Chapter 7
Selection and Use of Designer Biochars to Improve Characteristics of Southeastern USA Coastal Plain Degraded Soils

J.M. Novak and W.J. Busscher

Abstract The US Southeastern Coastal Plains have a long history of agricultural production. However, poor quality sandy soils hamper productivity. Soils have depleted organic carbon contents that lead to poor nutrient retention, reduced aggregation, and low plant-available soil water retention. Past soil management used reduced tillage to increase organic carbon but it deteriorated quickly in the hot, humid environment. Biochars can provide an alternative recalcitrant carbon source. Since biochar varies widely in characteristics, it must be designed to fit the needs of the soil—increased carbon, aggregation, nutrient retention, and plant-available water retention. Biochar design characteristics depend mainly on feedstock characteristics and method of pyrolysis. This review offers guidelines for designer biochar manufacture through feedstock selection and pyrolysis technique; it outlines potential usage to improve specific soil quality problems.

1 Introduction

The Southeastern Coastal Plains of the Carolinas have a long history of crop production by Paleo-Americans [63] and European settlers [15, 46, 103]. The region was initially settled by the Paleo-Americans [63], and they thrived by growing maize, beans, and squash and letting fields remain fallow after about 2 years of production. This rotation continued until the European settlers colonized the Carolinas in the seventeenth and eighteenth centuries [103]. With time, the European settlers shifted agriculture to more intensive corn, cotton, tobacco, rice, and timber production. Overuse of fields and poor land management accelerated depletion of

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soil nutrients and enhanced erosion of topsoil [16]. Fields of depleted soils were quickly abandoned.

In addition to the physical and chemical soil problems, the coastal plain climate hindered agricultural productivity. For example, the South Carolina Coastal Plain has an annual rainfall of about 1,310 mm [86], which is sufficient for row crop production [89]. But, crop water stress is common because of poor temporal rainfall distribution [85] and low soil water storage [36]. Droughts can last several weeks and reduce yields.

USDA agencies such as the Natural Resource Conservation Service and the Agricultural Research Service, have developed soil and water conservation management practices for these soils that promote productivity. Non-inversion, deep tillage that physically disrupts a subsurface hard pan can promote deep crop root penetration while minimally disrupting the surface to reduce water runoff and erosion [1, 2]. Unfortunately, the beneficial effects of deep tillage are temporary; deep disruption must be redone annually [13, 19] and soil organic carbon (SOC) levels are concentrated at the surface or deteriorate in the hot, wet weather [77, 105].

Minimal tillage, where crop residues are left on the soil surface, can increase SOC levels in sandy soils [50, 69], a soil characteristic that is known to improve aggregation [34], water infiltration, and nutrient retention [102]. An ideal OC-enriched amendment for these soils would be one that is long-lasting and increases aggregation, fertility, and water retention. Recently, Laird [57] described how a long-lost technology could be adopted as a management strategy to revitalize soils. In South America, pre-Columbian Amazonian inhabitants improved their infertile soils by applying biochar [45, 61]. These inhabitants obtained biochar from trees cleared from the forest and organic wastes such as bones, carcasses, and other fire pits debris; they added biochar to soils using a “slash and char” process which increased soil productivity [45]. Carbon in the form of biochar is resistant to degradation [99], having remained in tropical Amazonian soils for centuries [63]. Following the biochar vision of Laird [57], applying biochar to sandy agricultural soils of the Southeastern Coastal Plain would be a similar management strategy aimed at overcoming soil physical and chemical deficiencies.

