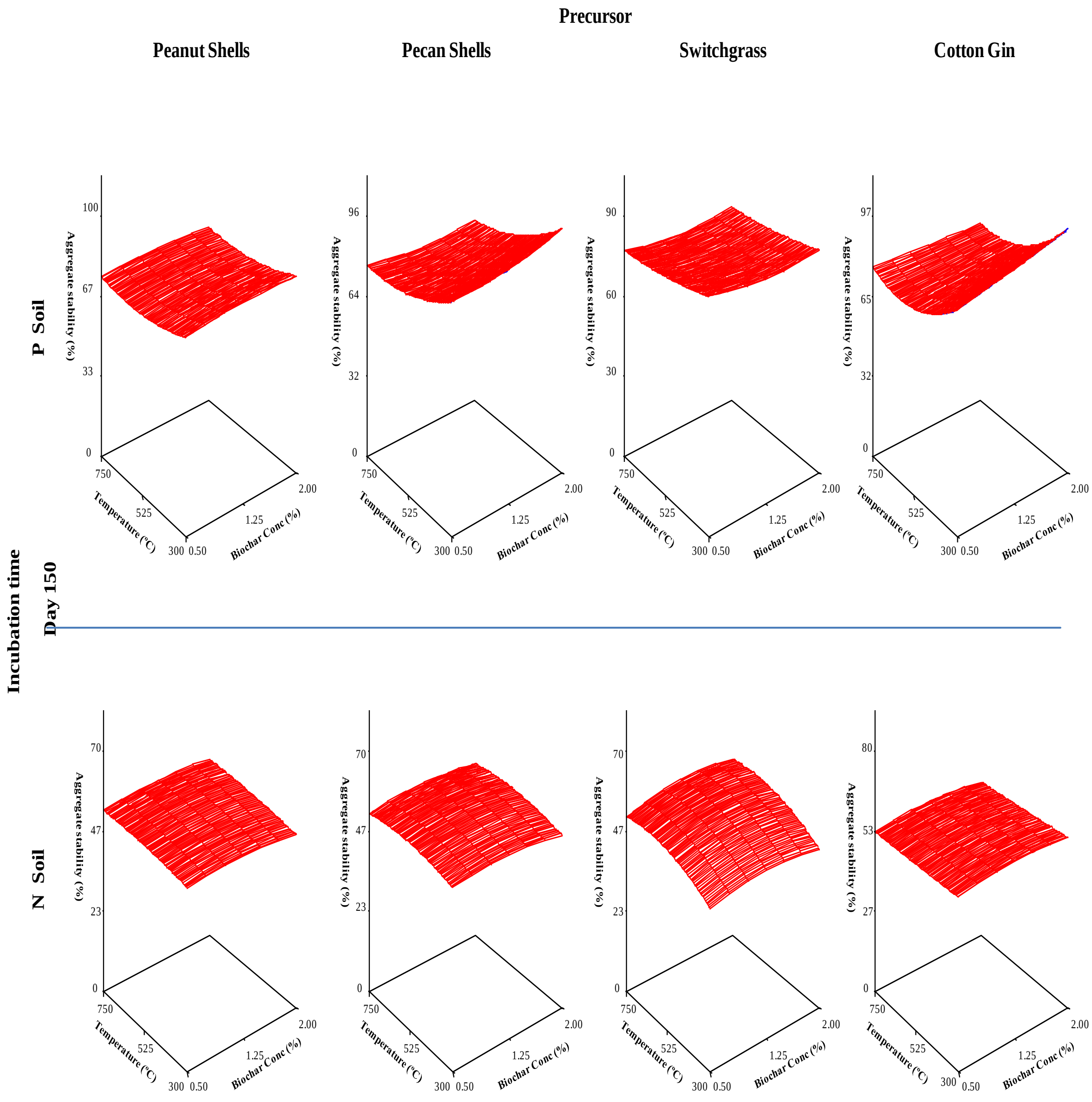

Figure 4.12. Effect of pyrolysis temperature and carbon application rate on aggregate stability of Mecklenburg and Norfolk soils. Note: Mecklenburg & Norfolk soils aggregate stability control at Day 150 = 71% and 52%, respectively.

Warnock, Lehmann, Kuyper, and Rillig (2007) stated that the aggregation is favored by interactions with soil organic matter and microorganisms or by additions of biochars and labile organic matter in combination since organic molecules sorb to appropriate biochars domains (Yu, Ying, & Kookana, 2006). Soil aggregation improvement by biochar addition is linked to its surface charge characteristics, which develop gradually by weathering and is affected by overall soil pH (Cheng et al., 2006) which in return promotes water infiltration. Thus, water infiltration through the soil, as opposed to runoff, could be increased benefiting plants (Major, Steiner, Downie, & Lehmann, 2009).

4.2.1.7. Water holding capacity. The addition of biochars has significantly increased the water holding capacity in both soil types. Biochars produced at high pyrolysis temperature and increased application rate had a positive effect on the water holding capacity (Figure 4.13). The positive effect of biochars' application rate on WHC was very clear, especially for SG, CG and PS biochars which exhibited increased ability to absorb and retain water in the soil. This is likely due to the high surface area and porosity of these biochars, especially for SG-derived biochar which had the highest WHC.

After 120 days of incubation, water retention by the Norfolk and Mecklenburg soils, with and without biochar incorporation varied considerably. The control Norfolk and Mecklenburg soils were able to retain only 36% and 26% by weight of the applied deionized water (based on mass collected after 30 h of free drainage), respectively. In contrast, water leaching of soil treated with the biochars revealed significant enhancement in water retention. For instance, application of switchgrass biochar (2%) resulted in the largest WHC increase by up to 53% and 38% in Norfolk and Mecklenburg soils, respectively.

This is a significant improvement in the mass of water retained by both soil. This enhancement in water retention can be explained either by the polarity of these biochars, or their micropores network which physically retain water or by improved aggregation that created pore space for water storage (Busscher et al., 2010).

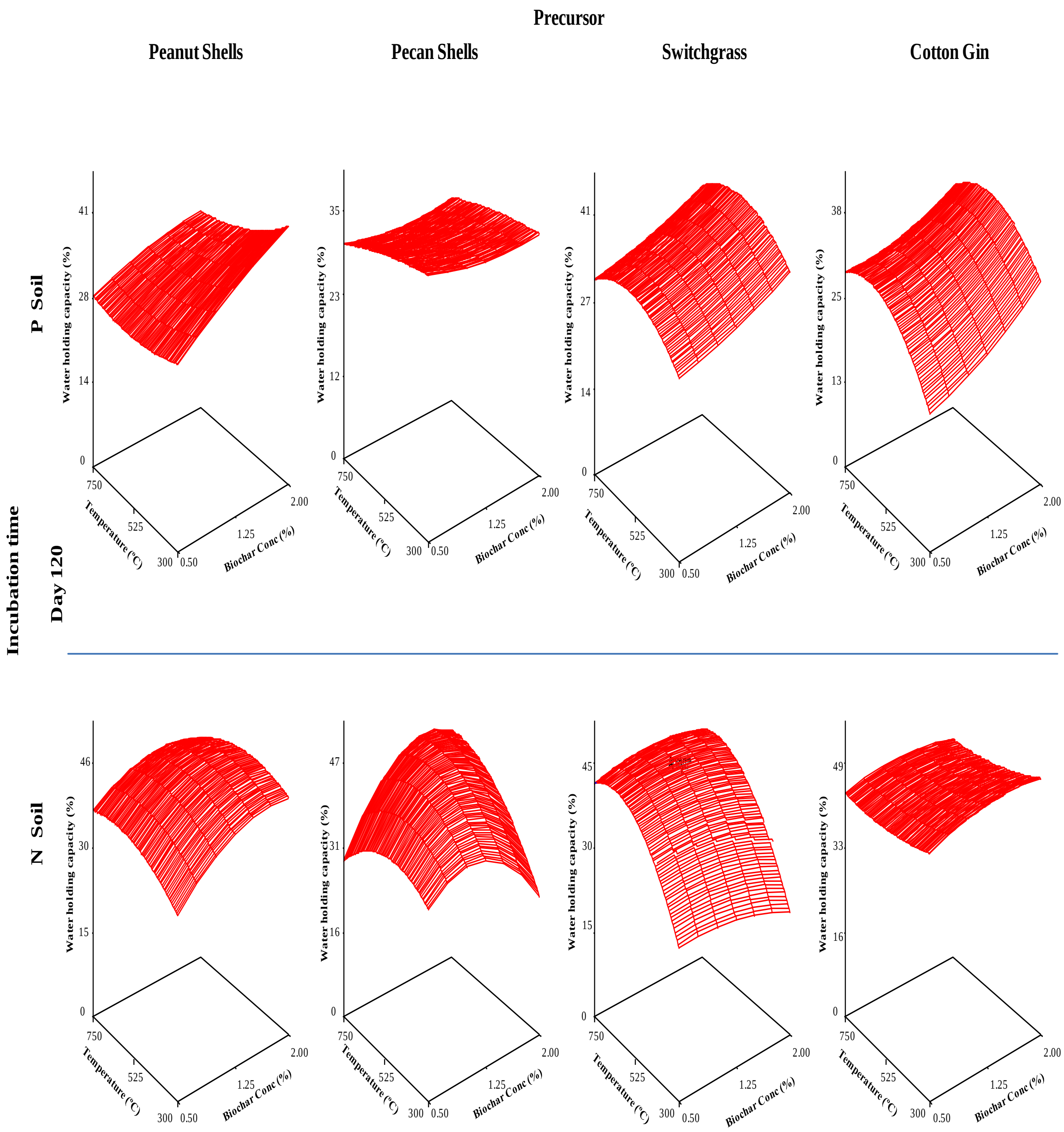

Figure 4.13. Effect of pyrolysis temperature and carbon application rate on water holding capacity of Mecklenburg and Norfolk soils. Note: Mecklenburg & Norfolk soils water holding capacity control at Day 120 = 26% and 36%, respectively.

Adding biochar to soil can have direct and indirect effects on soil water retention, which can be short or long lived. Water retention of soil is determined by the distribution and connectivity of pores in the soil-medium, which is largely regulated by soil particle size (texture), combined with structural characteristics (aggregation) and soil organic matter content (Verheijen et al., 2010). The direct effect of biochar application is related to the large inner surface area of biochar. Biochars with a wide range of porous structures will result from feedstocks as variable as straw, wood and manure. The hypothesized indirect effects of biochar application on soil water retention relate to improved aggregation or structure. Biochar can affect soil aggregation due to interactions with SOM, minerals, and microorganisms (Verheijen et al., 2010).

The surface charge characteristics, and their development over time, will determine the long term effect on soil aggregation which is in agreement with our findings, where the switchgrass biochar produced at 300 °C exhibited the highest surface charge and the one produced at 750 °C showed the highest surface area compared to other biochars.

Tryon (1948) studied the effect of biochar on the percentage of available moisture in soils of different textures. In sandy soil the addition of biochar increased the available moisture by 18% after adding 45% of biochar by volume, while no changes were observed in loamy soil and moisture content of clayey soil decreased with increase in biochar addition. This can be attributed to hydrophobicity of the biochar, although another factor could simply be that the biochar was replacing clay with a higher water retention capacity.

Verheijen et al. (2010) reported that the additional volume of water and soluble nutrients stored in the biochar micropores may become available as the soil dries and the matrix potential increases. This may lead to increased plant water availability during dry periods in sandy soils.

4.2.2. Biochar amendment and soil nutrients. The addition of biochars has significantly increased the concentrations of all the nutrients in both soils compared to their respective controls. Biochar produced at higher pyrolysis temperature showed a significant positive effect ($p < 0.05$) on the nutrients concentrations in treated soils (Figures 4.14–4.19), especially at higher application rate. The increase in the concentrations of P, K, and Mg was more significant ($p < 0.05$) in soils treated with switchgrass and cotton gin biochars. This is most probably due to the high concentrations of these elements in the corresponding feedstoks which was further increased in relative terms as the pyrolysis temperature increases.

Despite four months of regular leaching, the concentrations of the nutrients were still significantly higher than the control soil which lost more than 50% of elements such as K, Mg, and Zn in Norfolk soil and P, K, Mg in the Piedmont soil. This indicates a significant increase in the soil capacity to retain nutrients upon biochars addition.

Tryon (1948) also found increasing amounts of exchangeable bases after additions of 45% hardwood and conifer charcoals to sandy and loamy soils. Glaser et al. (2002) reported that most of the cations in the ash contained in the biochar were not bound by electrostatic forces but were present as dissolvable salts and, therefore, readily available for plant uptake. From these results it can be concluded that biochar is not only a soil conditioner which increases the CEC (Glaser, 1999; Glaser, Balashov, Haumaier, Guggenberger, & Zech, 2000; Glaser et al., 2001) but may also act as a fertilizer itself. Applications of charcoal which inevitably contain ash, add free bases such as K, Ca, and Mg to the soil solution increasing the pH value of the soil and providing readily available nutrients for plant growth.

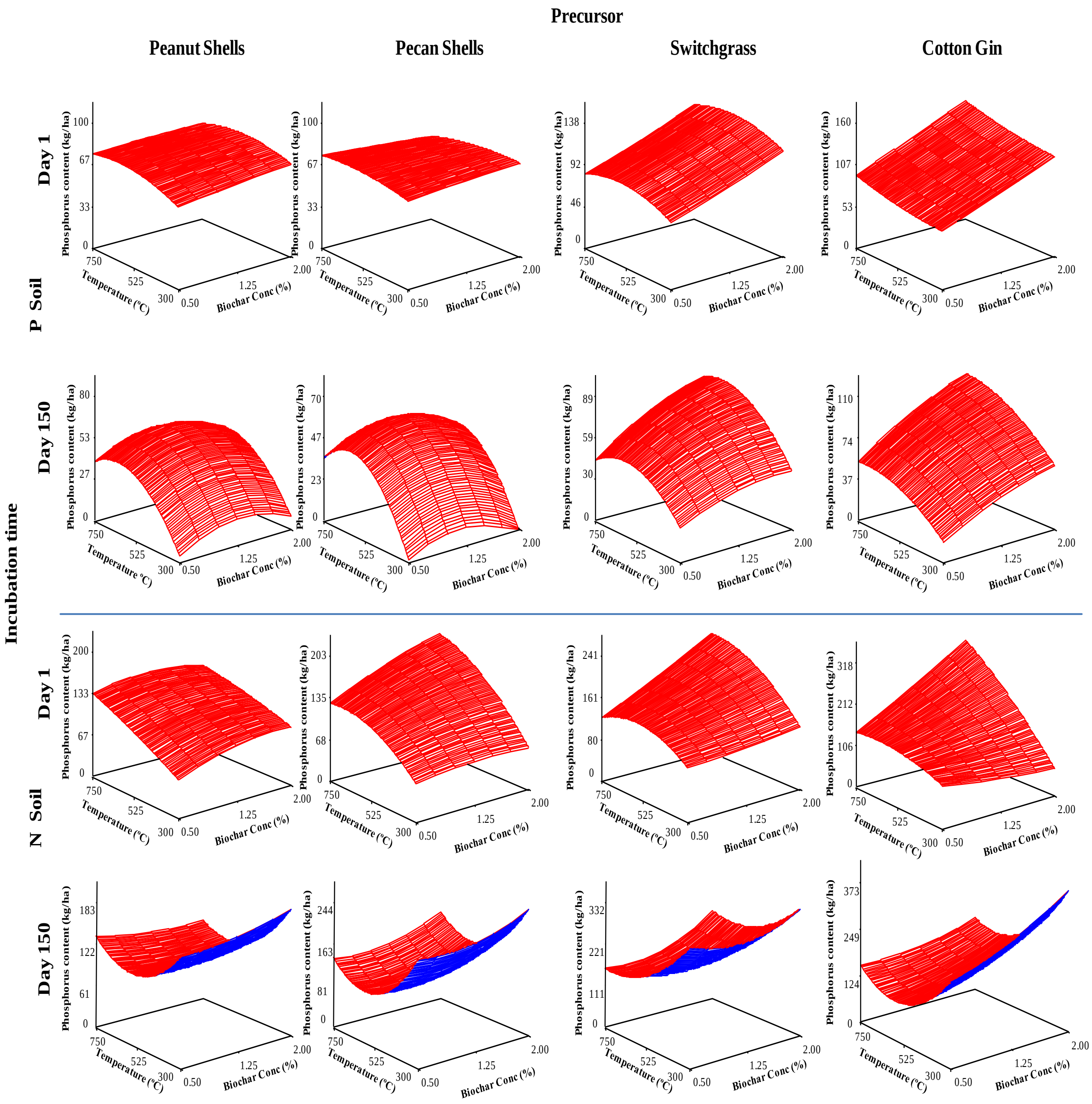

Figure 4.14. Effect of pyrolysis temperature and carbon application rate on phosphorus content of Mecklenburg and Norfolk soils. Note: Mecklenburg & Norfolk soils control Phosphorus at Day 1= 69.44 and 107.80 kg/ha, respectively. Mecklenburg & Norfolk soils control Phosphorus at Day 150 = 42.00 and 115.22 kg/ha, respectively.

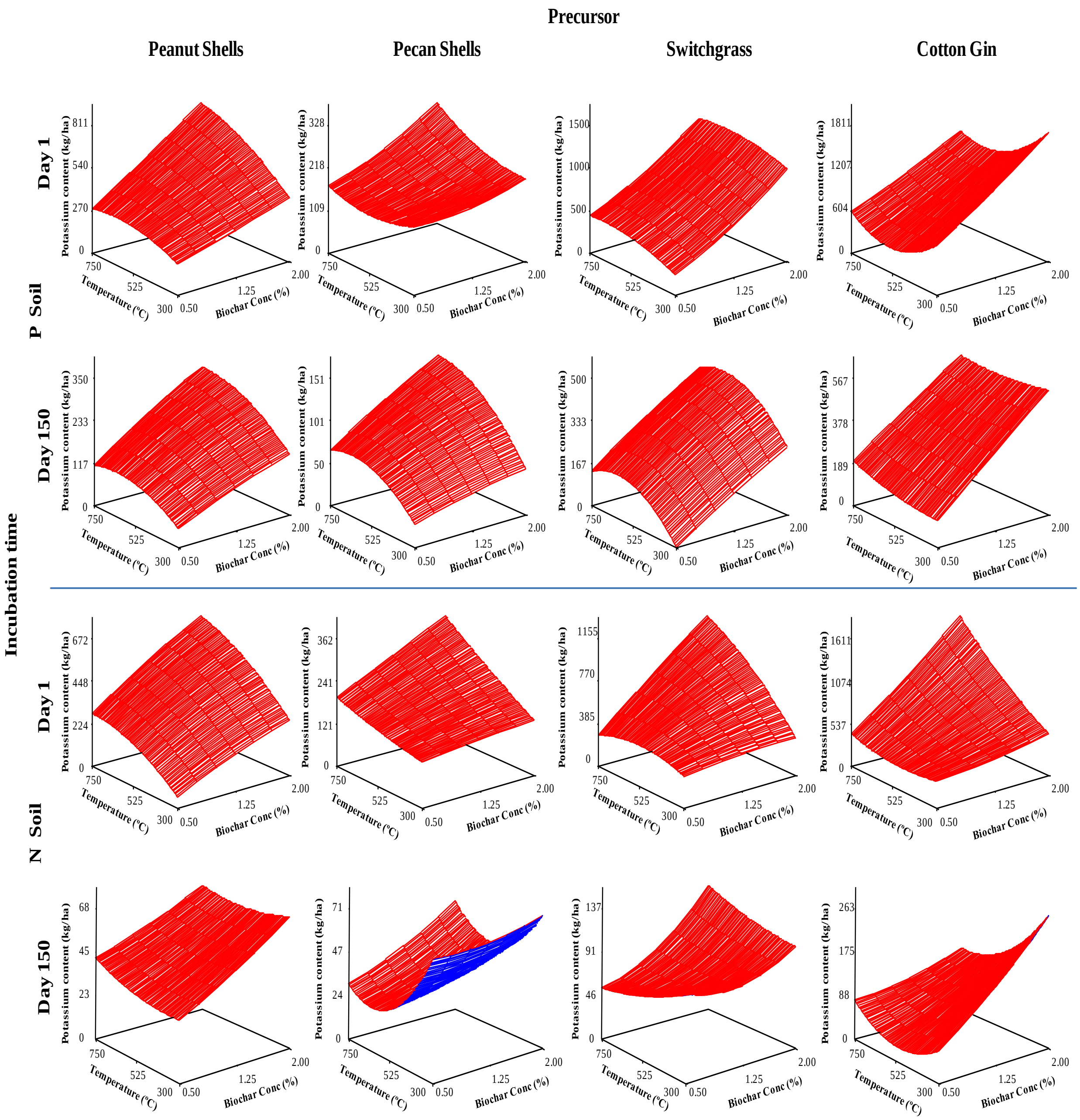

Figure 4.15. Effect of pyrolysis temperature and carbon application rate on potassium content of Mecklenburg and Norfolk soils. Note: Mecklenburg & Norfolk soils control Potassium at Day 1= 124.32 and 145.04 kg/ha, respectively. Mecklenburg & Norfolk soils control Potassium at Day 150 = 48.44 and 23.94 kg/ha, respectively.

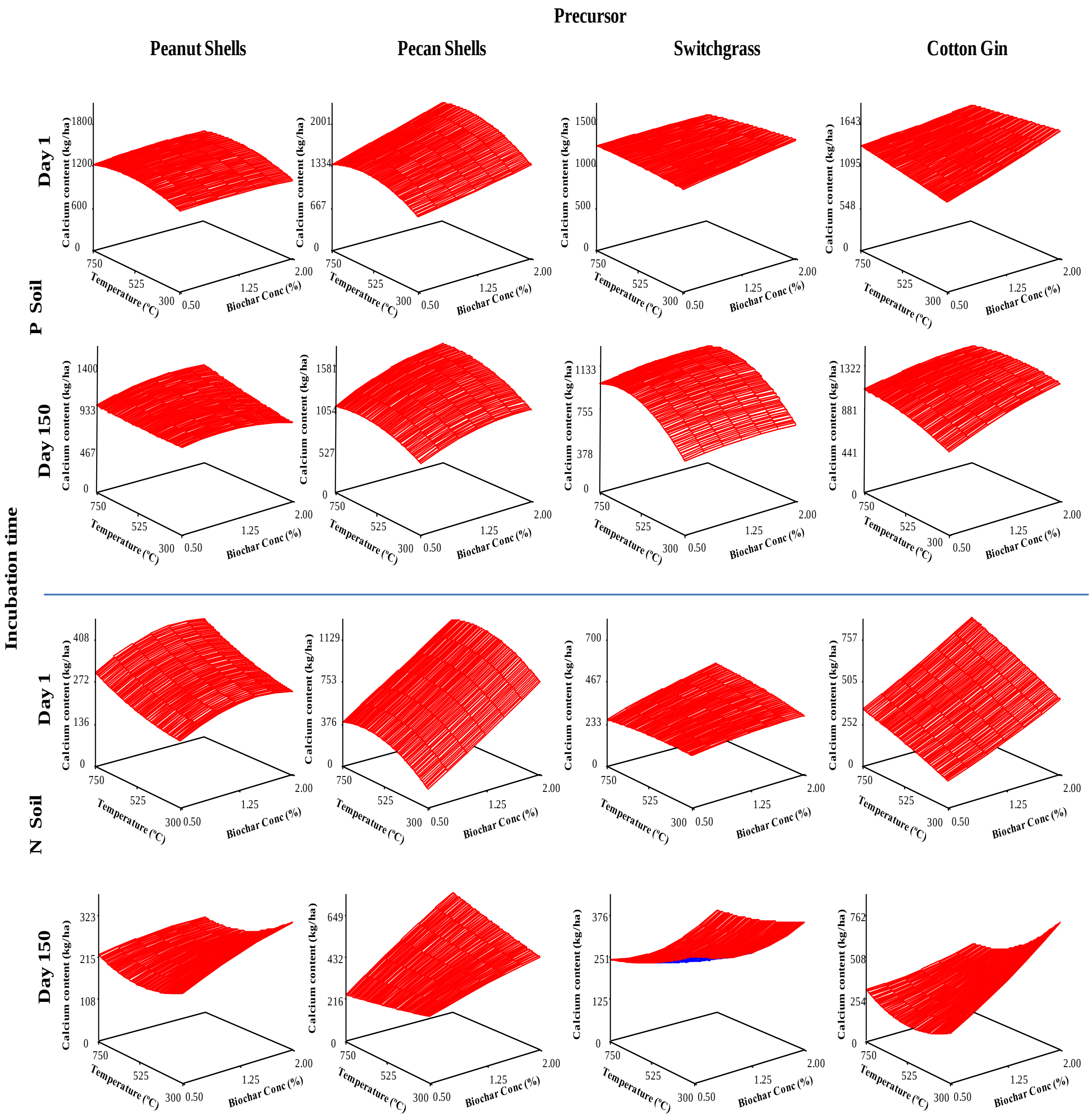

Figure 4.16. Effect of pyrolysis temperature and carbon application rate on calcium content of Mecklenburg and Norfolk soils. Note: Mecklenburg & Norfolk soils control Calcium at Day 1= 1161.43 and 268.52 kg/ha, respectively. Mecklenburg & Norfolk soils control Calcium at Day 150 = 980.56 and 194.39 kg/ha, respectively.

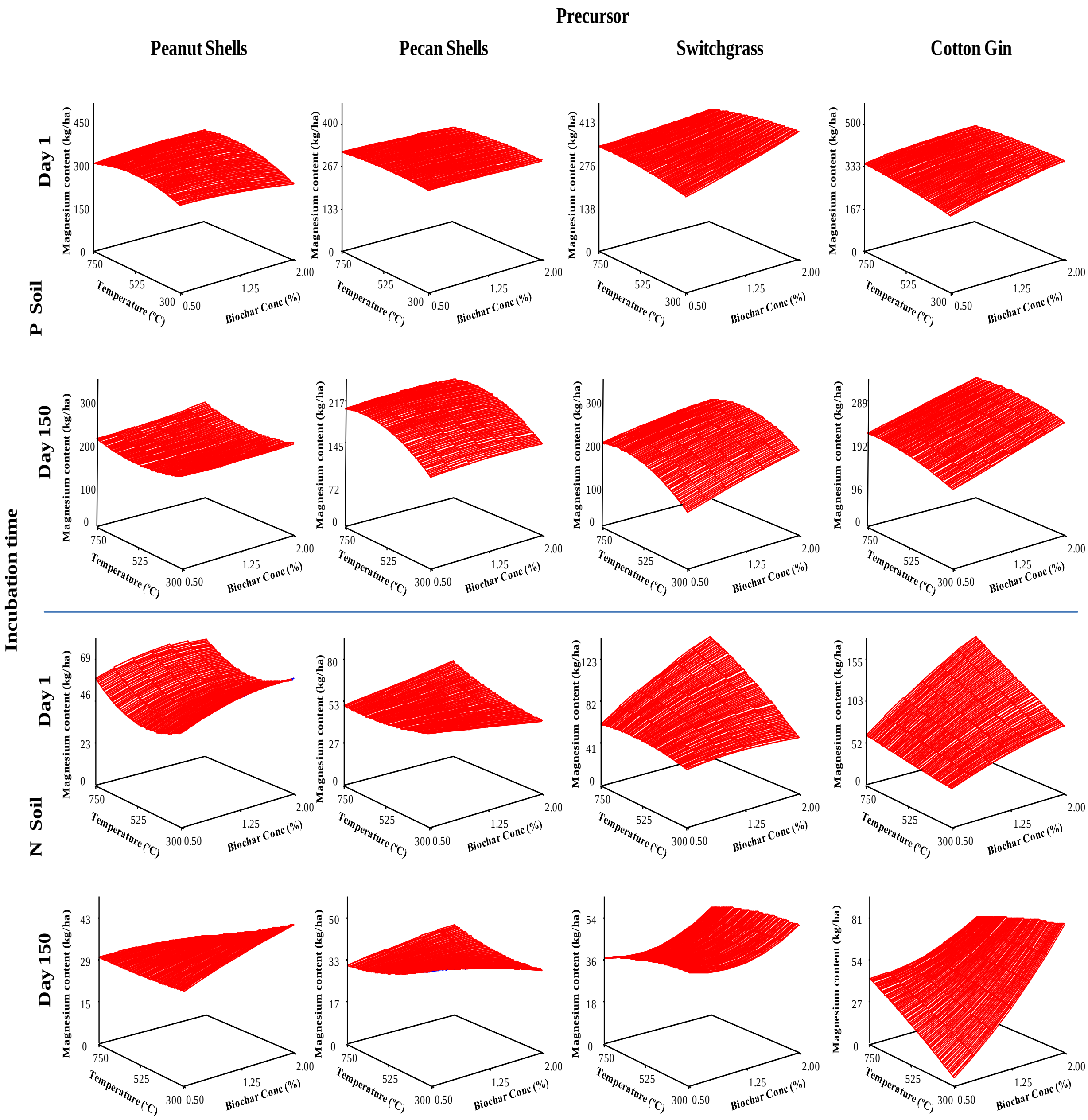

Figure 4.17. Effect of pyrolysis temperature and carbon application rate on magnesium content of Mecklenburg and Norfolk soils. Note: Mecklenburg & Norfolk soils control Magnesium at Day 1= 304.64 and 47.60 kg/ha, respectively. Mecklenburg & Norfolk soils control Magnesium at Day 150 = 176.12 and 27.58 kg/ha, respectively.

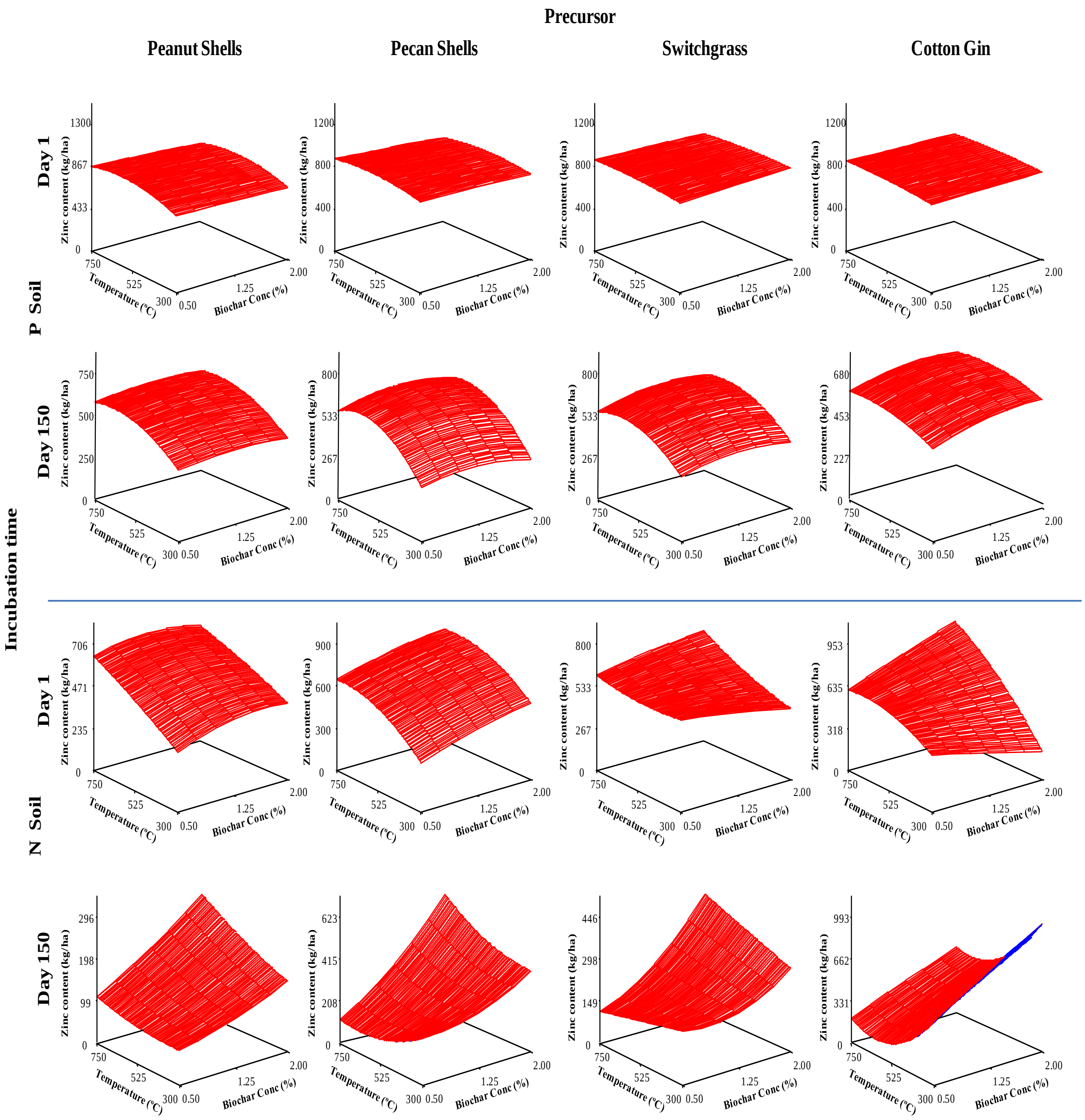

Figure 4.18. Effect of pyrolysis temperature and carbon application rate on zinc content of Mecklenburg and Norfolk soils. Note: Mecklenburg & Norfolk soils control Zinc at Day 1= 827.98 and 576.83 kg/ha, respectively. Mecklenburg & Norfolk soils control Zinc at Day 150 = 563.08 and 71.52 kg/ha, respectively.

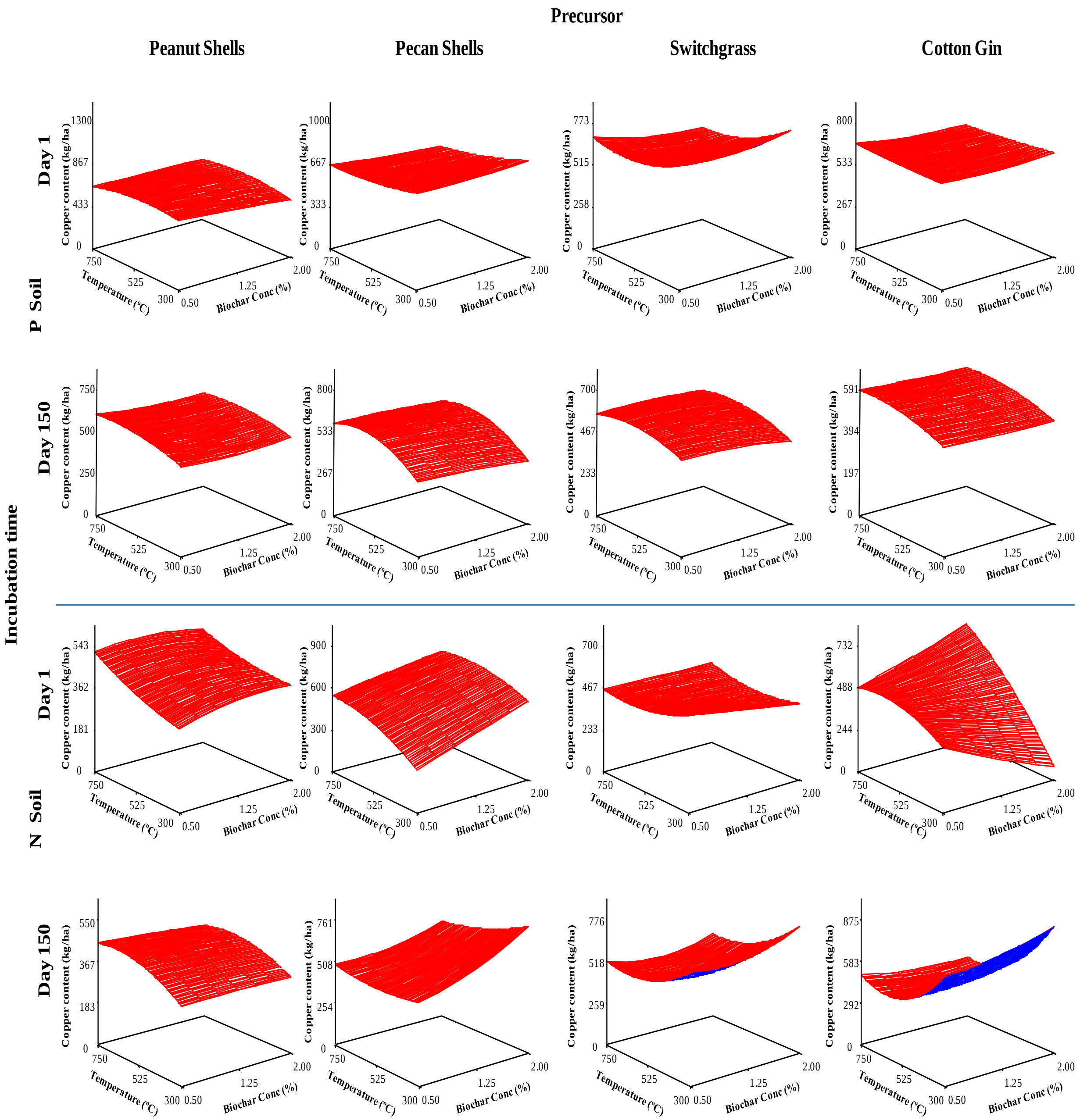

Figure 4.19. Effect of pyrolysis temperature and carbon application rate on copper of Mecklenburg and Norfolk soils. Note: Mecklenburg & Norfolk soils control Copper at Day 1= 682.83 and 500.64 kg/ha, respectively. Mecklenburg & Norfolk soils control Copper at Day 150 = 615.05 and 321.56 kg/ha, respectively.

Mixing relatively large amounts of hardwood biochar with soil increased the CEC by 50% compared to the unamended soil (Mbagwu & Piccolo, 1997; Tryon, 1948). But even low amounts of weathered biochar (Glaser, 1999) could increase the CEC of soil. Additionally, biochar has the potential to form organo-mineral complexes (Ma, Li, & Wang, 1979) which were also observed in biochar-containing soils (Glaser et al., 2000). It is assumed that slow oxidation (biotic and/or abiotic) on the edges of the aromatic backbone of biochar forming carboxylic groups is responsible for both the potential of forming organo-mineral complexes and the sustainably increased CEC (Glaser et al., 2002) which contribute to the nutrients retention.

Glaser et al. (2002) stated that a higher nutrient retention can also be achieved merely by retention of soil water in micro and mesopores. If water percolation through soil can be reduced, nutrient leaching will also decrease. By this mechanism nutrients can be retained which are normally not sorbed to soil and are very mobile and susceptible to leaching, such as NO_3^- at high pH, or base cations at low pH. These results show that charcoal may contribute to an increase in ion retention of soil and to a decrease in leaching of dissolved organic matter and organic nutrients.

Glaser et al. (2002) also reported that two processes are responsible for the high nutrient contents and nutrient retention capacity of soil amended with biochars which lead to improved nutrient supply for plants and reduced nutrient losses by leaching: (a) nutrients are physically trapped in the fine pores of amorphous carbonized materials, and (b) slow biological oxidation produces carboxylic units on the edges of the condensed aromatic backbone of the biochar which increases the CEC.

4.2.3. Mecklenburg and Norfolk soils leachates.

4.2.3.1. Leachate pH. It is important to examine the chemical composition of a deionized water extract (leachates) of an amended soil since, in some cases; the amendment can release elements that may cause plant growth issues (Novak, Lima, et al., 2009). The addition of biochars to soil had a positive effect on the pH of the soil leachates which fluctuated over time. Biochars significantly increased the pH of the leachates in both soils (Figures 4.20–4.21) at 1 and 2% application rates and as the pyrolysis temperature increases. Some pH variations were also observed within the pH of the same soil leachates as a function of the type of precursors used to produce the treatment biochars. This can be explained by the difference in initial composition of the precursors some of which (e.g., switchgrass and cotton gin) yield more basic cations than others in the final biochar.

Biochar pH is mostly neutral to basic (Figure 4.3). The liming effect has been discussed in the literature as one of the most likely mechanisms behind the observed increases in plant productivity after biochar applications and lower pH values in soils (greater acidity) often reduce the CEC and, thus the nutrient availability. Verheijen et al. (2010) reported in some studies that the average pre-amendment soil pH was 5.3 and post-amendment 6.2, although, in the case of poultry litter, biochar application on acidic soils increases from pH 4.8 to 7.8. Therefore, a scientific consensus on the short term liming effect of biochar applied to soil is apparent.

This implies that biochars with greater liming capacity can provide greater benefit to arable soils that require liming, through frequent application at lower rates to reduce or potentially cut conventional liming operations, and hence, provide cost saving.

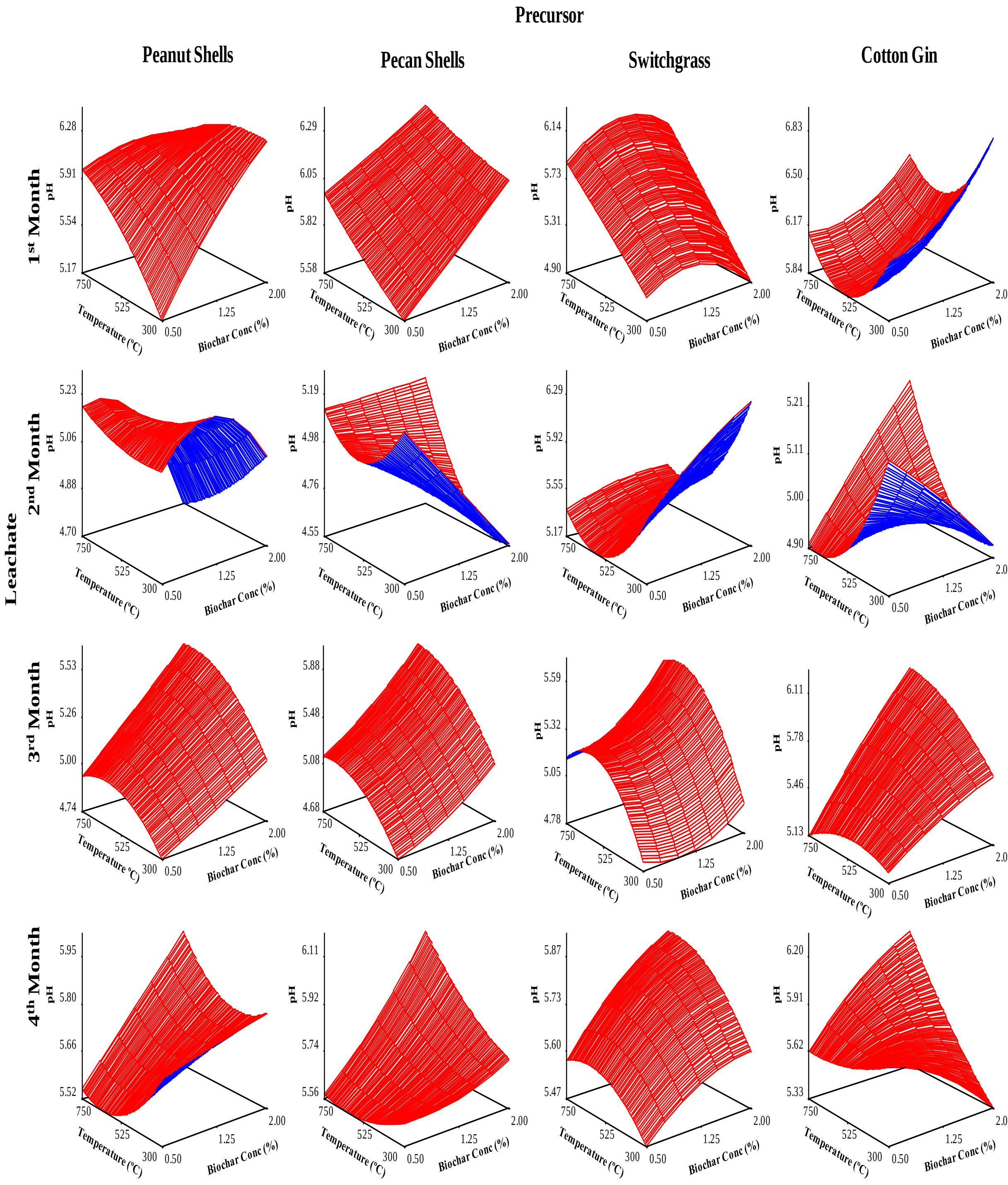

Figure 4.20. Effect of pyrolysis temperature and carbon application rate on the pH of Mecklenburg soil leachates.

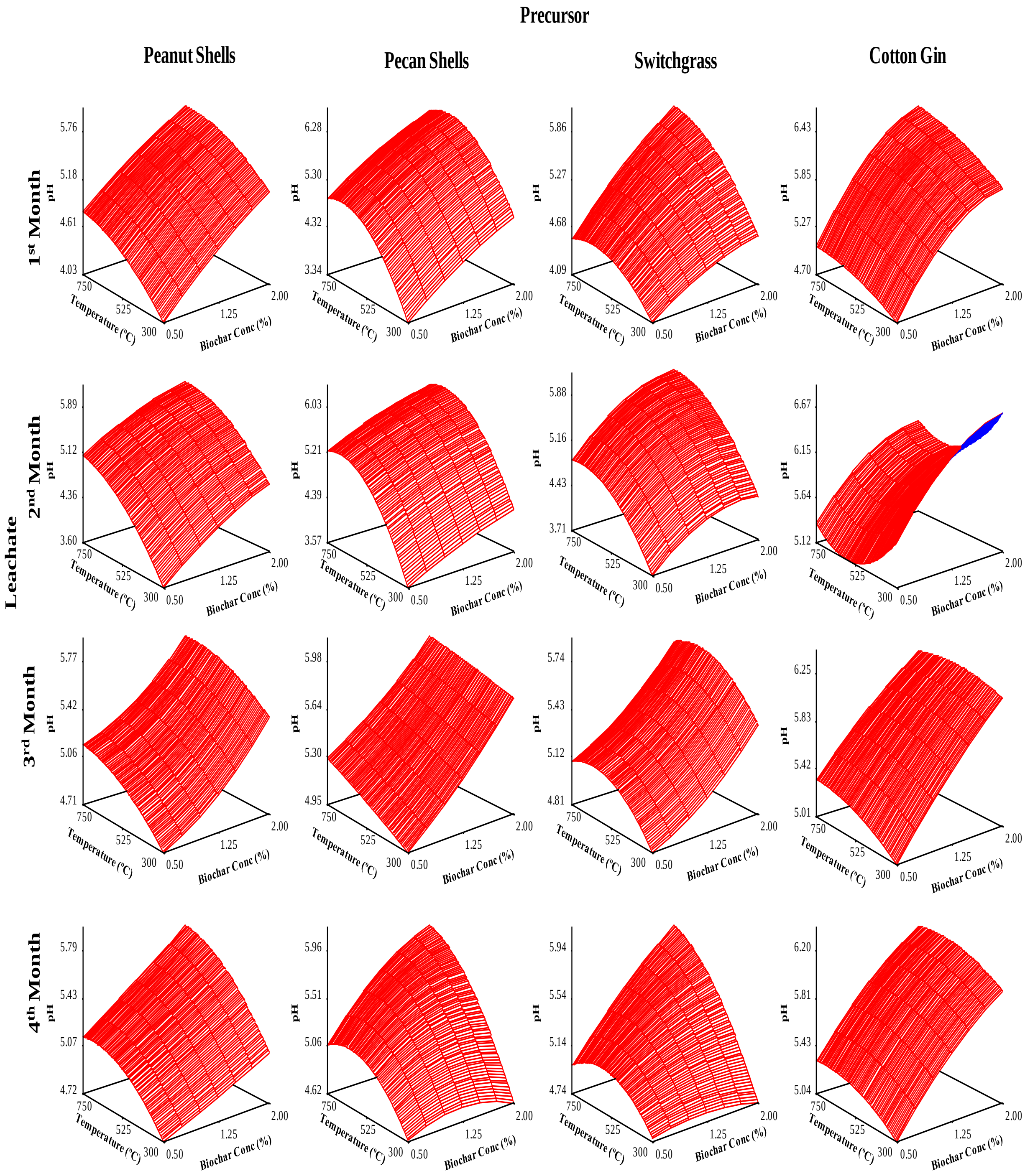

Figure 4.21. Effect of pyrolysis temperature and carbon application rate on the pH of Norfolk soil leachates.

4.2.3.2. Dissolved organic carbon and electrical conductivity. The addition of biochars to the soil has increased the dissolved organic carbon (DOC) of the soil leachates (Figures 4.22–4.23). Biochars produced at low temperature (300 °C) had the most positive effect on DOC which significantly increased ($p < 0.05$) in the leachates of both soil types, regardless of the types of precursors. The observed DOC enhancement was more significant ($p < 0.05$) for cotton gin-based biochar, especially in Norfolk soil. Biochars produced at low temperature are less resistant to biotic and abiotic degradation than the biochars produced at high temperatures. The latter tend to be harder and more resistant to abrasion and biodegradation in the soil (Novak, Lima, et al., 2009).

The addition of biochars to both soils significantly increased the electrical conductivity (EC) of the soils leachates compared to the controls with some fluctuations over time (Figures 4.24–4.25). The EC values of leachates were higher in Norfolk soil than in Mecklenburg soil, probably due to the clay nature of Mecklenburg soil that inherently possesses higher CEC. Among the feedstoks, cotton gin-based biochar showed highest EC concentrations, most likely because of its soft nature and high ash/mineral content.

It is important to mention that biochar porosity, especially its microporosity, contributes to nutrient adsorption by trapping nutrient-contained water held by capillarity forces in micropores which reduces the mobility of soil water through the matrix (Tseng & Tseng, 2006). In sandy soils where the volumetric amount of water held decreases sharply as the soil dries, biochar particles may act similarly to clay and hold large volumes of immobile water. Nutrients dissolved in this water would thus be retained near the soil surface if water is immobile or move slowly (Major et al., 2009).