Biochars quality can be variable [21] and different biochars react differently in soils [62, 70]. Biochar properties should be known to be beneficial to a soil to avoid creating unwanted chemical or physical legacies. One biochar type will not resolve all issues in all soils because of differences in its quality, and in its interaction with soil particles, and microbes. Arguably, it may be more prudent to design a biochar with specific chemical and physical attributes that can target specific soil problems. A biochar designed for a specific purpose was first introduced by Day et al. [27] to produce a material that acted as a nutrient carrier while being able to resist leaching. Day and his team were able to sequester C, H, and N from coal gas emissions into a char-based product for use as an N fertilizer source. Novak et al. [70] also recognized that biochars could be designed with specific chemical and physical properties through feedstock selection, pyrolytic temperature, and residence time manipulation. The designer biochar concept was further refined through a cooperative research [71]. This novel concept caught the attention of the scientific community, because shortly thereafter, others reported that biochar production can be managed to derive purposefully designed biochars that have properties tailored for specific end uses [6, 53, 98].

Biochar can be expensive to manufacturer with cost estimates of \$220 per Mg using current technologies [64]. If biochar is applied to soils at a common rate of between 1 and 30 Mg ha^{-1} [9]; its cost per ha can range from \$220 to \$6,615. To be a feasible option under these conditions, biochar marketing will need to establish a profit balance of bio-oil/biochars/syngas production from the parent feedstocks [94]. Also, if C offsets come to fruition, biochar could be seen as an amendment that would benefit reductions in atmospheric CO_2 concentrations by increasing soil C sequestration. Additionally, N_2O is a potent greenhouse gas influencing global warming and a linkage has been established showing reduced N_2O emissions from soils treated with biochar [90, 96].

In this article, we offer guidelines to pyrolytically design biochar, evaluate relationships between feedstock selection and biochar quality, and match the correct biochars or their blends to targeted soil and greenhouse gas production problems. It is important to first, understand what soil problem needs to be modified, and second, select a feedstock and pyrolysis condition that develops a biochar specific for that targeted problem. Therefore, the objectives of this review are to (1) appraise the geomorphic, chemical, and physical characteristics of degraded southeastern sandy coastal plain soils, (2) describe past physical and chemical remediation strategies to revitalize these sandy soils, and (3) establish guidelines for manufacture and use of designer biochars and their blends that could improve soil deficiencies and reduce greenhouse gas emissions.

2 Description of Southeastern USA Coastal Plain Soils

2.1 Geomorphic Properties

The coastal plain is an expansive geomorphic region of the Southeastern USA that extends from southern New Jersey along the Atlantic coast through the coast of the Gulf of Mexico to South Texas. It comprises nearly 2/3 of the land area of South Carolina (Fig. 1); most of which is either in agriculture or forestry. The coastal plain was initially deposited during a series of sea level rises and recessions; it has been subject to depositional and erosional forces moving and relocating sediments from the Pliocene Epoch (1.8–5 million years ago, [91]) to today. Below Pliocene age sediments are geologic strata consisting of beds of multicolored sands, intermixed with gravel and clay beds laid down during the Tertiary Epoch from 5 to 38 million years ago [91].

Terraces and scarps commonly occur across the coastal plain that are reflective of glacioeustatic changes in ocean level, deposition of sediments, and river dissection during the last 5 million years [30]. The terraces are gently eastward-sloping on the surface, which are bounded by seaward-facing scarps [25]. These scarps are a

Fig. 1 View of the coastal plains of the Southeastern USA (*left*) and of South Carolina (*right*) from the fall line to the coast

few meters in height and demark a time when sea levels were higher. Some of the scarps are definitive on the landscape [32] and are used to divide the area into physiographic divisions consisting of (1) lower, (2) middle, and (3) upper coastal plain, based on topography, sediments, elevations above mean sea level, and soils [30]. Their elevations range from sea level to about 150 m.

2.2 Pedogenic Activity Shapes Soil Morphology

Because coastal sediments were deposited by sea level changes, fluvial activity, and by erosional processes over the past 35,000–5 million years [32], pedogenic activity has had millions of years to form sediments into soils. Stable coastal surfaces developed aged soils that include an eluvial (E) horizon, weathered clays [28], and a reddened argillic B horizon [29].