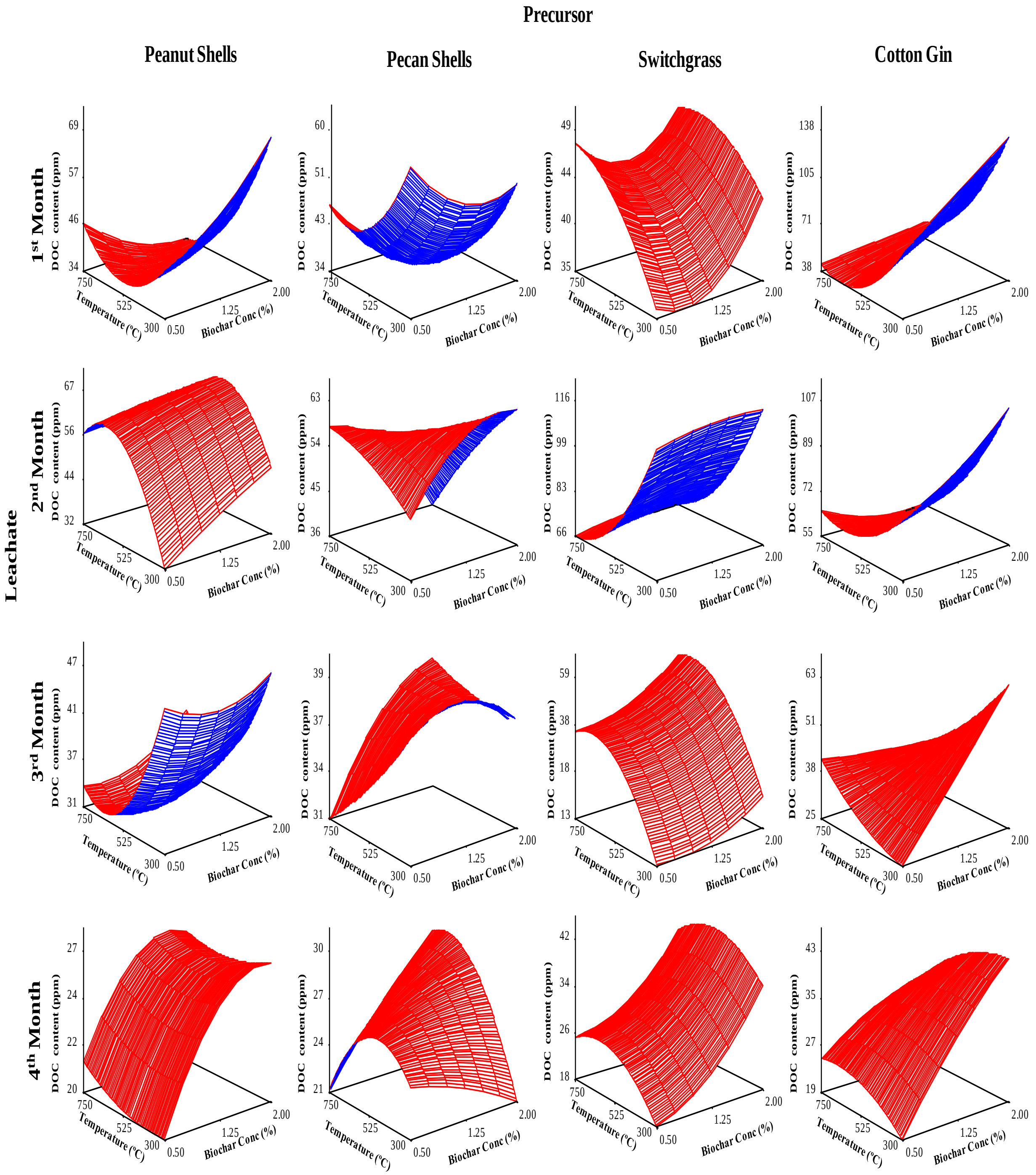

Figure 4.22. Effect of pyrolysis temperature and carbon application rate on the DOC of Mecklenburg soil leachates.

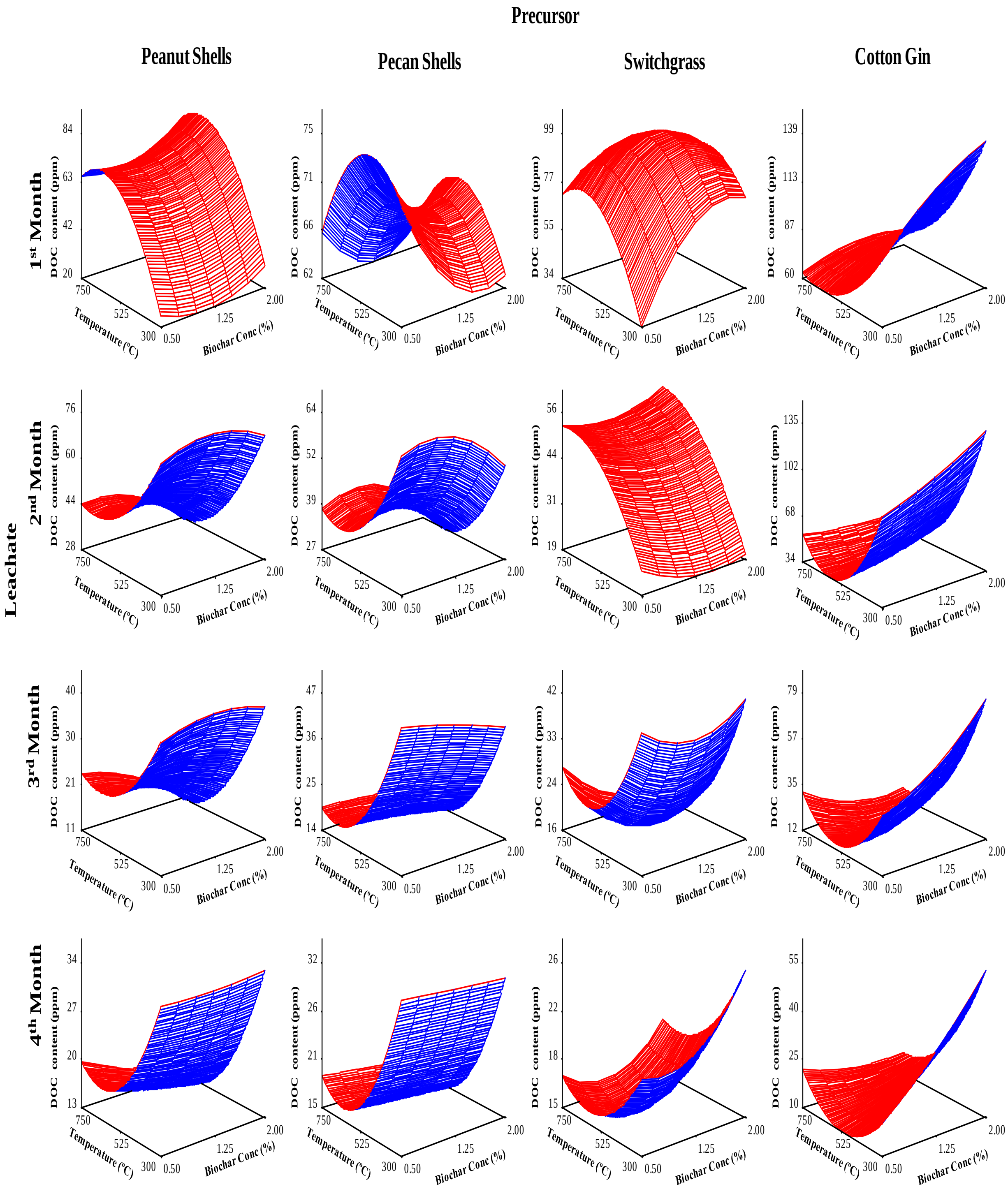

Figure 4.23. Effect of pyrolysis temperature and carbon application rate on the DOC of Norfolk soil leachates.

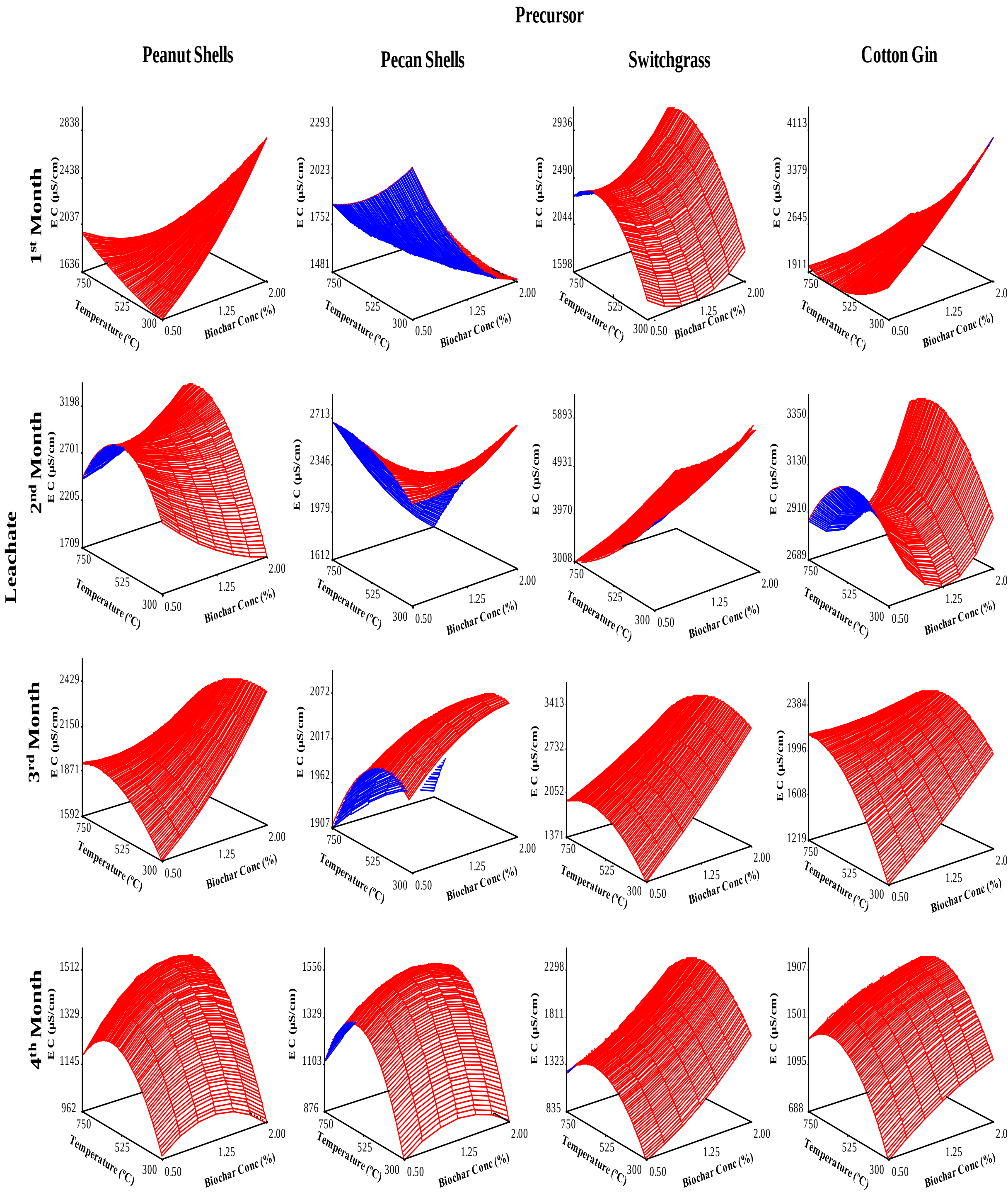

Figure 4.24. Effect of pyrolysis temperature and carbon application rate on the EC of Mecklenburg soil leachates.

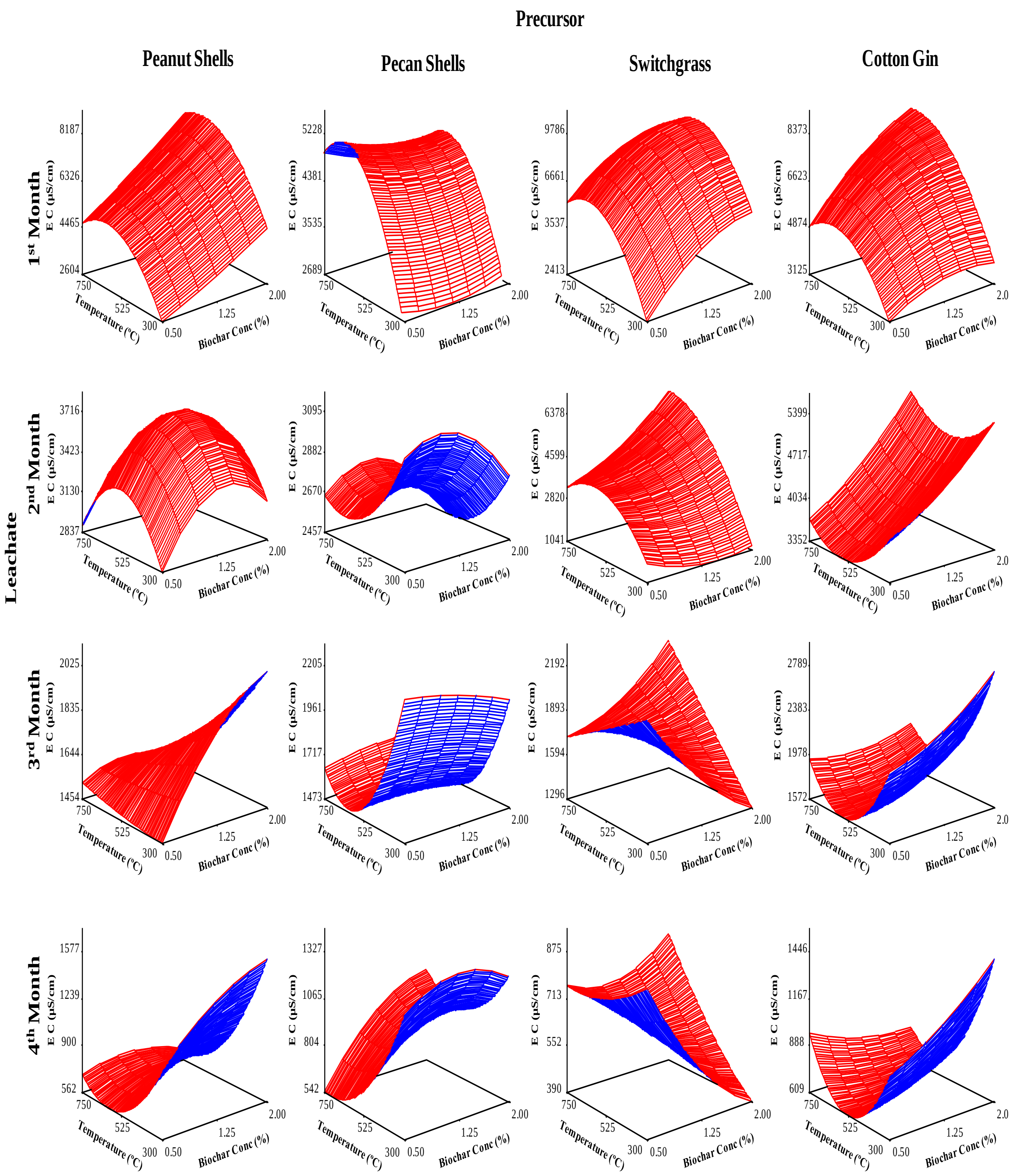

Figure 4.25. Effect of pyrolysis temperature and carbon application rate on the EC of Norfolk soil leachates.

4.2.3.3. Total nitrite and nitrate (NOxN). The temporal changes of total nitrate/nitrites ((NO_3^-/(NO_2^-) are shown in Figures 4.26 and 4.27. The leaching of nitrate/nitrites from the controls and treated soils tended to vary differently in Mecklenburg and Norfolk soil, with values ranging from 0 to 68 ppm and 36 to 58 ppm for Norfolk and Mecklenburg soil, respectively. The observed peak for both the control and treated soils appeared in the first month for the Norfolk soil and third month for the Mecklenburg soil. Thereafter, the concentration of nitrate/nitrites in the control soil decreased to zero for Norfolk soil and 36 ppm for Mecklenburg soil. This difference in soils is probably due to the high clay and organic matter content of Mecklenburg soil.

The concentration of nitrate/nitrites in biochar-treated soils decreased significantly with the increase of biochars application rate and with high pyrolysis temperature used in carbon production. Overall, the concentration of nitrate/nitrites increased significantly in the first month to peak at the end of first month and the third month for Norfolk and Mecklenburg soils, respectively. After this peak, the nitrate/nitrites concentrations showed a trend of moderate decline.

Biochars produced at elevated temperature and used at higher application rate have significantly decreased ($p < 0.05$) the concentration of nitrate/nitrites in both soil types. In contrast, low pyrolysis temperature and high biochar application rate increased the nitrate/nitrites concentrations in the soil, This is due to the differences in biochar decomposition because of their C:N ratios; higher pyrolysis temperatures caused wider C:N ratios in the biochar because of loss of N and concentration of C (Novak, Lima, et al., 2009).

Overall, these results suggest that nitrate/nitrites can be retained in the surface soil layer for a longer time through biochars addition produced at high pyrolysis temperature. This reduces the leaching rate of nitrate/nitrites which is beneficial to crops.

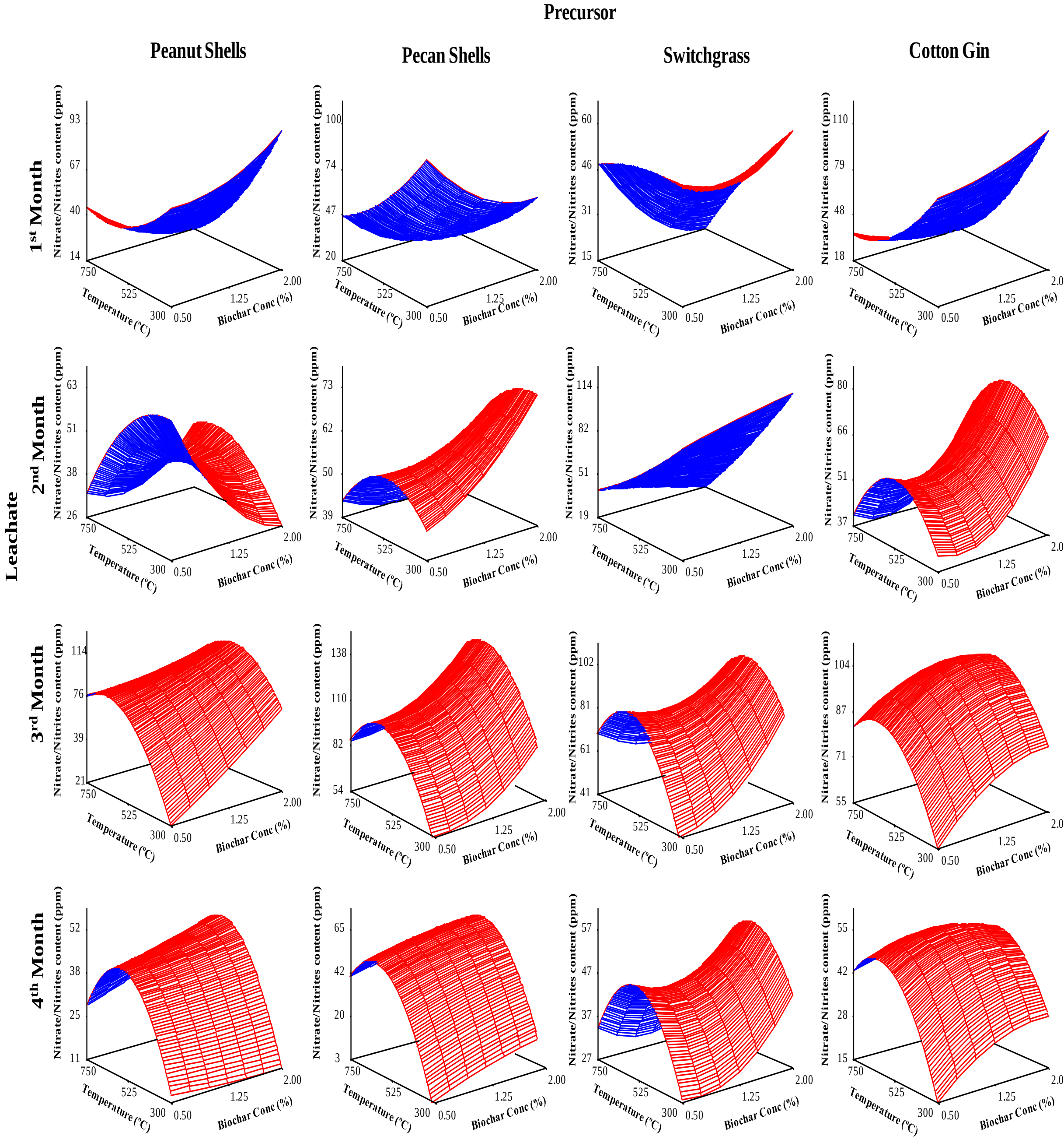

Figure 4.26. Effect of pyrolysis temperature and carbon application rate on the NOxN of Mecklenburg soil leachates.

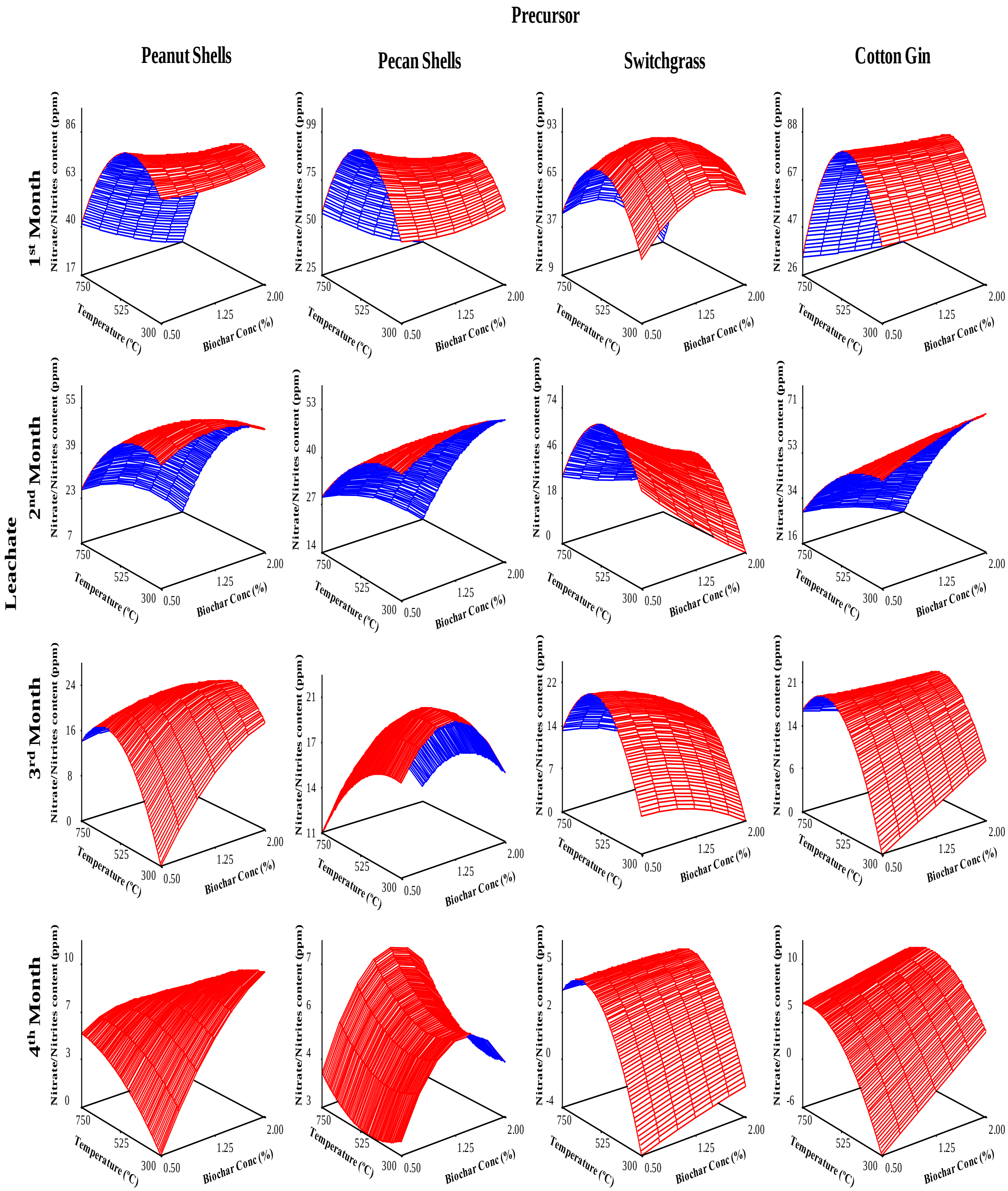

Figure 4.27. Effect of pyrolysis temperature and carbon application rate on the NOxN of Norfolk soil leachates.

The majority of soil N exists in complex organic forms that must be ammonified to NH_4^+ and then nitrified to NO_3^- prior to uptake by plants (Stevenson & Cole, 1999). Nitrogen mineralization is the process whereby organic N is converted to inorganic N through the processes of ammonification (where NH_4^+ is formed) and nitrification (where NO_3^- is formed). Biochar has been found to increase net nitrification rates in temperate and boreal forest soils that otherwise demonstrate no net nitrification (DeLuca, MacKenzie, Gundale, & Holben, 2006). Gundale and DeLuca (2006) reported that biochars produced by heating biomass in a muffle furnace were found to stimulate net nitrification in forest soils.

The addition of field-collected biochar to soil expressing no net nitrification readily stimulated nitrifier activity in a 24 hour aerated soil slurry assay as reported by Deluca and Sala (2006). Deluca et al. (2006) also reported that a small increase in nitrification was observed in sterile control samples amended with sterile biochar, suggesting that the oxide surfaces on biochars may stimulate some quantity of auto-oxidation of NH_4^+.

Similar results were reported by Gundale and DeLuca (2006) where they evaluated how biochars produced at different temperatures (350 °C and 800 °C) from the bark and wood of two different tree species (ponderosa pine and Douglas-fir) influences N mineralization and nitrification. All biochars treatments increased nitrification, except for Douglas-fir wood, for which a reduction in ammonification was observed compared to the control possibly due to NH_4^+ adsorption to biochars (Berglund, DeLuca, & Zackrisson, 2004).

Biochar additions to agricultural soils of the tropics have been reported to either reduce N availability (Lehmann, Da Silva, et al., 2003) or to increase N uptake by crops (Steiner et al., 2007). The reduced N availability may be a result of the high C/N ratio of biochars and, thus, greater potential for N immobilization or due to biochar adsorption of NH_4^+ which in turn reduces the potential for N leaching losses and sustained higher N fertility over time in surface soils (Steiner et al., 2007).

4.2.3.4. Atrazine. The effects of biochars application rates and pyrolysis temperature on the leaching of atrazine over time from Mecklenburg and Norfolk soils are shown in Figures 4.28 and 4.29. The addition of biochars to the soil significantly decreased the leaching of atrazine as evidenced by the low atrazine concentrations in the soil leachates compared to leachates from soil controls. The 2% biochar application rate had the most significant effect on binding of atrazine into soil. A 96% and 92% reduction was observed at 2% biochar application rate for Mecklenburg and Norfolk soils respectively compared to soil control.

This may be explained by several mechanisms, including diminished O functionality on the edges of biochar’s graphitic sheets due to heat treatment which resulted in enhanced hydrophobicity and affinity for both polar and nonpolar compounds, thereby reducing competitive adsorption by water molecules and hence leaching of atrazine (Wang, Sato, & Xing, 2006; Zhu, Kwon, & Pignatello, 2005). The treated biochar also revealed an increase in micropore volume and pore surface area, resulting in better accessibility of solute molecules and an increase in sorption sites allowing the retention of atrazine.

Previous studies have convincingly demonstrated that adsorption to biochar is mainly influenced by the structural and chemical properties of the contaminant (i.e. molecular weight, hydrophobicity, planarity) (Cornelissen & Gustafsson, 2004; Cornelissen et al., 2005; Zhu et al., 2005), as well as pore size distribution, surface area and functionality of the biochar (Wang et al., 2006; Chen, Zhu, & Sun, 2007). The influence of pyrolysis temperatures mostly in the 340-400 °C range (James et al., 2005; Tsui & Roy, 2008) and feedstock type (Pastor-Villegas, Pastor-

Valle, Meneses Rodriguez, & García García, 2006) on such a phenomena has been recently evaluated for various wood biochars by a number of authors.

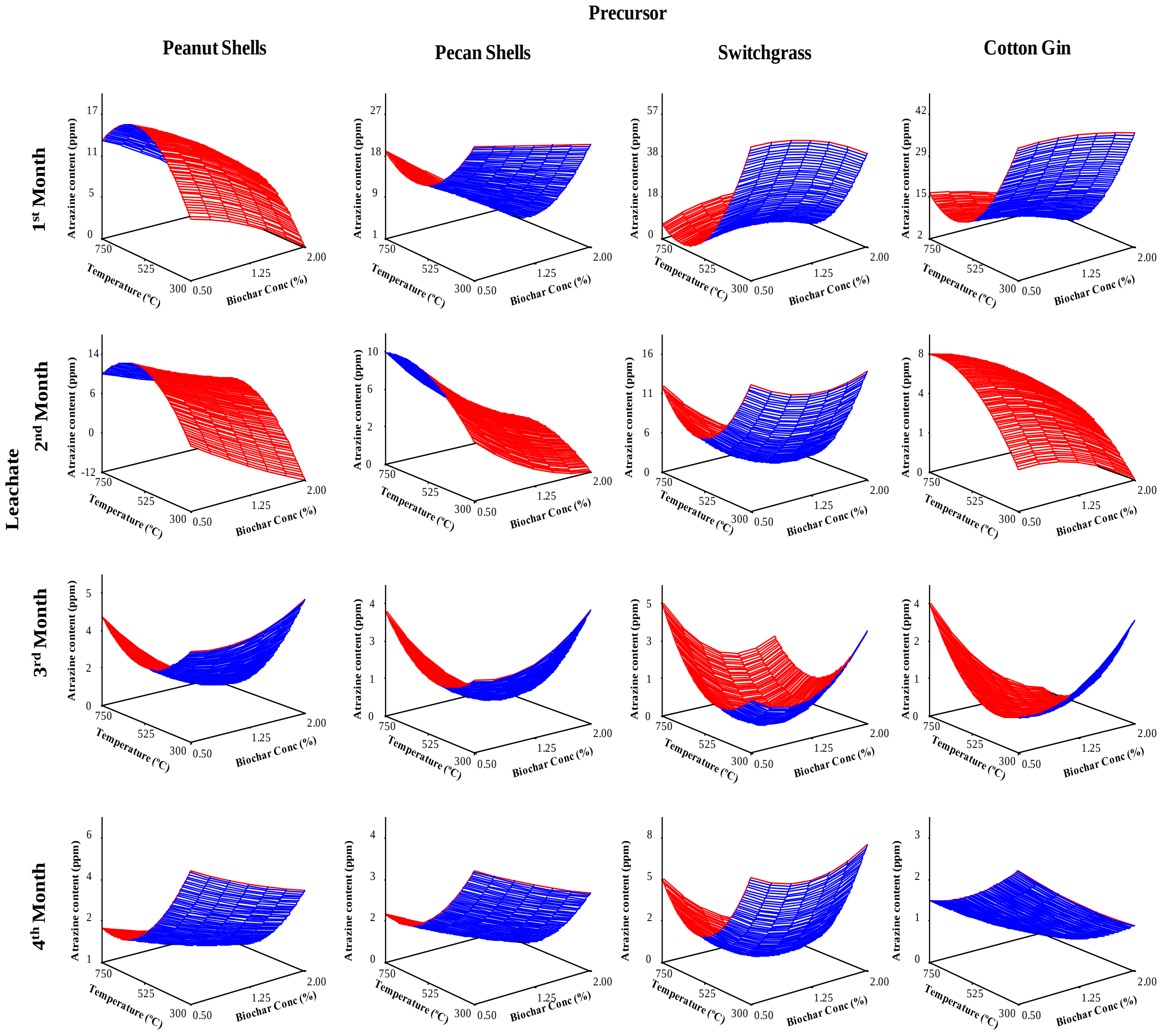

Figure 4.28. Effect of pyrolysis temperature and carbon application rate on the atrazine content of Mecklenburg soil leachates.

Interestingly, sorption to high-temperature biochars appears to be exclusively by surface adsorption, while that to low-temperature biochars derives from both surface adsorption and (at a smaller scale) absorption to residual organic matter (Chun, Sheng, Chiou, & Xing, 2004). Once released in the environment, the original adsorption properties of biochar may be affected by aging due to environmental factors, such as the impact of coexisting substances. The presence of organic compounds with higher hydrophobicity and/or molecular sizes have shown reduced adsorption of lower molecular weight compounds to biochars (Sander & Pignatello, 2005; Wang et al., 2006).

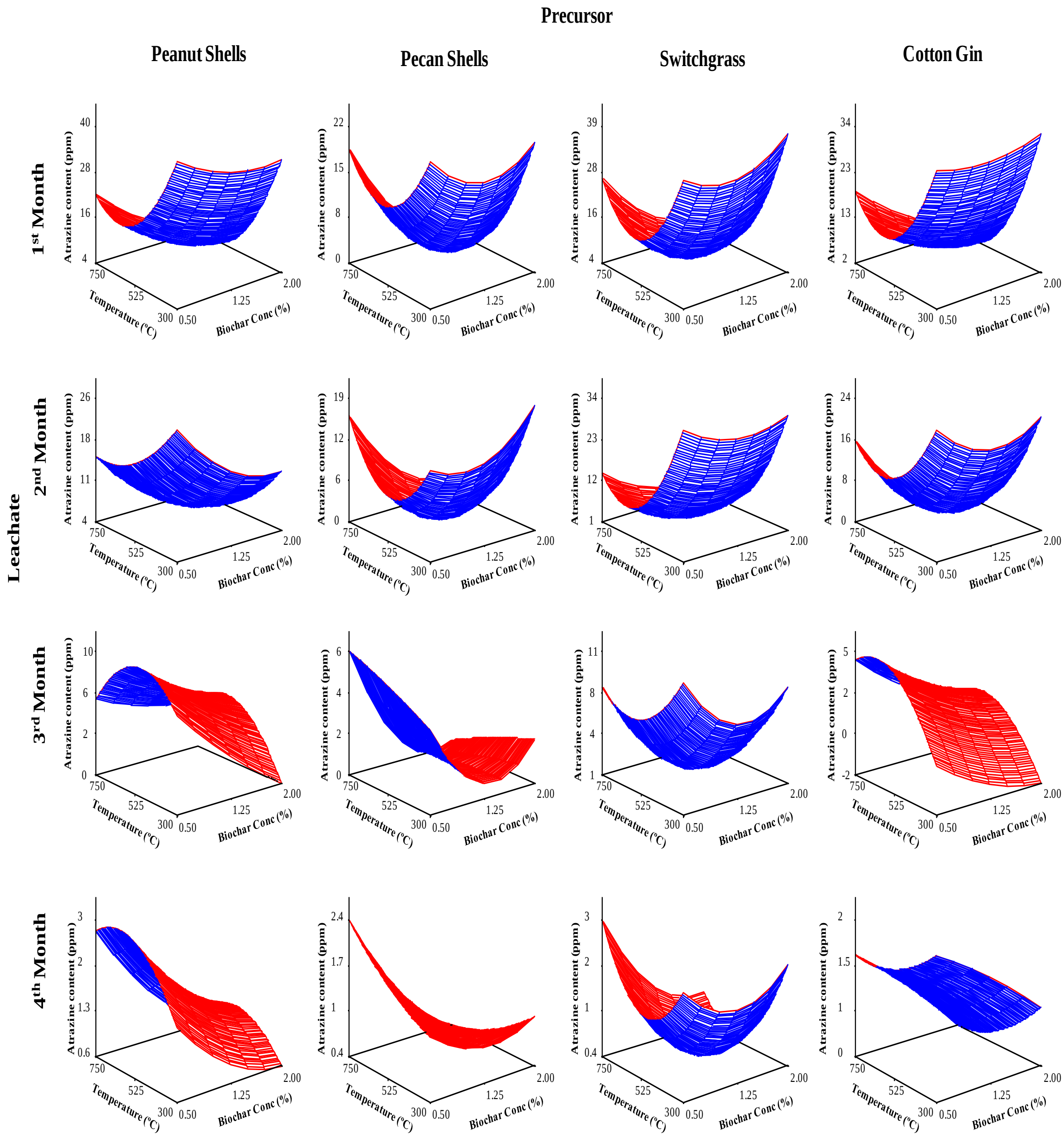

Figure 4.29. Effect of pyrolysis temperature and carbon application rate on the atrazine content of Norfolk soil leachates.

4.2.3.5. Micro and macronutrients. Figures 4.30 through 4.39 illustrate the effect of biochars application rates and pyrolysis temperature on the soil elemental leachates from Mecklenburg and Norfolk soils over time following treatment with biochars from four precursors at four different leaching times. For Mecklenburg soil, the biochar application rates and pyrolysis temperature had either significant positive or negative effects on elements' leaching, depending on whether the elements were mono or polyvalent cations.

For instance, the leaching of monovalent cation K increased as biochar application rate to soil increased, whereas leaching of multivalent cations (Ca, Mg, Cu, and Zn) decreased over time with increasing biochar application rate, with the 2% showing the most significant effect. The strength of cation retention or repulsion from negatively charged surfaces increases with increasing ion charge and with the distance between the charged surface and either the source of charge or the soluble ion. Consequently, multivalent cations were preferentially adsorbed over monovalent cations on exchange sites, and hence, the monovalent K cation would be more available for movement with the leachate (Novak, Lima, et al., 2009).

In the case of the Norfolk soil, the addition of biochars increased the leaching of Ca, K, and Mg but decreased the leaching of the heavy metal (Cu and Zn) which was most significant at 2% biochars application rates compared to the soil control leachates. During the first month leaching, the concentration of Cu in the Mecklenburg soil leachate was zero which means that the Cu was totally retained by the soil. This may be due to the combined effect of the biochar and the high concentration of clay in the Mecklenburg soil compared to the Norfolk soil.

Similar data were reported by several studies. For instance, Lehmann, Da Silva, et al. (2003) showed that in Amazonian Dark Earths that contain large amounts of aged biochar, leaching of Ca was approximately 20% lower than in oxisols with low biochar contents. Dunisch et al. (2007) also found that biochar/ash mixtures impregnated with fertilizer in the laboratory leached proportionally lower amounts of nutrients back into deionized water when compared to equal weights of wood feedstock.

Leaching of nutrients from agricultural soil depletes soil fertility, increases the need for artificial or organic fertilizer input, and leads to eutrophication of ground and surface waters (Laird et al., 2010). Evidence from several laboratory and field studies show that biochar application can reduce nutrient leaching from soil (Ding et al., 2010; Lehmann, Da Silva, et al., 2003; Novak, Lima, et al., 2009; Steiner et al., 2008). The capability of biochar to retain nutrients is mainly attributed to biochars (often) great surface area providing adsorption sites for inorganic nutrients (bound by ion and covalent bindings). Moreover biochars apparent ability to increase the water holding capacity of soils may improve nutrient retention time in the topsoil.

The attachment to biochar of organic matter or minerals with sorbed nutrients (aggregation) may further increase the nutrient retention (Glaser et al., 2002). Lehmann, Czimczik, Laird, and Sohi (2009) also reported that biochar can change the pore-size distribution of the soil and possibly alter percolation patterns, residence times of soil solutions and flow paths. Moreover; the high porosity of biochar is accompanied with by high surface areas to which both hydrophilic and hydrophobic molecules can sorb, depending on the functional groups displayed on the biochars. These results show that biochar may contribute to an increase in ion retention of soil and to a decrease in leaching of dissolved organic matter and organic nutrients.

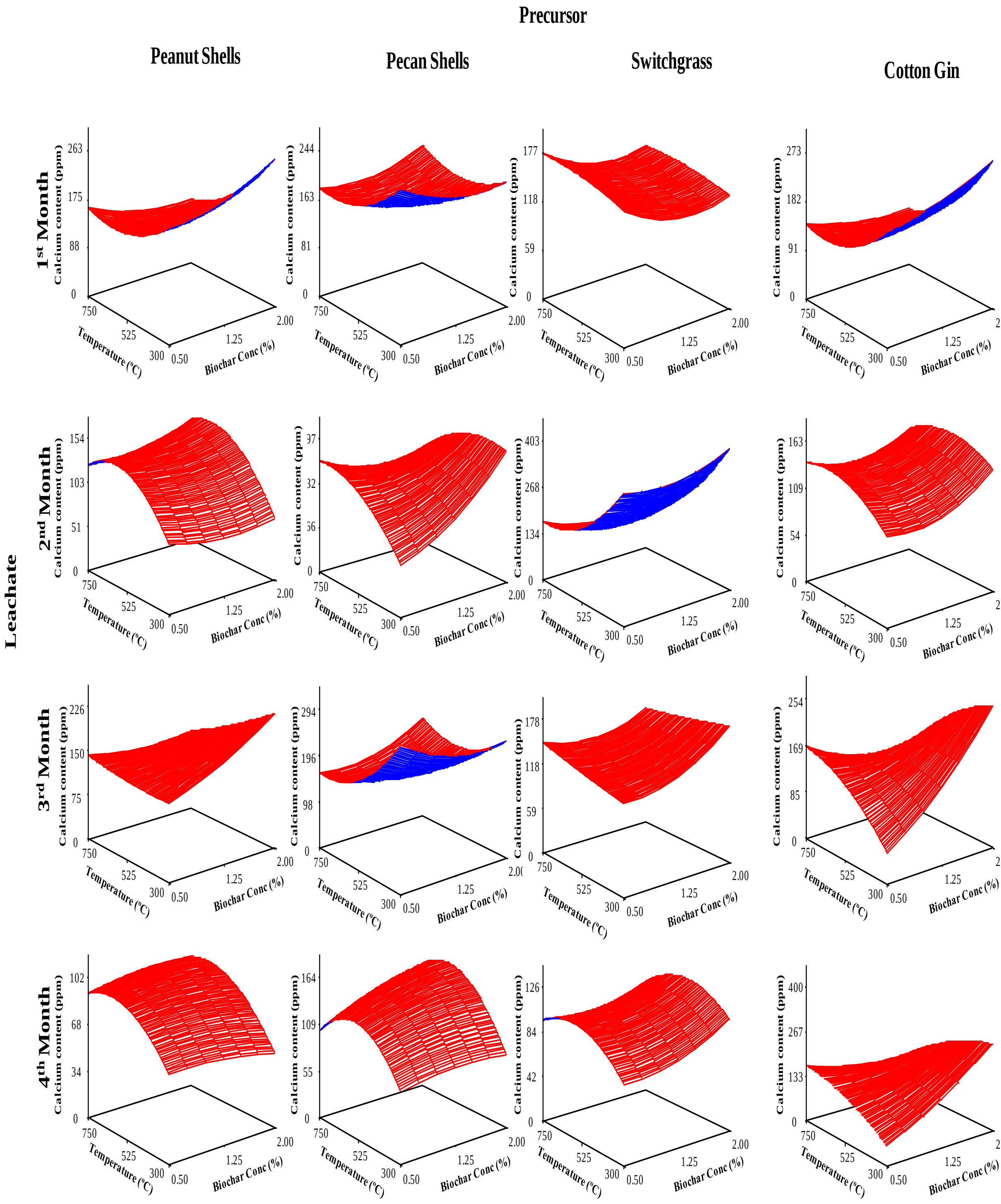

Figure 4.30. Effect of pyrolysis temperature and carbon application rate on calcium in Mecklenburg soil leachates.

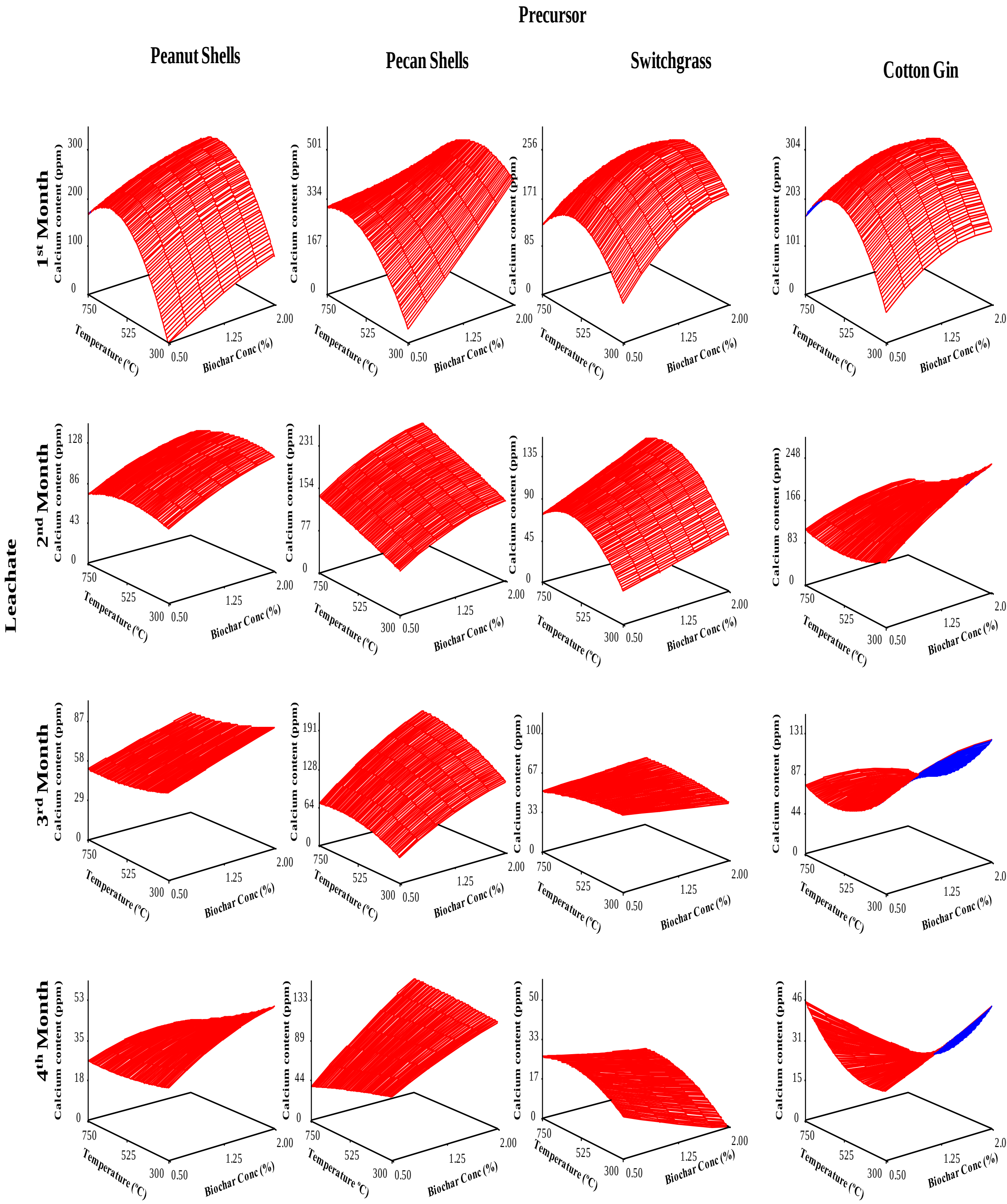

Figure 4.31. Effect of pyrolysis temperature and carbon application rate on calcium in Norfolk soil leachates.

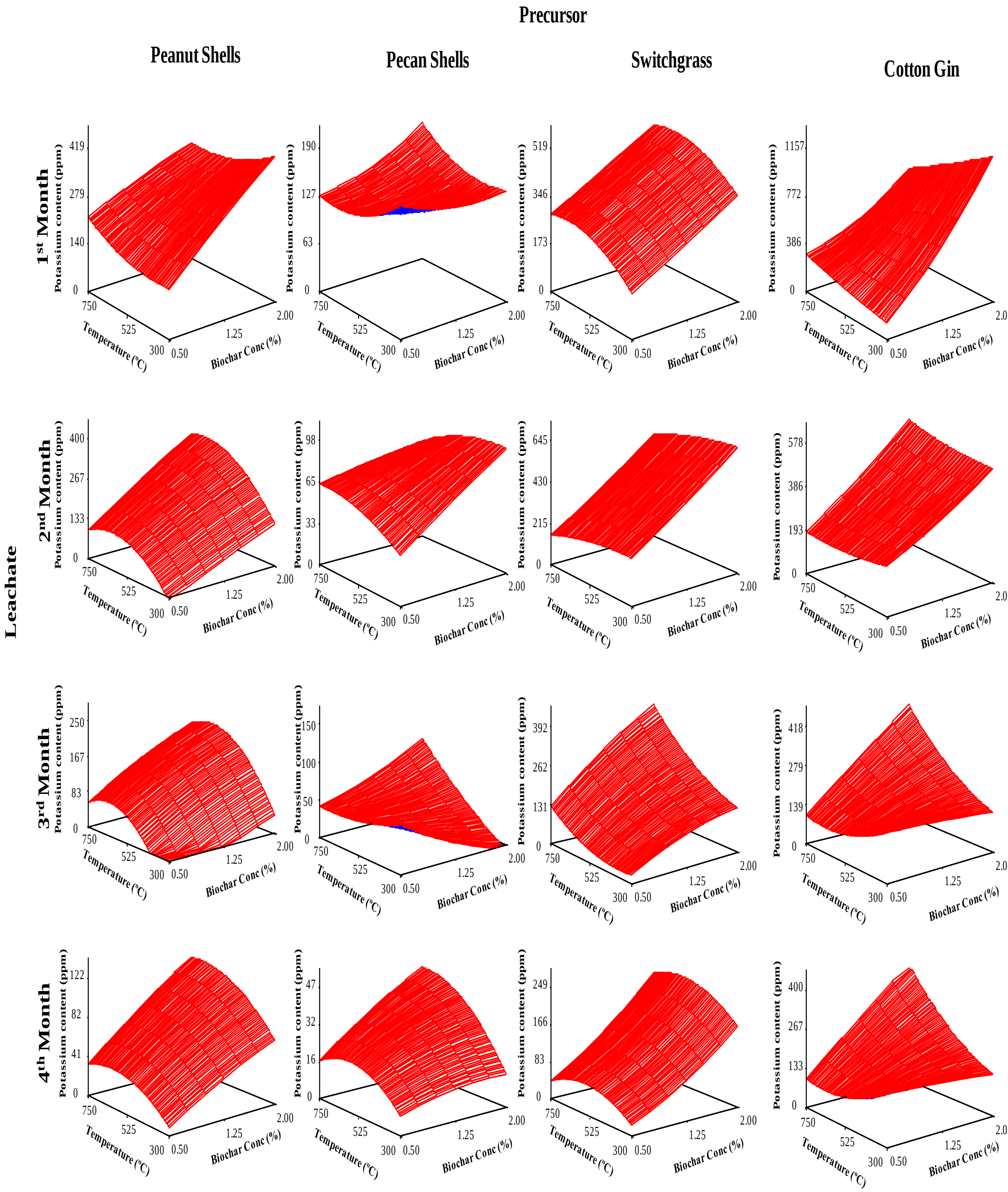

Figure 4.32. Effect of pyrolysis temperature and carbon application rate on potassium in Mecklenburg soil leachates.