The upper coastal plain is highly dissected by streams, and is covered by extensively weathered well-drained soils [32]. The middle coastal plain is gently undulating with a swell and swale relief of 0.3–1.5 m [31]. Here, upland soils are well drained when located closer to drainage ways and depressions are poorly drained. Circular depressions are referred to as Carolina Bays [30].

The Norfolk and Bonneau soil series are examples of well-drained upland soils of the middle coastal plain (Fig. 2). They are classified as Paleudults and have well-developed E and clay-enriched argillic B horizons. Particle size and fertility analyses show that their topsoils are sandy and mildly acidic [72]. Their low pH is caused by leaching of sandy parent material and the predominance of alumino-hydroxy species on cation exchange sites [32]. The clay fraction also attests to the soil age; it can be composed primarily of kaolinite, gibbsite, and hydroxy-interlayer vermiculite with minor amounts of hydroxy (Fe and Al) interlayer chlorite [73, 88]. All of this leads to a soil with low cation exchange capacities (<2 to 4 $\mathrm{cmol_c\,kg^{-1}}$, [55]).

Another characteristic of the Norfolk series is a subsurface hard layer (Fig. 3, left) that is caused by physical cementation and/or chemical precipitation of soluble Si between particles during wetting/drying cycles [22, 66]. This hard layer when dry

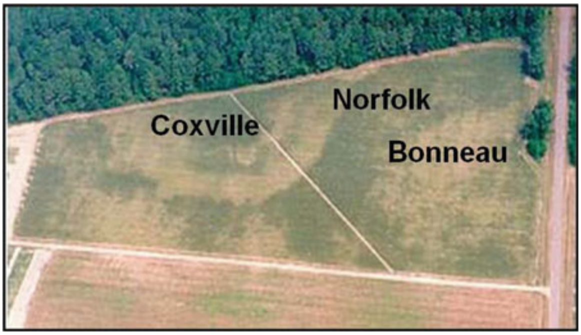


Fig. 2 Coxville (poorly drained), Norfolk (well-drained), and Bonneau (excessively well-drained) soil series in a Coastal Plain agricultural field (Darlington, SC)

Fig. 3 Poorly aggregated, massive structure of the E horizon (hard layer) of the Norfolk soil series (*left*). A deformed probe attempting to measure penetration resistance in the hard layer (*right*, photos courtesy of ARS Florence)

has penetration resistances that can deform the steel probe used to measure its strength (Fig. 3, right). In some cases, crop roots will grow along the top of the hard layer because high soil strength and lack of aggregation deters their penetration.

The Bonneau series also forms in upland areas. It has a thicker, hard E horizon and its argillic B horizon can have a lower boundary up to 102-cm deep. As shown in Fig. 2, the lack of vegetation on the Bonneau soil was due to crop moisture stress during a drought (2002). Crop growth was limited in this series because roots were unable to penetrate the hard layer to exploit water stored in the argillic B horizon.

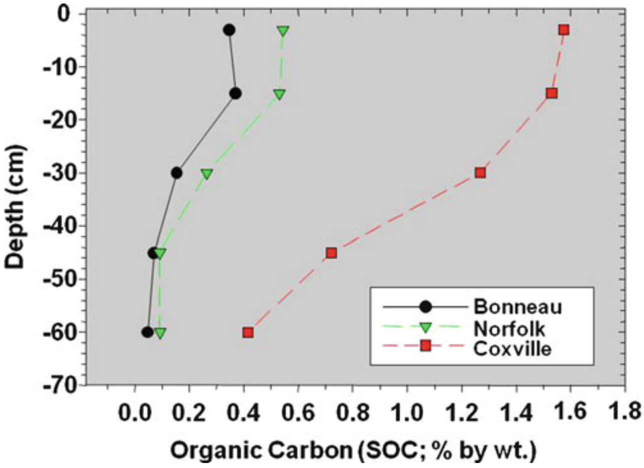


Fig. 4 Percentage by weight of soil organic carbon (SOC) in the profile of Bonneau, Norfolk, and Coxville soil series (profile data from field in Fig. 2)