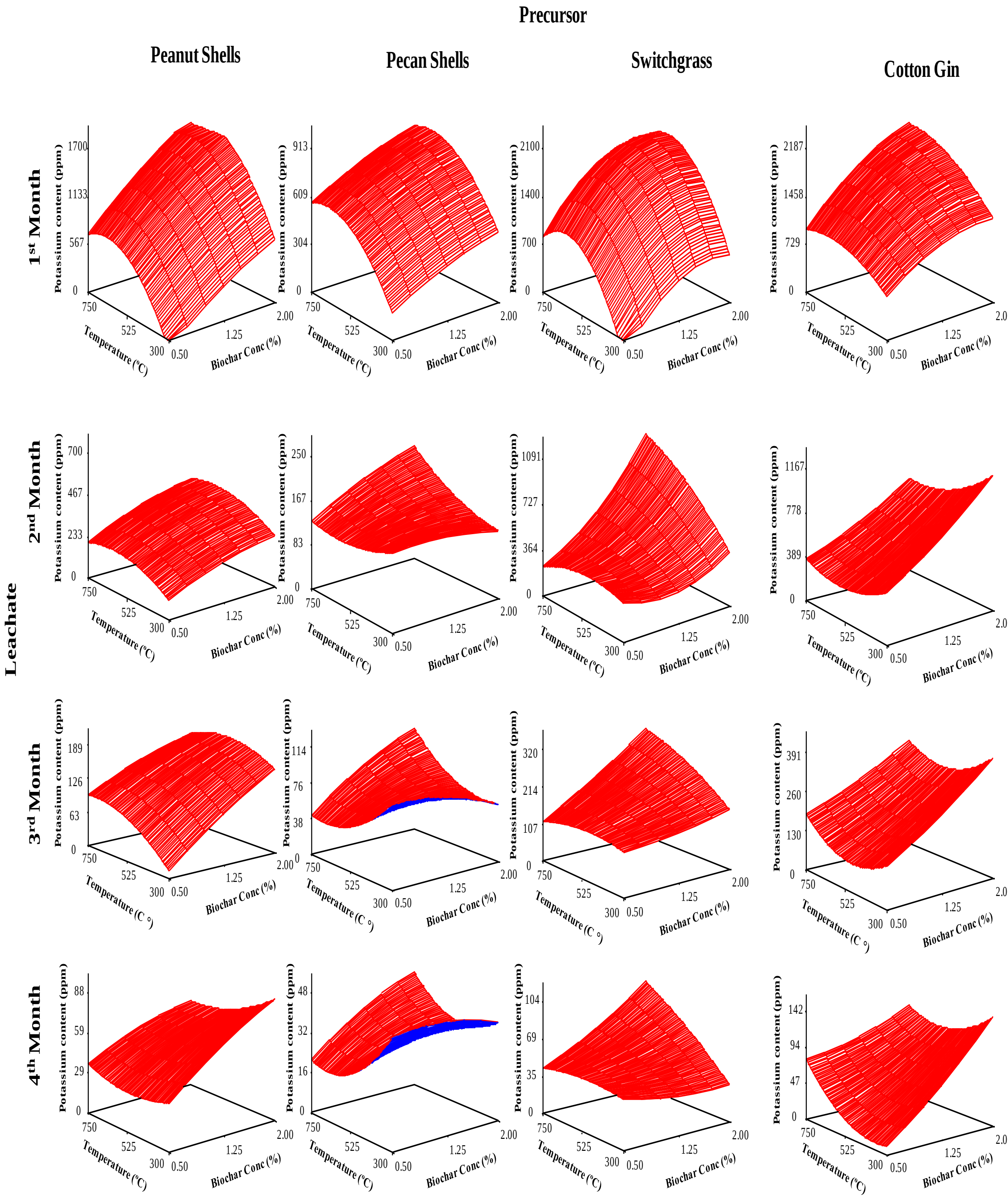

Figure 4.33. Effect of pyrolysis temperature and carbon application rate on potassium in Norfolk soil leachates.

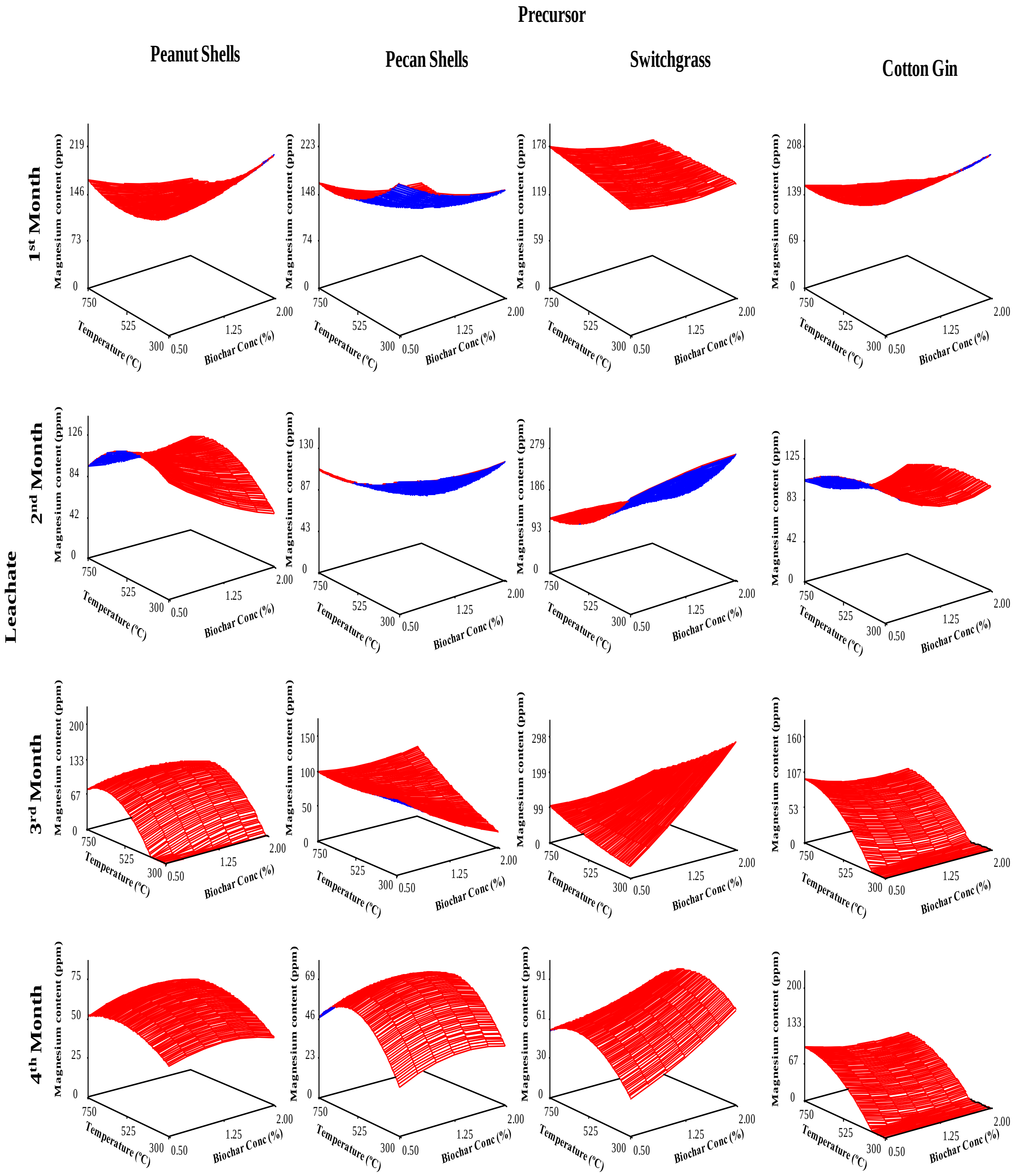

Figure 4.34. Effect of pyrolysis temperature and carbon application rate on magnesium in Mecklenburg soil leachates.

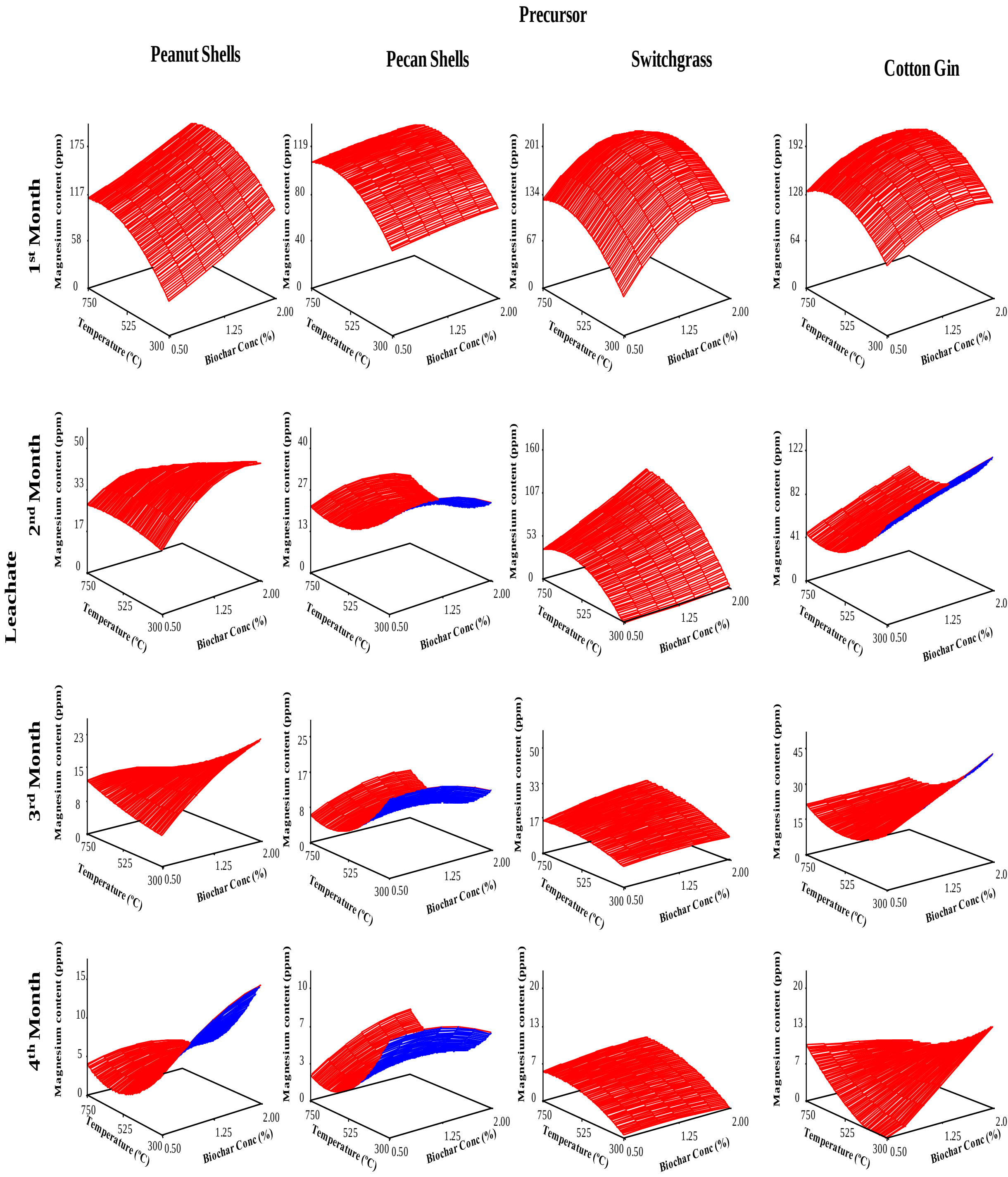

Figure 4.35. Effect of pyrolysis temperature and carbon application rate on magnesium in Norfolk soil leachates.

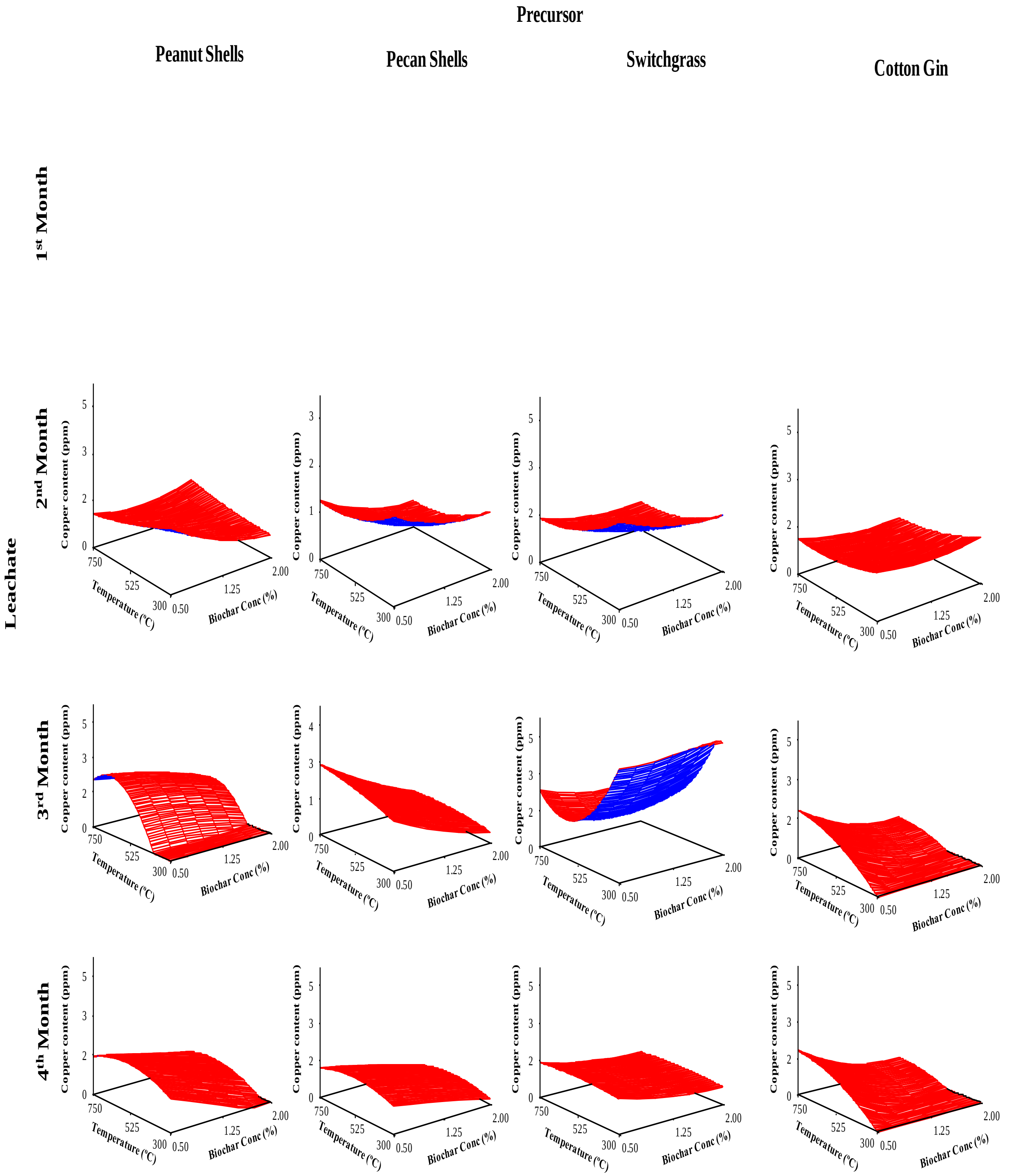

Figure 4.36. Effect of pyrolysis temperature and carbon application rate on copper in Mecklenburg soil leachates. Note: the concentration of Cu was below detection limit for the first month.

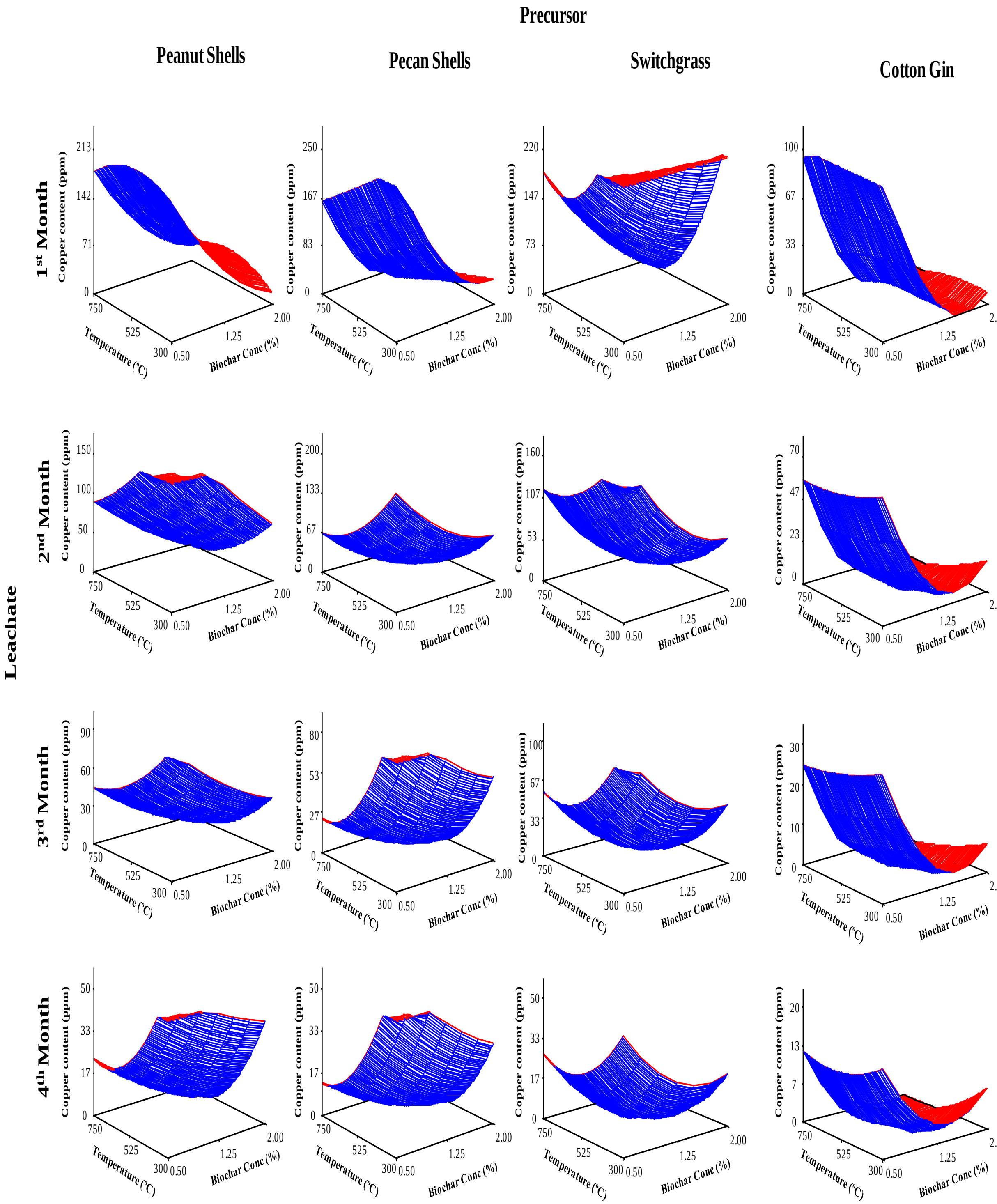

Figure 4.37. Effect of pyrolysis temperature and carbon application rate on copper in Norfolk soil leachates.

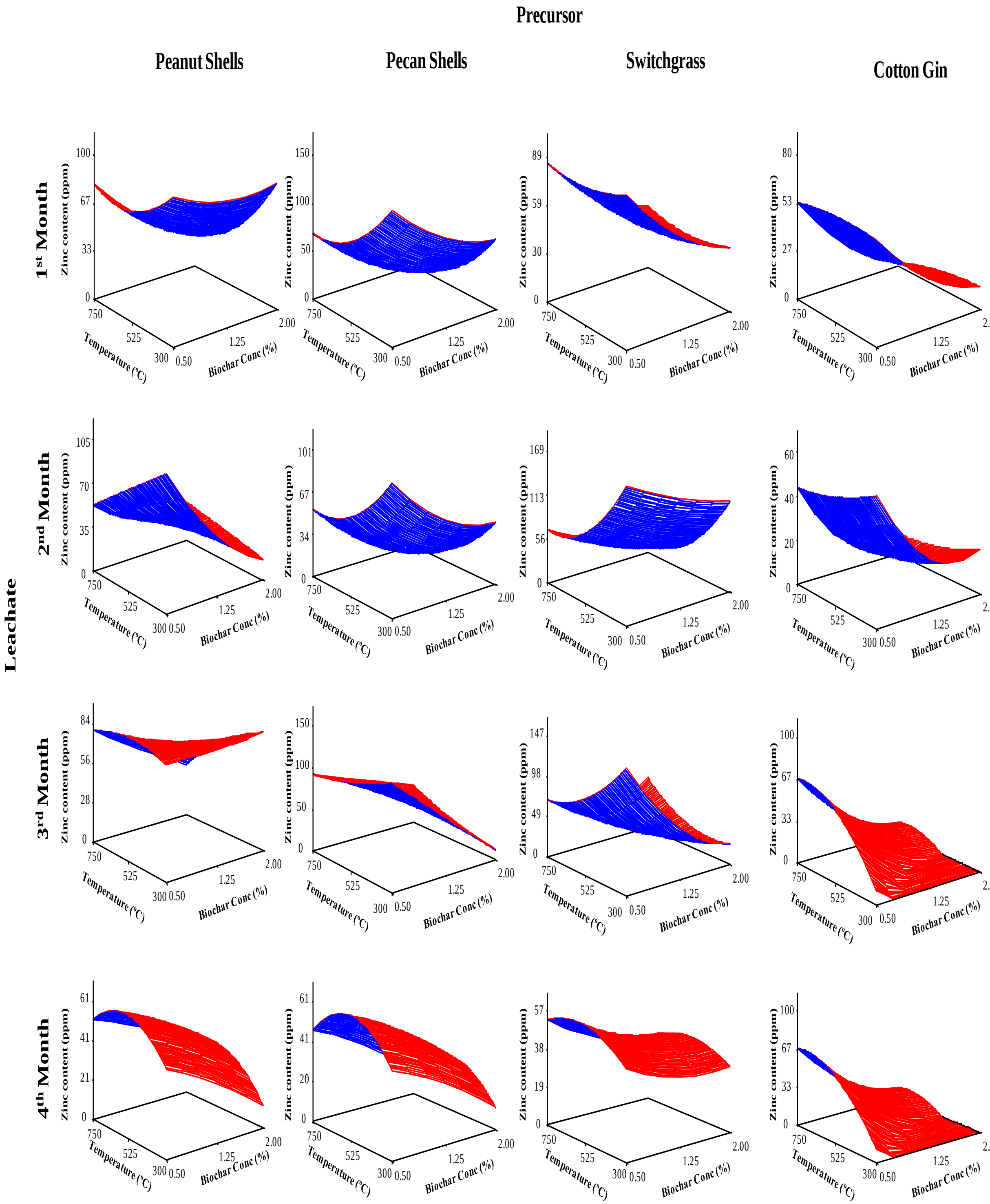

Figure 4.38. Effect of pyrolysis temperature and carbon application rate on zinc in Mecklenburg soil leachates.

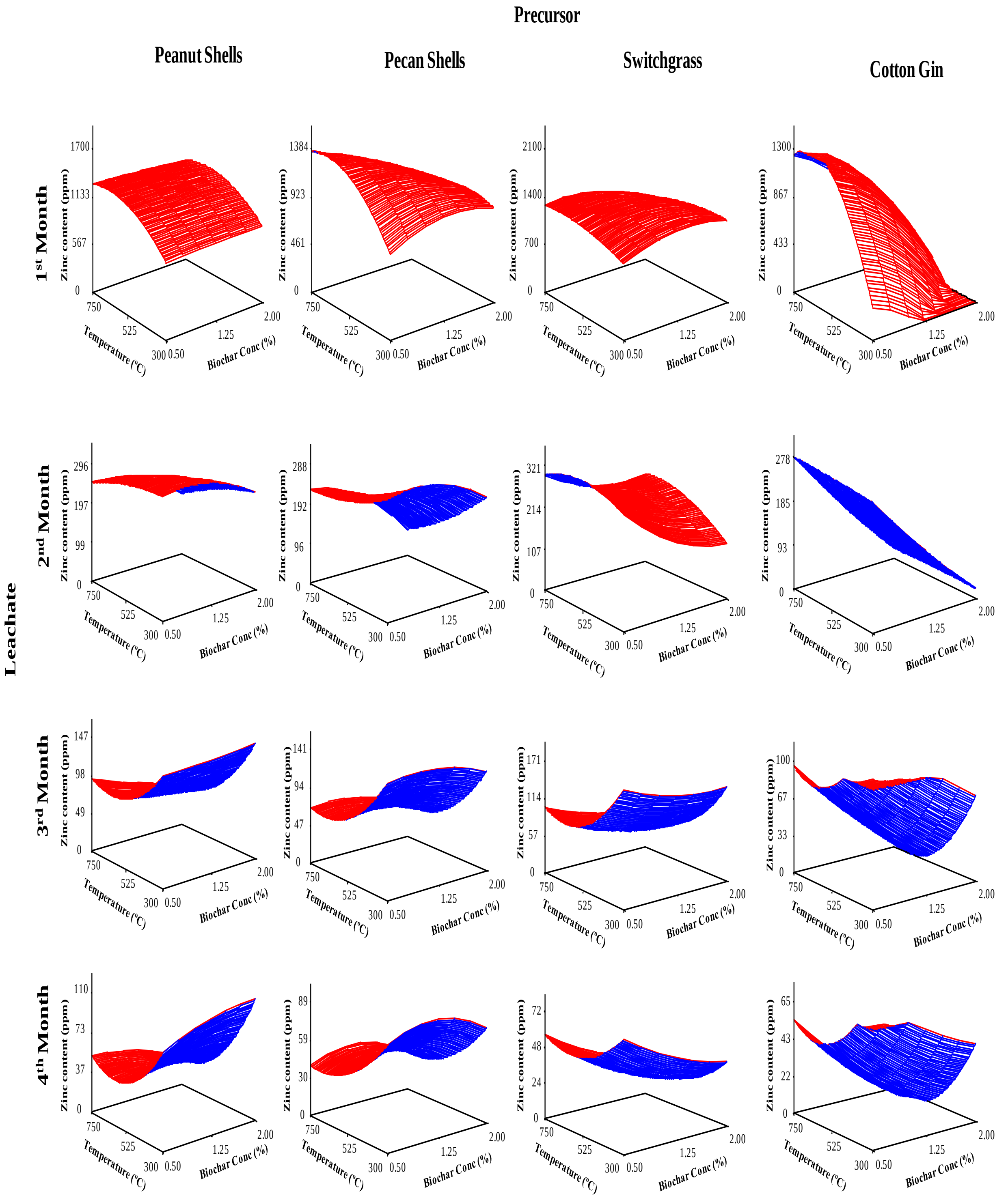

Figure 4.39. Effect of pyrolysis temperature and carbon application rate on zinc in Norfolk soil leachates.

4.3. Selection of the Best Biochars

Following 150 days of biochars-soil incubation, cluster and principal components analysis were used to select the best biochars based on a set of the most important soil parameters for plant growth (pH, CEC, EC, TC, water holding capacity, aggregate stability, leachate C/N ratio, DOC, atrazine content, micro and macronutrients). The soil characteristics play an important role in the plant's ability to extract water and nutrients. If plants are to grow to their potential, the soil must provide a satisfactory environment for plant growth.

For instance, the soil pH is one of the most important soil properties that affects the availability of nutrients. Macronutrients tend to be less available in soils with low pH and micronutrients tend to be less available in soils with high pH. For plants to be healthy, they need a steady supply of nutrients from the soil. Nitrogen (N), phosphorus (P), potassium (K), sulfur (S), calcium (Ca) and magnesium (Mg), are required in relatively large quantities (macronutrients). Others are required in small quantities (micronutrients) such as: copper (Cu), zinc (Zn) and manganese (Mn). A shortage or absence of any one of these essential nutrients can severely retard plant growth (Miller, Donahue, & Shickluna, 1977).

The best biochars were then used in the GHGs emission experiment and plant growth trails using lettuce as a model crop. The output of cluster and principal components analyses are presented in Figures 4.40, 4.41, 4.42, and 4.43. The codes in cluster and principal components graphs represent the name of biochar precursors (CG = Cotton Gin, SW = Switch Grass, PC = Pecan Shells, and PS = Peanut Shells) followed by their production conditions and application rate. The control (soil + 0% biochar) was coded with the first letter of the soil type used (P = Piedmont and N = Norfolk). The cluster on the right side of the graph (highlighted in bold) represent the biochars treatments most different from the soil control treatment (on the left side of the graph) in terms of all the soil characteristics.

Cluster analysis is concerned with forming groups of similar objects based on several measurements of different kinds made on the objects. The key idea is to identify classifications of the objects that would be useful for the aims of the analysis. In our study, we used the analysis to identify the best biochar treatments based on their positive effect on soil properties which will in return have a positive effect on the plant growth and productivity. Figure 4.40 represents different clusters of treatments that are significantly different from the control treatment (soil without biochar addition) and other treatments. The farthest cluster from the control treatment in terms of variables used (pH, CEC, EC, TC, bulk density, water holding capacity, aggregate stability, leachate C/N ratio, DOC, atrazine content, micro and macronutrients), indicates the best performing carbons.

Principal component analysis was used to produce a scatter plot of the relationship between the control treatment (soil without biochar addition) and the actual treatments (soil with biochar addition) in terms of their fertility characteristics (Figure 4.41). Three quadrants were separated by the intersection of the zero values along the x and y axes. The biochar treatments most similar to control treatment are expected to cluster in the quadrant containing the latter.

Results of principal component and cluster analyses (Figures 4.40 and 4.41) were used to determine the cluster that is the most significantly different from the control treatment (PCon0) and from other treatment clusters and revealed the ten best treatments selection as shown below. From the four precursors, only two (cotton gin and switchgrass) were selected by the multivariate analysis based on their ability to enhance soil fertility parameters compared to the two remaining precursors (pecan and peanut shells), especially in term of pH, CEC.

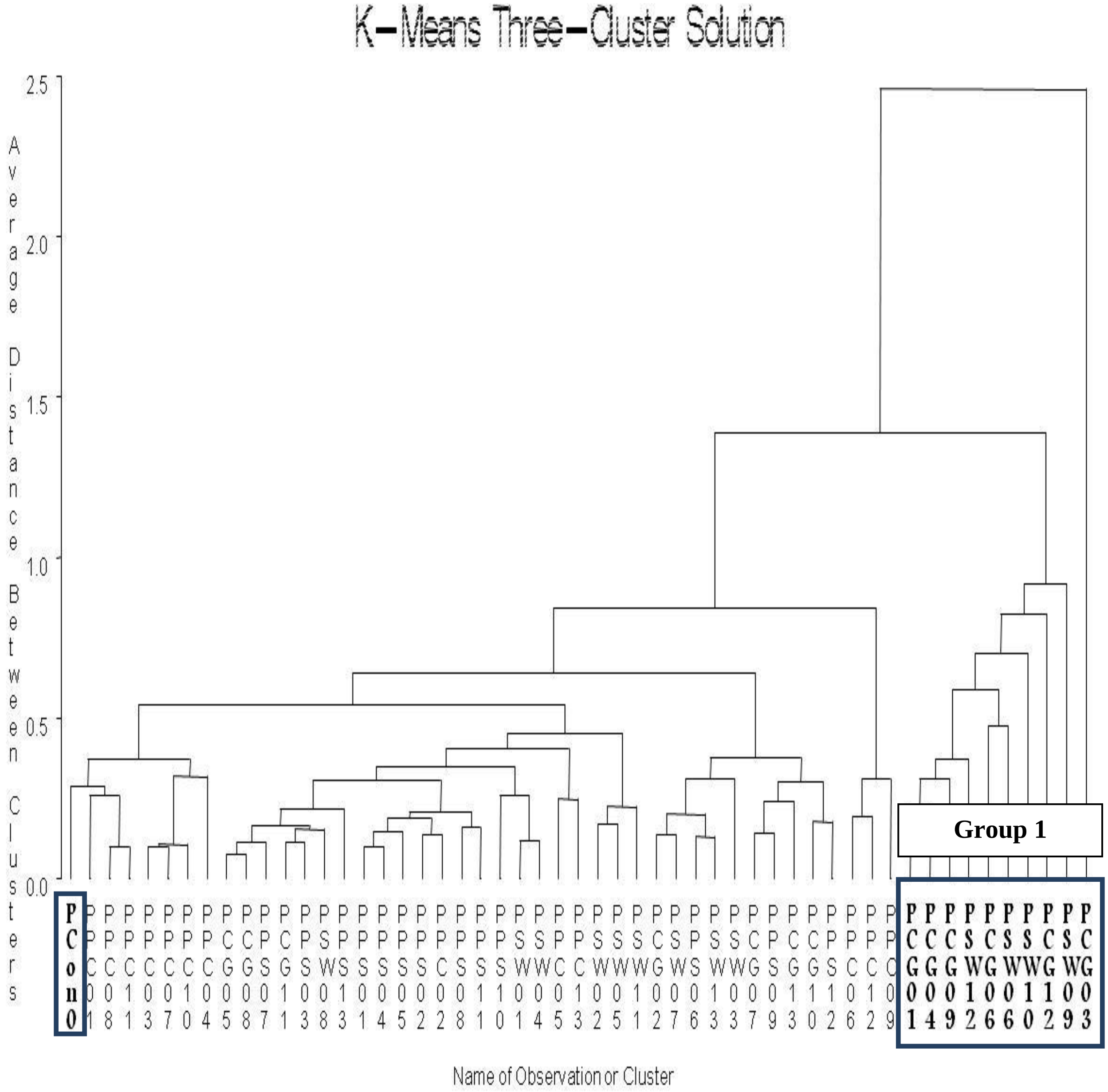

Figure 4.40. Cluster analysis for the selection of the best biochars based on their impact on soil properties.

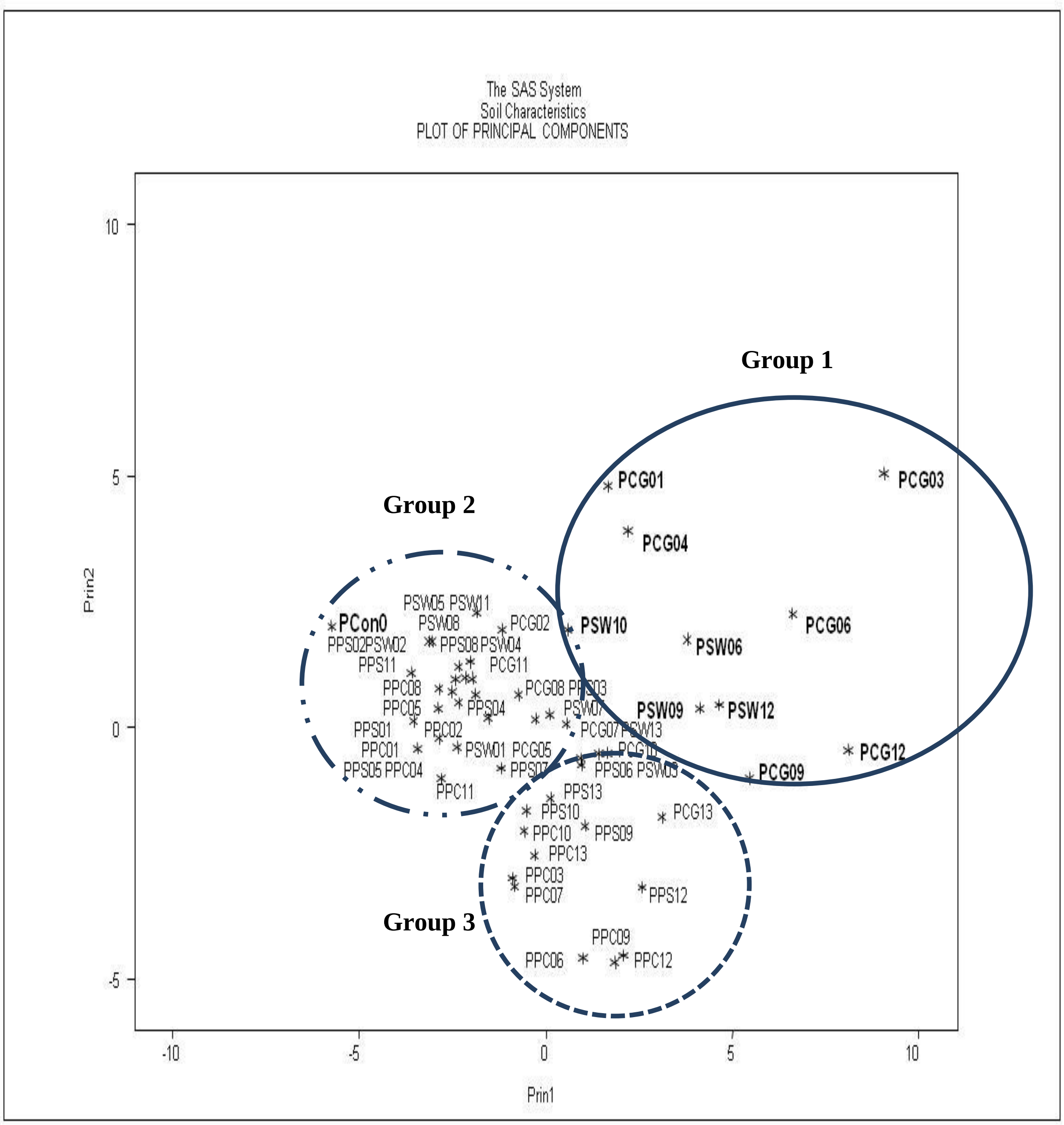

Figure 4.41. Principal components analysis for selection of the best biochars based on their effect on soil properties and dissimilarities with untreated control soil samples.

The ten selected biochars from the clusters (upper right quadrant or Group 1) showed higher pH, CEC, phosphorus, potassium, magnesium concentrations, better water holding capacity and atrazine adsorption in treated soils compared to the control and other treatments (Groups 2 & 3). Biochars cluster in Group 2 and the control treatment (PCon0) were similar in terms of pH, CEC, EC, aggregate stability.

Generally, results of cluster analysis were in agreement with those of principal component analysis. Both techniques revealed that ten biochar (Table 4.2) treatments (PCG01, PCG03, PCG04, PCG06, PCG09, PCG12, PSW06, PSW09, PSW10, and PSW12) were significantly different from the control treatment in most properties used and, thus would make good choices for use in plant growth and decreasing GHGs emission.

Table 4.2

Selected biochars and their codes

Treatment Code	**Precursor Type**	**Pyrolysis Temp (°C)**	**Pyrolysis Time (Hrs)**	**Application rate (%)**
PCG01	Cotton Gin	300	8	1
PCG03	Cotton Gin	300	16	2
PCG04	Cotton Gin	300	24	1
PCG06	Cotton Gin	500	4	2
PCG09	Cotton Gin	500	12	2
PCG12	Cotton Gin	750	2	2
PSW06	Switchgrass	500	4	2
PSW09	Switchgrass	500	12	2
PSW10	Switchgrass	750	1	1
PSW12	Switchgrass	750	2	2

Another cluster and principal component analysis were used to select the top 2 best biochars from the initially selected cluster containing 10 biochars as shown in the graphs below (Figures 4.42 and 4.43). Since it was hard to make a good selection from the group as they are very close in terms of their effect on the soil fertility, a secondary selection was carried out based on the biochars that have highest yield and that require less energy for production (lower pyrolysis time and temperature).

The two best biochars selected based on the primary clustering, principal component analysis, and the above secondary inclusion criteria were biochars produced from switchgrass and cotton gin at 500 °C pyrolysis temperature and 4 hours pyrolysis time and used at the 2% application rate (PCG06 and PSW06). Figure 4.43 shows that all the clusters (groups 1, 2, and 3) are different from the control treatment in term of the soil fertility mentioned above.

The following group of biochars (PCG09, PSW09, PSW10, PCG12, and PSW12) was excluded because of their low carbon yield and high energy consumption during production. The remaining group was not selected (PCG01, PCG03, and PCG04) due to their low effect on the soil pH, CEC, water holding capacity, and atrazine adsorption compared to the two selected as best biochars (PCG06 and PSW06).

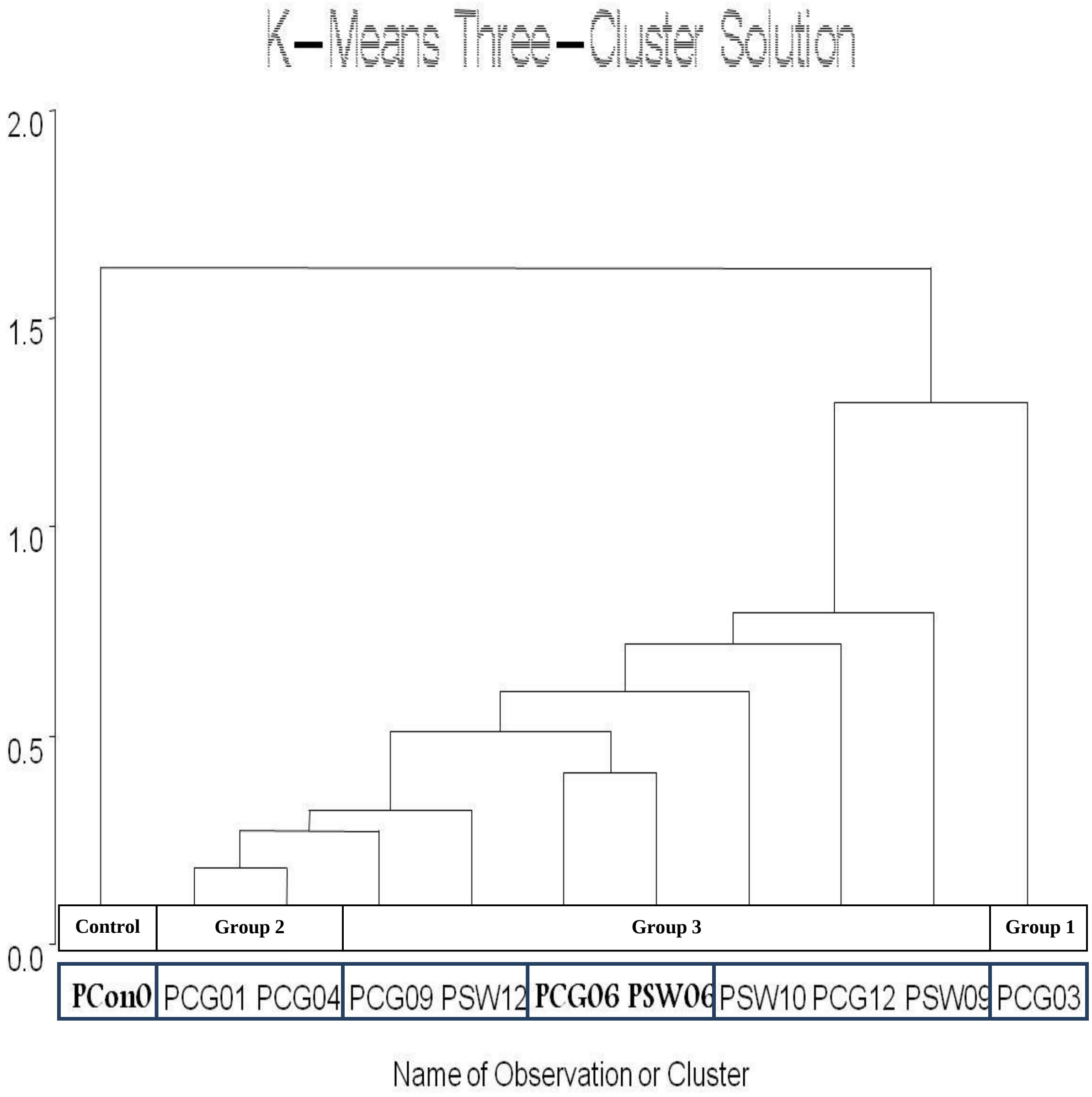

Figure 4.42. Cluster analysis for the selection of the best biochars based on biochar effect on soil properties.

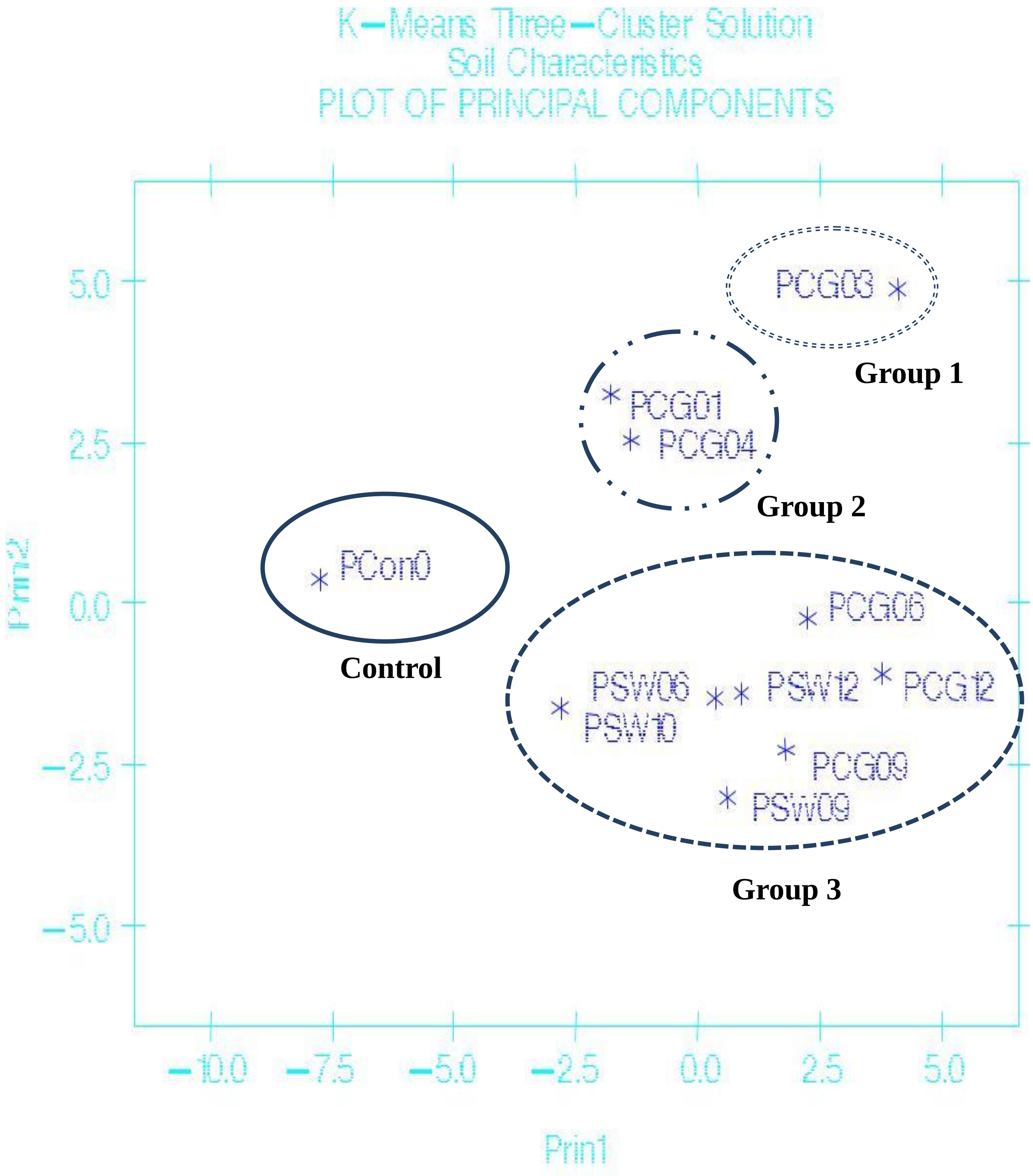

Figure 4.43. Principal components analysis for the selection of best biochars based on performance as soil amenders.

4.4. Green House Gas Emission Experiment

After the selection of the two best biochars, the latter were used in soil incubation experiments designed to determine their effect on the greenhouse gases (GHGs) emission by performing measurements of two GHGs (CO_2 and CH_4) productions from batches of precursors and corresponding biochars in sealed glass vials.

Figures 4.44 and 4.45 show CO_2 flux over the study period. Carbon dioxide flux is an indicator of decomposition and microbial activity. The CO_2 flux reached its maximum on the 11th day of incubation and then remained steady throughout the incubation period for the soil mixed with raw feedstocks. The lack of change after the 11th day suggests that the raw material decomposed rapidly and nitrification took place, leaving no additional organic CO_2 production.

As expected, the CO_2 emission increased sharply during the first two weeks of incubation for the soil containing raw feedstocks. The biochar incubated alone did not show any gas emission during the entire 10 weeks incubation indicating a higher degree of recalcitrant C in the biochars produced at 500 °C and the removal of most of the volatile compounds during the pyrolysis process at 500 °C.

The addition of biochars to soil did not show any significant difference CO_2 emission compared to the soil control (without biochar). The same trend was seen in both types of biochar, except in the cotton gin biochar where the CO_2 emission was slightly higher in the soil with biochars compared to the soil control (without biochar). This could be attributed to the presence of dirt in the feedstock itself.

The presence of organic matter in the soil (native soil organic C) has triggered the CO_2 emission during the incubation which explains why the soil control (soil without biochars or raw material) showed emission of CO_2 gas.

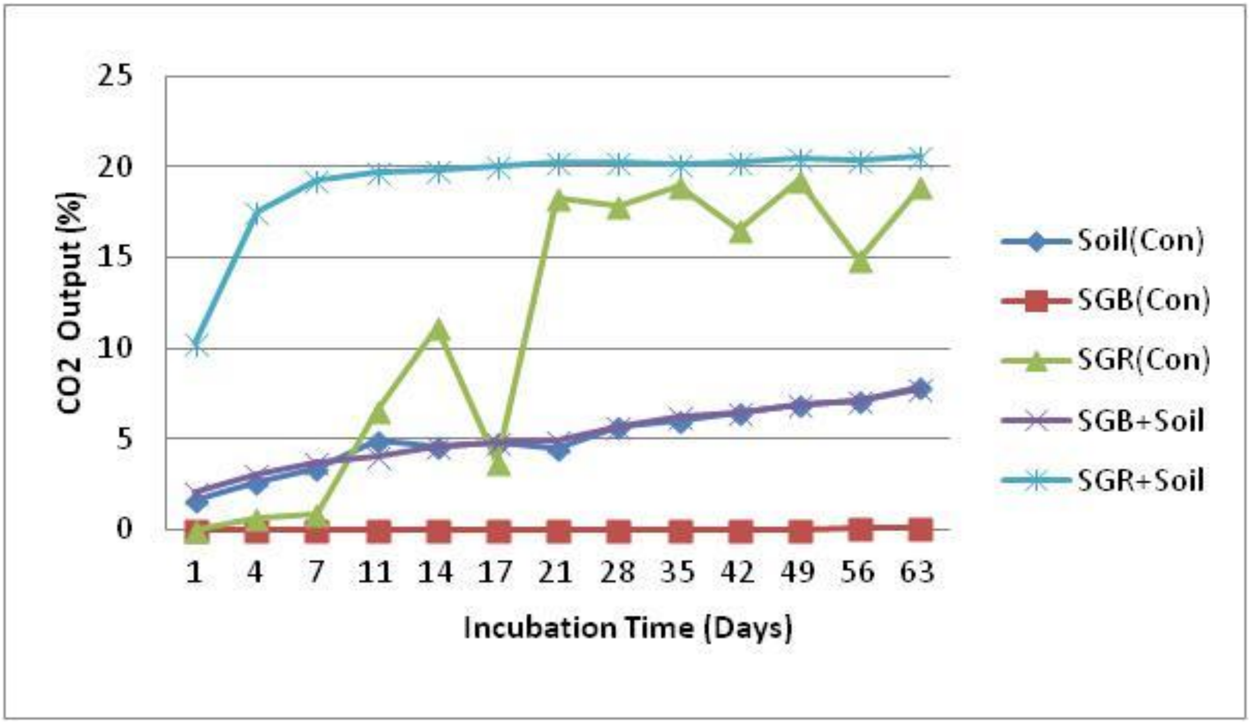

Figure 4.44. Soil CO_2 production for switchgrass biochar.

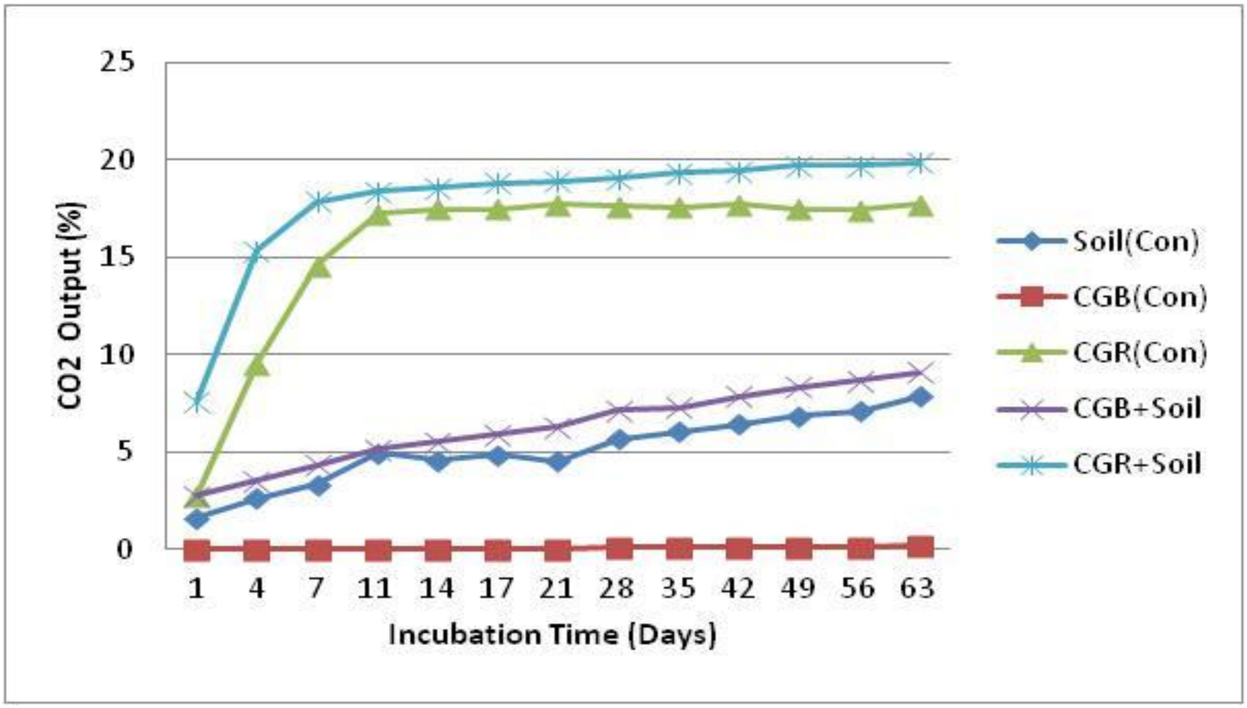

Figure 4.45. Soil CO_2 production for cotton gin biochar.

The observed difference in the CO_2 emission between the soil treated with raw material (Low C:N ratio) and biochars (High C:N ratio) suggests that the treatments with lower C:N ratio were more easily mineralized and the probability of nitrification and de-nitrification was high. The C:N ratio had a significant negative relationship on the rate of mineralization which also suggests the high C:N ratio posed a nutrient limitation on decomposers during the decomposition phase (Spokas, Koskinen, Baker, & Reicosky, 2009).

Spokas and Reicosky (2009) reported both increases and decreases in CO_2 emissions from soils amended with 16 different types of biochar, suggesting that biochar quality has a significant influence on the interaction between biochar and soil organic matter. In another study where biochar was mixed with dried swine manure, biochar addition consistently increased CO_2 emission relative to no-biochar controls with cumulative CO_2–C emissions equivalent to 17 to 23% of biochar C applied (Rogovska et al., 2011).

Smith, Collins, and Bailey (2010) also reported an increase in CO_2 production from soil amended with biochar produced from switchgrass at 500 °C for two hour. The increase went up with increasing rates of biochar application. However, the effect diminished by day 6 of the incubation indicating that most of the biochar carbon is slowly decomposing suggesting that there is a distinct labile C pool associated with young biochar that may be significant in the short-term. It is likely that a fraction of the condensates from the bio-oil formed during pyrolysis absorbed to the biochar during cooling. These condensates are likely the source of the labile C pool and thus do not originate from the stable carbonized components of the biochar.

Since only about 10 to 20% of the soluble component is mineralized to CO_2, it is probable that the aromatic and aliphatic compounds may precipitate forming larger more complex molecules (Smith et al., 2010). In the long-term, we suggest these materials would be resistant to decomposition and would become part of the slow to resistant C pools in soils. Thus the claims in the literature that the greenhouse effect of increased CO_2 could be reduced by converting organic biomass to biochar and used as a soil amendment may have merit (Smith et al., 2010).

Jones et al. (2011) stated that a mixed hardwood derived biochar, produced at 450 °C for 48 hours, induced a net release of CO_2 from the soil; however, this C loss was very small relative to the amount of C stored within the biochar itself (0.1%). Although biochar-induced significant changes in the physical characteristics of the soil, overall this made no contribution to changes in soil respiration suggesting that biochar consistently repressed soil organic matter (SOM) turnover over the 3 week experimental period.

This response could be due to a range of mechanisms including: (a) The biochar induced release of soluble humic substances which bind to and inhibit extracellular enzymes involved in SOM breakdown; (b) Sorption of extracellular enzymes on the biochar surface causing inactivation and a spatial disconnect with potential substrates (Virchenko, Povzhitkova, Lysenko, & Kozhekova, 1986); (c) Release of labile soluble C from the biochar providing an alternative substrate for the soil microbial community; (d) A biochar-induced shift in soil pH which induces changes in soil microbial structure and function; (e) Sorption of DOC released from SOM preventing movement to microbial consumers; and (f) Biochar induces growth of the microbial community which partitions more SOM-derived C into anabolic versus catabolic microbial processes causing an apparent reduction in CO_2 release from soil organic matter (Blagodatsky, Blagodatskaya, Yuyukina, & Kuzyakov, 2010).

4.5. Plant Growth Experiment

A greenhouse study investigated a short term impact of biochar on crop performance and soil quality over a 53 days period using lettuce as a model crop where two type of biochars previously selected were added to a Mecklenburg soil at different application rates (0%, 1%, and 2% on a dry weight basis). The crop growth parameters were measured during and after the harvest along with the soil fertility analysis.

Lettuce growth parameters are shown in Figures 4.46 through 4.49. Overall, there were no significant differences in the growth performance of the lettuce crop after biochar application ($p > 0.05$) except for the 1% application rate for cotton gin biochar that exhibited a significant difference (decrease) compared to the control treatment and other treatments.

Biochar had no significant effect on the plant height, leaves number, plant shoots and roots dry weights. However, a significant difference was observed for the cotton gin biochar applied at 1% application rate compared to the control treatment ($p < 0.05$) where the control plant dry weight (Figure 4.48), which represent plant yield, was greater than both biochar treatments. The 2% application rate showed a higher number of leaves (Figure 4.47) compared to the 1% application rate and the control but the difference was not statistically significant ($p > 0.05$).

The same observation holds for the plant height where the control plant height was greater than both application rates and precursors but it did not show any significant difference ($p > 0.05$). The number of leaves per plant was increased with biochar application (Figure 4.47).

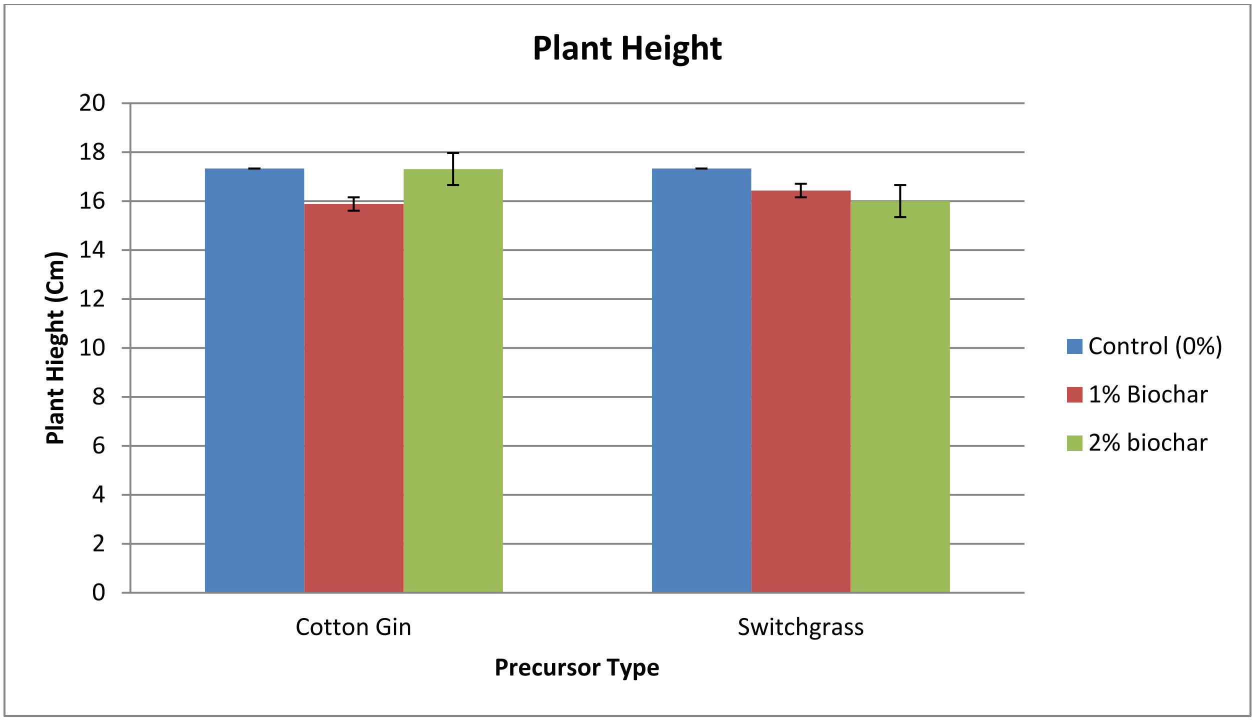

Figure 4.46. Effect of biochar precursor and application rate on the plant height.

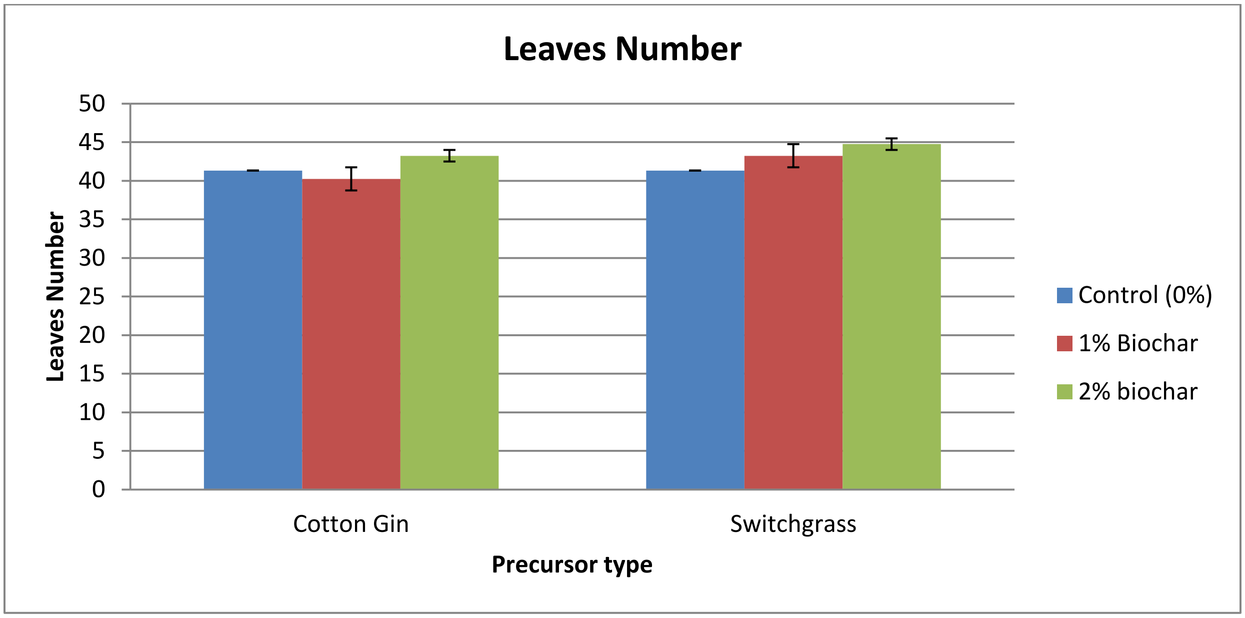

Figure 4.47. Effect of biochar precursor and application rate on the number of plant leaves.

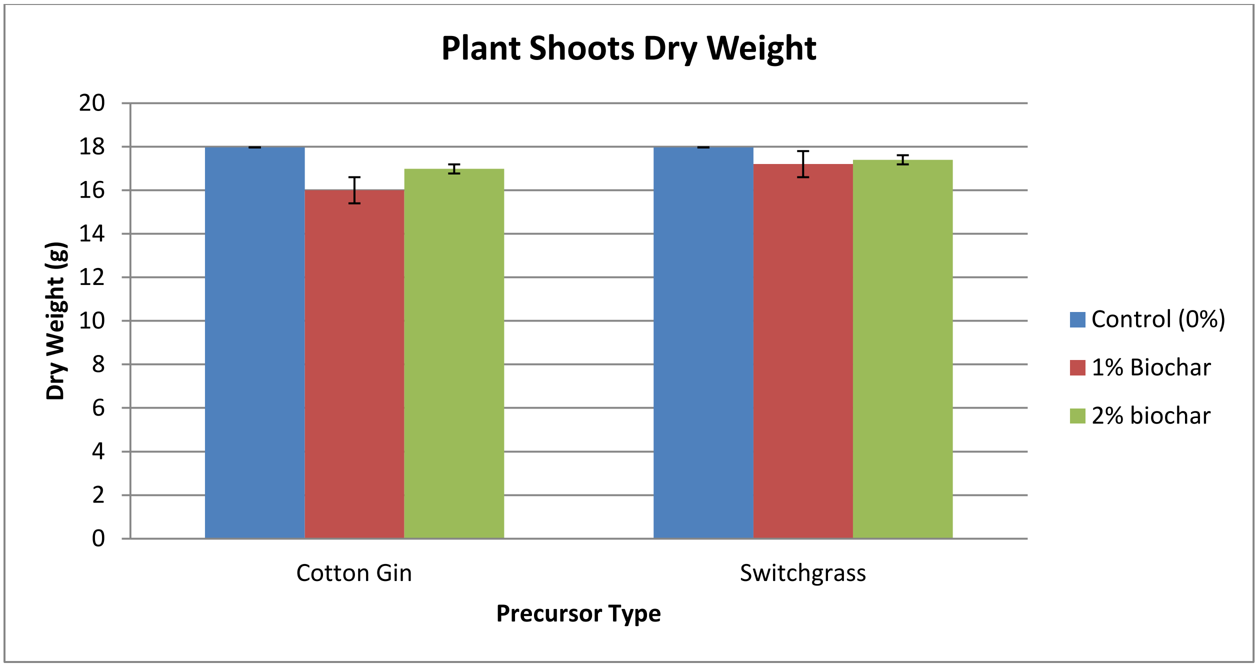

Figure 4.48. Effect of biochar precursor and application rate on dry weight of plant shoots.

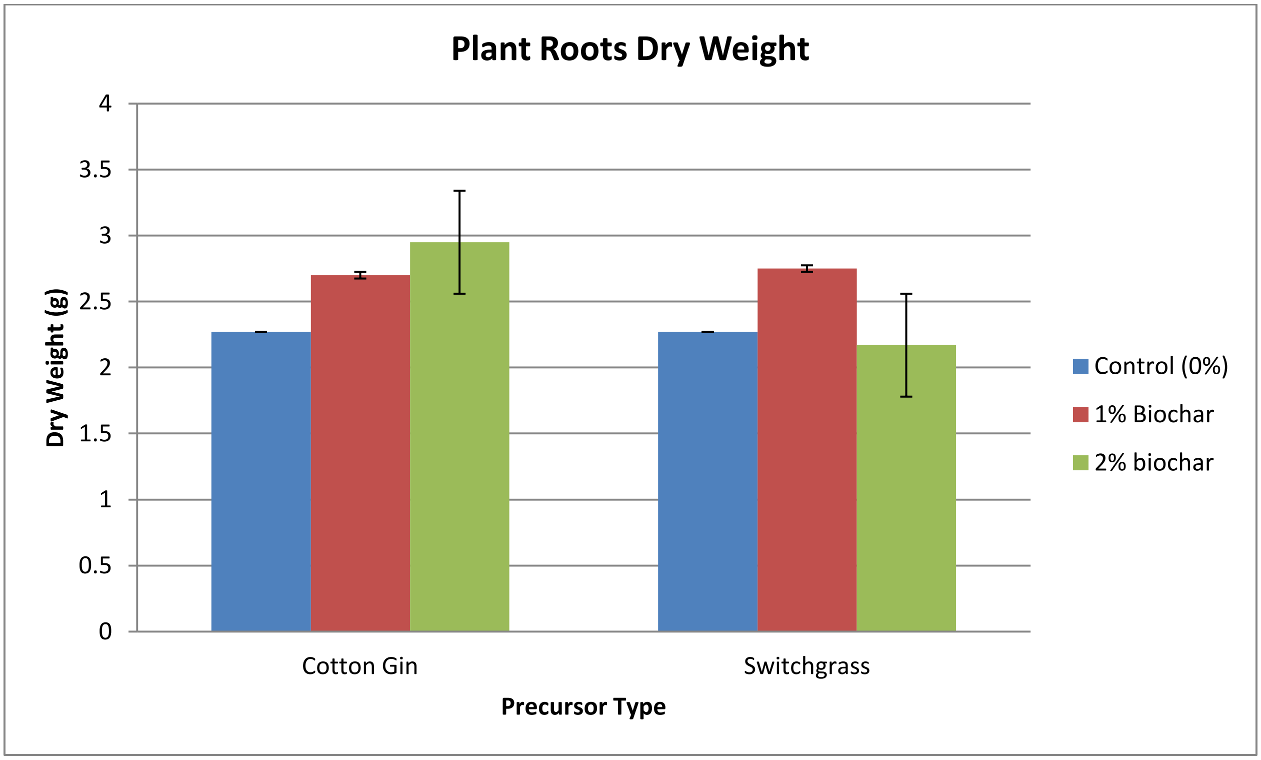

Figure 4.49. Effect of biochar precursor and application rate on dry weight of plant roots.

Results for soil fertility properties sampled after lettuce harvest under the different biochar treatments are presented in Table 4.3. Biochar amendments of soils used in plant growth significantly increased ($p < 0.05$) soil pH, CEC, P, K, Mn, and sulfur concentrations but had no effect on humic matter (HM), Mg, Cu, and Zn in both cotton gin and switchgrass biochars treatments (Table 4.3). No significant difference was observed between cotton gin and switchgrass biochars treatments in term of CEC. However, a significant difference in soil pH was observed between the two biochars where the cotton gin biochar treatment induced a higher soil pH compared to the switchgrass treatment probably due to the high concentrations of the base cations in the cotton gin biochar. Overall, the soil HM, pH, CEC, P, K, S increased as the biochar application rate increased in both biochar types (Table 4.3).

Earlier studies have shown that biochar amendments increased crop productivity by improving the physical and biochemical properties of cultivated soils (Asai et al., 2009; Major, Rondon, Molina, Riha, & Lehmann, 2010). Crop response to biochar amendment depends on the chemical and physical properties of the biochar, climatic conditions, soil conditions and crop type (Zwieten, Kimber, Morris, et al., 2010; Yamato, Okimori, Wibowo, Anshori, & Ogawa, 2006; Gaskin et al., 2010; Haefele et al., 2011).

Asai et al. (2009) reported a decreased yield of upland rice (Oryza sativa L.) following application of biochar amendment without N fertilization in an N deficient soil. In another study, this author also found a significant increase in rice yield with a biochar application rate of 4 t/ha. However, Kimetu et al. (2008) reported the cumulative maize yield to double after three repeated biochar applications of 7 t/ha over 2 years in a degraded Ultisol (an acid, highly weathered and nutrient poor soil) from Kenya. Similar results were reported by Blackwell, Riethmuller, and Collins (2009) in poor tropical soils using high biochar application rates.

Table 4.3

Soil fertility parameters following plant growth

Parameter	**Treatment**					
	Initial Soil*	**Control Soil**	**Soil+CG**	**Soil+CG**	**Soil+SG**	**Soil+SG**
Application Rate (%)	0	0	1	2	1	2
HM (%)	0.36	0.48 ± 0.10^{a}	0.47 ± 0.10^{a}	0.49 ± 0.09^{a}	0.50 ± 0.08^{a}	0.53 ± 0.10^{a}
CEC	6.3	6.67 ± 0.32^{a}	7.43 ± 0.45^{ab}	8.05 ± 0.24^{abc}	7.20 ± 0.36^{ab}	7.90 ± 0.26^{abc}
pH	5.9	5.97 ± 0.06^{a}	6.65 ± 0.06^{b}	7.25 ± 0.06^{c}	6.30 ± 0.08^{d}	6.60 ± 0.08^{e}
P-kg/ha	52.8	94.40 ± 11.34^{a}	145.20 ± 13.93^{b}	182.40 ± 10.18^{c}	135.60 ± 13.36^{d}	177.00 ± 12.30^{e}
K-kg/ha	70.38	80.81 ± 33.71^{a}	497.55 ± 26.97^{b}	1016.60 ± 41.26^{c}	372.43 ± 39.32^{d}	925.70 ± 44.74^{e}
Ca-kg/ha	22400	23200 ± 400^{a}	23300 ± 200^{a}	22900 ± 383^{a}	22100 ± 200^{b}	20500 ± 383^{b}
Mg-kg/ha	6323.2	6404.27 ± 140.41^{a}	6444.80 ± 140.41^{ab}	6201.60 ± 140.41^{ac}	6688.00 ± 140.41^{ad}	6323.20 ± 0.00^{ae}
Mn-kg/ha	75.2	90.88 ± 6.25^{a}	112.24 ± 6.12^{ab}	105.84 ± 10.37^{ab}	104.64 ± 7.71^{ab}	107.68 ± 7.71^{ab}
Zn-kg/ha	26.48	26.43 ± 0.84^{a}	27.02 ± 1.65^{a}	26.28 ± 0.84^{a}	27.44 ± 1.52^{a}	28.38 ± 1.16^{a}
Cu-kg/ha	2	2.24 ± 0.04^{a}	2.30 ± 0.08^{a}	2.30 ± 0.10^{a}	2.27 ± 0.10^{a}	2.27 ± 0.06^{a}
S-kg/ha	43.2	127.04 ± 7.21^{a}	150.24 ± 12.50^{b}	164.64 ± 12.31^{b}	139.68 ± 7.03^{a}	143.76 ± 8.74^{a}
Na-kg/ha	46	92 ± 0.00^{a}	92 ± 0.00^{a}	92 ± 0.00^{a}	92 ± 0.00^{a}	92 ± 0.00^{a}

*the initial soil is without fertilizer addition.

On the other hand, Major et al. (2010) showed no change of maize yield in the first year and significant increase in the subsequent 3 years following a single dose of wood biochar at 20 t/ha in a Colombian savanna Oxisol (similar in chemical properties to Ultisols). A significant improvement in maize yield (4%) and population density (15%) was reported during the first year by Laird, Fleming, Wang, and Karlen (2009) after a 4.4 and 8.2 ton/acre (9.8 and 18.4 t/ha, respectively) biochar application rate to a fertile central Iowa soil, and a non-significant increase of 1.5% in the second year.

Lehmann, Kern, et al. (2003) found improved rice growth in an Oxisol when application rates of biochar made from woody material was increased from 95 to 180 t/ha. Similarly, Chan (2007) and Chan, Zwieten, Meszaros, Dowine, and Joseph (2008) showed increasing crop growth from 50 to 100 t/ha when 10 to 50 t/ha of green waste or poultry manure biochar were added to an acid Alfisol. Rondon et al. (2007) reported improved bean growth in response to increasing rates of eucalyptus wood biochar (from 66 to 122 t/ha) addition to a highly weathered savanna soil, but decreasing growth upon further increases of application rate to 188 t/ha.

Improvements in pH or nutrient retention observed for many other locations with poorer soils (Lehmann, Kern, et al., 2003; Steiner et al., 2007; Zwieten, Kimber, Downie, et al., 2010) did not have a large effect on crop growth especially at high application rates, as observed in our study. Similar results were reported by Rajkovich et al. (2012) who stated that biochar made from plant residues such as hazelnut shells, pine, and oak showed little improvement of the relatively fertile Alfisol, with the exception of biochar from corn stover which significantly improved crop growth on average by 16% (range between −36% and +32% depending on pyrolysis temperature and application rates). Pyrolysis of animal manures, food waste, and paper mill waste generated biochars that were either beneficial or detrimental to crop performance.

Chen, Shinogi, and Taira (2010) also reported data showing very different sugar cane growth responses using biochar made from either bagasse or biosolids. These results stress the importance of quantifying yield responses to biochars made from different feedstocks before large-scale application (Rajkovich et al., 2012). Data reported in this study are in agreement with reported literature and point to this conclusion and the need to custom-design carbon for the intended application taking into account the nature of the precursor, charring conditions, and optimal biochar application rate.

CHAPTER 5

Conclusion

This study demonstrated the feasibility of developing biochars that can effectively alter the physicochemical properties of the soil and design biochars that can target specific soil properties such as pH, water holding capacity or aggregate stability.

Biochars produced from different biomass under a range of pyrolysis process conditions exhibited major differences in their physical, chemical and adsorption properties. These dissimilarities were caused by differences among precursors and the effect of the charring conditions. More biochar was recovered at the lower pyrolysis temperatures due to minimal condensation of aliphatic compounds and lower losses of CH_4, H_2 and CO.

Among the eight biochars, switchgrass-derived biochar produced at 750 ºC had the highest surface area (276 m^2/g) followed by pecan shell biochar (185 m^2/g). pH values significantly increased as pyrolysis temperature increases from 300 °C to 750 °C passing from a value of 6 to almost 10 which is probably due to the release of the basic cations such as Ca and Mg during pyrolysis process at increasing temperatures, Biochar produced from cotton gin had the highest pH values ranging between 8.2 and 9.8, followed by pecan shell-based biochar.

Biochars produced at lower temperatures (300 °C) had measurable total surface charge with peanut shells biochar having the highest value (3.16 meq), while biochars produced between 500 and 750 ºC had low or no measurable total surface charge. This is due to the gradual loss of the alkyl aromatic units in the biochars with a variety of oxygen-containing functional groups, including hydroxyl, carboxyl, carbonyl, ether, and lactone structures as the pyrolysis temperature increases.

For all materials, ash contents increased with pyrolysis temperature. Cotton gin biochar exhibited high ash content ranged from 11 to 34% which may be partially attributed to the sand/soil contained in the cotton gin during the collection. The different biochars show dissimilarities in terms of elemental composition. This variability can be attributed to the different feedstocks and different conditions under which the four biochars were produced. K and Mg were most concentrated in the cotton gin biochar, with biochar produced at high pyrolysis temperature having the highest Mg/K concentration, followed by switchgrass.

On the other hand, pecan shells showed a very high concentration of Ca compared to others biochars followed by cotton gin. Overall, higher pyrolysis temperatures resulted in biochars with lower yield, and total surface charges but higher surface areas, pH, and ash contents. The precursors used to produce the two best biochars were cotton gin and switchgrass and were both produced at 500 °C pyrolysis temperature and 4 hours pyrolysis time.

Biochar properties and their effects on soil fertility vary widely with biochar feedstock and processing conditions. Higher pyrolysis temperature and carbon application rate increased significantly the soil pH. This change was observed for all the precursors and at both incubation times (day 1 and day 150). The increased soil pH is attributable to buffering effect of biochars pH.

A significant increase in CEC was observed at low (300 °C) and high (750 °C) temperatures, especially at high biochars concentration (2%) in both soils. Low pyrolysis temperature (300 °C) may have contributed to the relatively high level of surface oxidation of the biochars and hence the significant increase of the CEC in soil. On the other hand, the increase observed in biochars produced at high temperature is possibly due to their high surface area and porosity.

Regardless of the type of precursor, the addition of biochars has significantly increased the Total Carbon (TC) of both soil types compared to the soil control. In both soils, C/N ratio increased as the biochar rate increases and the C/N ratio was significantly higher than the control and remained higher during 150 days of incubation time. The C/N ratio significantly decreased over time probably due to the mineralization process and the effect of monthly leaching during the incubation period.

The combined effect of the biochars application rate and pyrolysis temperature has significantly increased the aggregate stability in both soils, with more pronounced increase in aggregate stability in the treated Norfolk soil. The Norfolk soil composition is mainly sand and is known to have very low aggregates compared to Mecklenburg soil which contains more clay contributing to the formation of more aggregates. Therefore the addition of organic matter to the Norfolk soil is expected to significantly increase the aggregates. Hence, the effect of biochar on soil aggregation was more visible in Norfolk soil than in Mecklenburg soil.

The addition of biochars has significantly increased the water holding capacity in both soil types. Biochars produced at high pyrolysis temperature and increased application rate had a positive effect on the water holding capacity. SG-derived biochar exhibited highest WHC which is likely due to its high surface area and porosity.

The addition of biochars has significantly increased the concentrations of all the nutrients in both soils. The increase in the concentrations of P, K, and Mg was more significant in soils treated with switchgrass and cotton gin biochars. This is most probably due to the high concentrations of these elements in the corresponding feedstoks which was further increased as the pyrolysis temperature increases.

The addition of biochars to the soil has increased the dissolved organic carbon (DOC) of the soil leachates. Biochars produced at low temperature (300 °C) had the most positive effect on DOC which significantly increased in the leachates of both soil types, regardless of the types of precursors. The low temperature biochar are less resistant to biotic and abiotic degradation compared to high temperature biochar.

Biochars produced at elevated temperature and used at higher application rate have significantly decreased the concentration of nitrate/nitrites in both soil types. In contrast, low pyrolysis temperature and high biochar application rate increased the nitrate/nitrites concentrations in the soil, This is due to the differences in biochar decomposition because of their C:N ratios. The leaching of nitrate/nitrites tended to vary differently in Mecklenburg and Norfolk soil. This difference in soils is probably due to the high clay and organic matter content of Mecklenburg soil.

The addition of biochars to the soil significantly decreased the leaching of atrazine as evidenced by the low atrazine concentrations in the soil leachates compared to leachates from soil controls. The 2% biochar application rate had the most significant effect on binding of atrazine into soil. This is probably due to high surface area and porosity for biochars produced at high temperature and high surface charge to low temperature biochars.

The leaching of monovalent cation K in piedmont soil increased as biochar application rate to soil increased, whereas leaching of multivalent cations (Ca, Mg, Cu, and Zn) decreased over time with increasing biochar application rate, with the 2% showing the most significant effect. In the case of the Norfolk soil, the addition of biochars increased the leaching of Ca, K, and Mg but decreased the leaching of the heavy metal (Cu and Zn) which was most significant at 2% biochars application rates compared to the soil control leachates.

Biochar characterization and short-term soil incubations can provide some insight into the short-term effects of applying biochar that can be used to narrow down a pool of potential biochars. The characterizations and soil indicators used in this study identified two biochars that would likely show at least some positive effects when applied to the Mecklenburg soil and provide data to further refine the selection.

Among all the biochars used in the soil incubation, cotton gin and switchgrass biochars produced at 500 °C pyrolysis temperature and 4 hours pyrolysis time were selected as the best ones using cluster and principal components analysis based on their ability to enhance soil fertility parameters compared to the two remaining precursors (pecan and peanut shells), especially in term of pH, CEC.

The biochar incubated alone did not show any gas emission during the entire 10 weeks incubation indicating a higher degree of recalcitrant C in the biochars. The addition of biochar to soil did not show any significant difference CO_2 emission compared to the soil control. A difference in the CO_2 emission was observed between the soil treated with raw material (Low C:N ratio) and biochar (High C:N ratio), suggests that the treatments with lower C:N ratio were more easily mineralized and the probability of nitrification and de-nitrification was high. Thus, the greenhouse effect of increased CO_2 could be reduced by converting organic biomass to biochar and used as a soil amendment.

Overall, there were no significant differences in the growth performance of the lettuce crop after biochar application ($p > 0.05$) compared to the control treatment. The 2% application rate showed a higher number of leaves (Figure 4.47) compared to the 1% application rate and the control but the difference was not statistically significant ($p > 0.05$).

Biochar amendments of soils used in plant growth significantly increased ($p < 0.05$) soil pH, CEC, P, K, Mn, and sulfur concentrations but had no effect on humic matter (HM), Mg, Cu, and Zn in both cotton gin and switchgrass biochars treatments. These improvements in the main soil parameters did not have a significant effect on crop growth.

The application of biochar to agricultural soils has the potential to greatly improve soil physical and chemical conditions. In addition to biochar properties, growth responses will vary on different soils and with different crops. The complexity of possible interactions between crop, soil, and biochar may be very large, as evident from the present experiment with only one crop and one soil. More importantly no negative aspects were apparent in this trial.

These results are important in terms of satisfying the environmental risk assessment required to formulate legislation for the use of biochar in agriculture. Decisions tools need to be developed that capture this complexity and should be continuously refined. Moreover, the application of biochar from crop residues may offer additional carbon negative benefits through carbon sequestration, avoiding burning in field, and bio-resource recycling, which have been a great concern with air pollution of U.S.A’s agriculture.

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Appendix A

Experimental Soil Description

Mecklenburg Series

The Mecklenburg series consists of very deep, well drained, slowly permeable soils that formed in residuum weathered from intermediate and mafic crystalline rocks of the Piedmont uplands. Slopes range from 2 to 25 percent. Mean annual precipitation is 45 inches, and mean annual temperature is 59 degrees near the type location.

Taxonomic Class: Fine, mixed, active, thermic Ultic Hapludalfs.

Typical Pedon: Mecklenburg loam--pastured. (Colors are for moist soil unless otherwise stated.)

Ap--0 to 8 inches; reddish brown (5YR 4/4) loam; moderate medium granular structure; friable; many fine roots; common fine pores; common fine black concretions; slightly acid, clear smooth boundary (2 to 11 inches thick).

Bt1--8 to 17 inches; yellowish red (5YR 4/6) clay; moderate medium subangular blocky structure; firm, sticky, plastic;

common fine roots; few fine pores; many fine black concretions; common distinct clay films on faces of peds; slightly acid; gradual wavy boundary.

Bt2--17 to 25 inches; yellowish red (5YR 4/8) clay; common fine distinct brownish yellow (10YR 6/6) mottles; moderate medium subangular blocky structure; firm, sticky, plastic; few fine roots; few fine pores; common black concretions; common distinct clay films on faces of peds; slightly acid; gradual wavy boundary. (Combined thickness of the Bt horizon is 12 to 35 inches.)

BC--25 to 36 inches; yellowish red (5YR 4/8) clay loam; common medium faint reddish yellow (7.5YR 6/6) and common fine distinct yellowish brown (10YR 5/4) mottles; weak subangular blocky structure; firm, sticky, plastic; few fine black concretions; common fine lenses of gray clayey saprolite; slightly acid; gradual wavy boundary (3 to 15 inches thick).

C--36 to 60 inches; mottled yellowish red (5YR 4/8), reddish yellow (7.5YR 6/6) and yellowish brown (10YR 5/4) highly weathered saprolite that has a sandy clay loam texture; massive; friable; many black and gray minerals; slightly acid.

Type Location: Davidson County, North Carolina; 0.7 mile west of Linwood on SR 1134; 20 feet north in pasture at bend in road.

Range in Characteristics: Solum thickness ranges from 20 to 60 inches. Depth to bedrock is greater than 5 feet. The soil ranges from strongly acid to slightly acid in the A horizon and is moderately acid to neutral in the B and C horizons. Content of rock fragments of gravel and cobble size range from 0 to 30 percent by volume in the A horizon and 0 to 10 percent in the B horizon. Manganese concretions are few to many in the A and B horizons. Content of flakes of mica ranges from none to few.

The A or Ap horizon has hue of 2.5YR to 7.5YR, value of 3 to 6, and chroma of 2 to 6. A or Ap horizons with moist values less than 4 are less than 6 inches thick. The A horizon is fine sandy loam, sandy loam, silt loam, loam, or their gravelly analogues. Eroded phases are sandy clay loam or clay loam.

The BE or BA horizon, where present, has hue of 2.5YR or 5YR, value of 3 to 6, and chroma of 4 to 8. It is loam, sandy clay loam, or clay loam.

The Bt horizon has hue of 2.5YR or 5YR. In the upper part, value is 3 to 6 and chroma is 4 to 8. In the lower part, value is 4 to 6 and chroma is 4 to 8. Few to common mottles in shades of brown, yellow or red are in the lower Bt horizon in most pedons. The Bt horizon is clay with clay content from 40 to 60 percent.

The BC horizon has hue of 2.5YR to 7.5YR, value of 4 to 7, and chroma of 4 to 8 and is often mottled in these colors. It is loam, sandy clay loam, or clay loam, and contains up to 25 percent saprolite.

The C horizon is mottled or multicolored saprolite weathered from mafic crystalline rock. It is variable in texture but typically is loamy.

Competing Series: These are Brantley, Canton Bend, Capshaw, Cowton, Enon, Gundy, Hampshire, Maben, Magnet, Meth, Spray, Zion, and Zuber series in the same family. Those in closely related families are Coronaca, Iredell, and Wilkes series. Brantley, Canton Bend, Capshaw, Cowton, Maben, and Meth soils are more acid in the B horizons than Mecklenburg. Coronaca soils have moist colors of values of less than 4 throughout. Enon, Hampshire, Iredell, and Zuber soils have hue of 7.5YR or yellower in the Bt horizon; and in addition Zuber soils have sandy A and AB horizons. Gundy soils are more permeable and developed from slate or fine grained schist. Magnet soils are more permeable and formed in residuum from syenite and other intrusive igneous rocks. Spray soils developed from mudstone, siltstone, or shale. Wilkes and Zion soils have bedrock at a depth of less than 40 inches.

Geographic Setting: Mecklenburg soils are on nearly level to moderately steep Piedmont uplands. Slope gradients are 0 to 25 percent, most commonly between 2 and 10 percent. These soils have developed in weathered intermediate and mafic crystalline rocks. Average annual precipitation is about 45 inches. Mean annual soil temperature is about 59 degrees F.

Geographically Associated Soils: In addition to the competing Coronaca, Enon, Iredell, Wilkes, Winnsboro, and Zion Series, these are Cecil, Cullen, Davidson, Gaston, Lloyd, and Pacolet series. These soils have a base saturation less than 35 percent.

Drainage and Permeability: Well drained. Runoff is slow to medium and internal drainage is slow. Permeability is slow.

Use and Vegetation: Cleared areas are used primarily for corn, soybeans, small grain, hay, and pasture.

Forested areas are in shortleaf, loblolly and Virginia pines, yellow- poplar, sweetgum, southern red oak, northern red oak, white oak and hickory. Flowering dogwood, Eastern red cedar, sourwood, winged elm, sassafras, greenbrier, and American holly are common in the understory.

Distrubution and Extent: Alabama, Georgia, North Carolina, South Carolina and Virginia. The series is of moderate extent.

MLRA Office Responsible: Raleigh, North Carolina.

Series Established: Mecklenburg County, North Carolina; 1910.

Remarks: Diagnostic horizons and features recognized in this pedon are:

Ochric epipedon - the zone from the surface of the soil to a depth to 8 inches.

Argillic horizon - the zone between depth of 8 and 25 inches.

Ultic Hapludalfs feature - base saturation of 35 to 60 percent in the zone between 36 and 60 inches.

MLRA = 136

SOI-5 Soil Name Slope Airtemp FrFr/Seas Precip Elevation

NC0072 MECKLENBUR 2- 25 58- 66 180-225 37- 60 400- 900

SOI-5 FloodL FloodH Watertable Kind Months Bedrock Hardness

NC0072 NONE 6.0-6.0 - 60-60

SOI-5 Depth Texture 3-Inch No-10 Clay% -CEC-

NC0072 0- 8 L FSL SL 0- 5 80-100 8-25 4- 20

NC0072 0- 8 GR-L GR-SL GR-FSL 2- 10 55- 85 8-25 4- 20

NC0072 0- 8 CL SCL 0- 5 90-100 20-35 10- 25

NC0072 8-25 C 0- 5 85-100 40-60 15- 35

NC0072 25-36 L SCL CL 0- 5 85-100 20-35 10- 20

NC0072 36-60 VAR - - - -

SOI-5 Depth -pH- O.M. Salin Permeab Shnk-Swll

NC0072 0- 8 5.6- 7.3 .5-2. 0- 0 0.6- 2.0 LOW

NC0072 0- 8 5.6- 7.3 .5-2. 0- 0 0.6- 2.0 LOW

NC0072 0- 8 5.6- 7.3 .5-1. 0- 0 0.6- 2.0 LOW

NC0072 8-25 5.6- 7.3 0.-.5 0- 0 0.06- 0.2 MODERATE

NC0072 25-36 5.6- 7.3 0.-.5 0- 0 0.6- 2.0 LOW

NC0072 36-60 - - - -

Appendix B

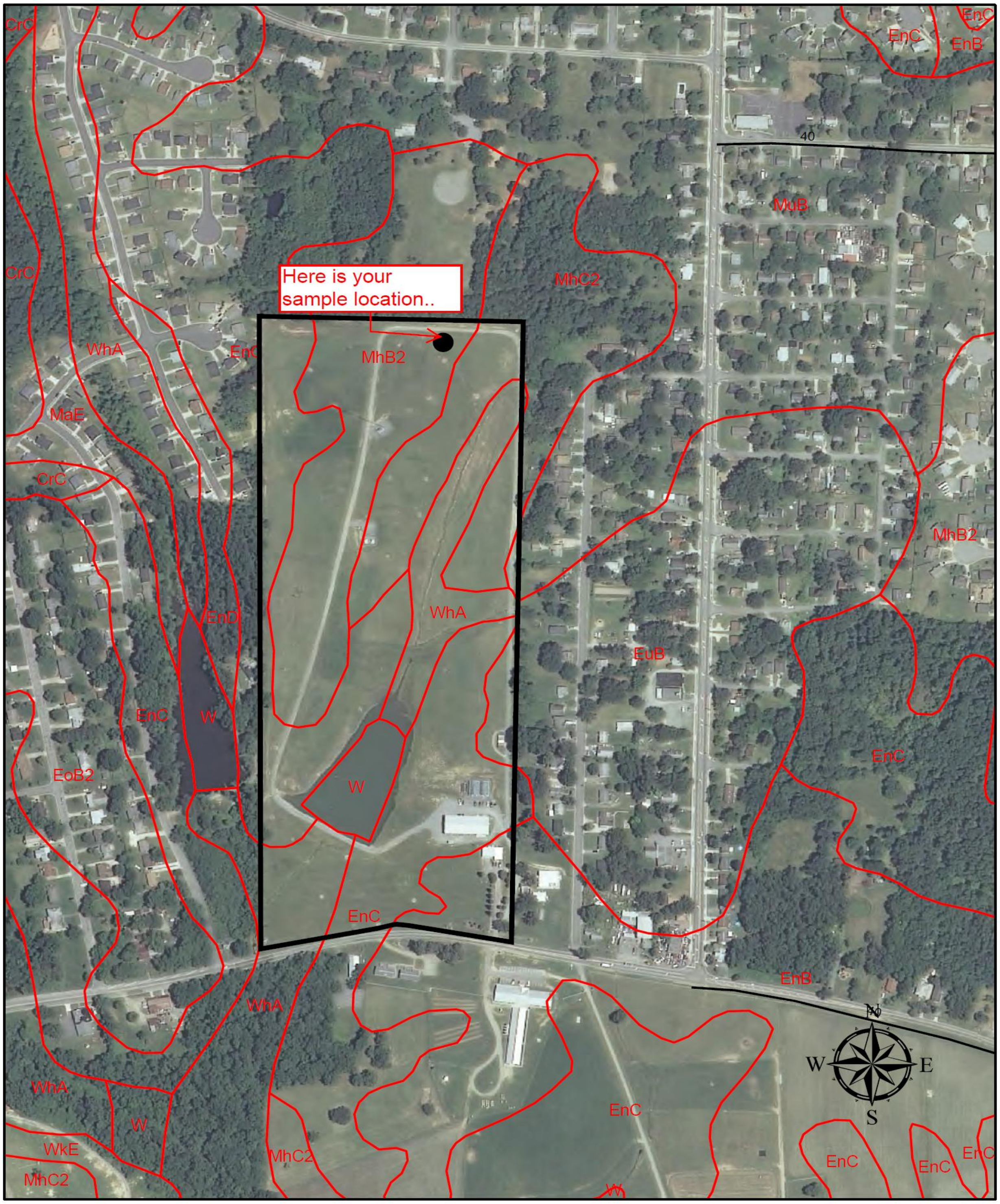

Figure 4.50. Mecklenburg Soil Sample Location.