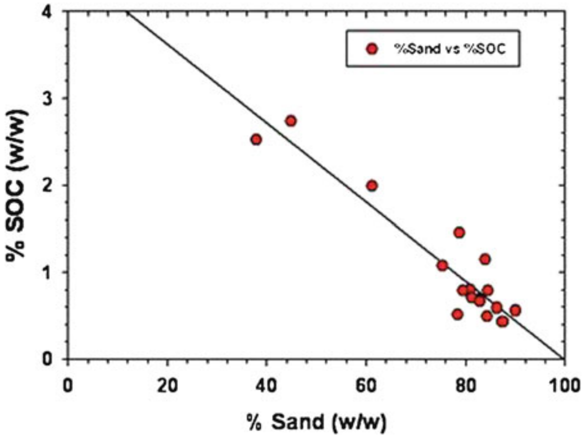


Fig. 5 Relationship between sand and SOC in topsoil (0–15-cm) of Norfolk, Bonneau, and Coxville soil series (samples collected from field shown in Fig. 2)

Deep coring into the Norfolk and Bonneau soil profiles shows that they have low SOC contents (Fig. 4). This can be explained by their high sand content (Fig. 5), and their lack of clay-size particles that are known to sorb SOC compounds and slow organic matter mineralization [101]. In contrast, the Coxville is a poorly drained Paleaquult, which forms in Carolina Bays (Fig. 2). Sediments from soils in upslope locations have eroded into the bay over millennia causing the Coxville to contain more clay. As shown in Fig. 4, the Coxville soil has more SOC in the profile than the Norfolk or Bonneau soil. Accumulation of SOC in the Coxville is also facilitated

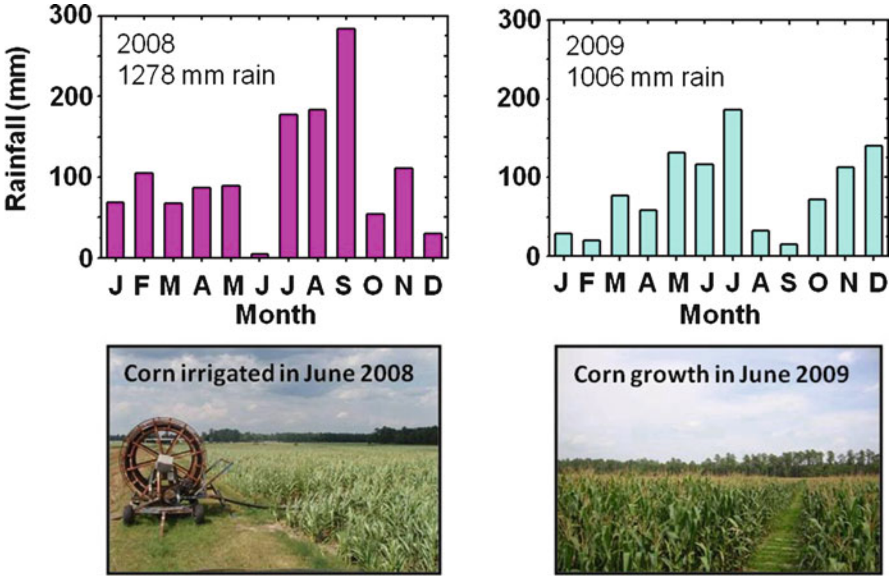


Fig. 6 Monthly rainfall totals during 2008 (*left*) and 2009 (*right*) recorded at the Clemson University, Pee Dee Research and Education Center, Florence, SC, USA and its influence on corn yields show the importance of water availability. Corn grows from mid April to early August. Its yields were 3.8–4.7 Mg ha^{-1} in 2008 and yields = 8.4–9.3 Mg ha^{-1} in 2009

by its poor internal drainage that slows oxidation [101]. The Coxville series has a greater ability to retain nutrients than the Norfolk and Bonneau because of its larger cation exchange capacity (5–15 $cmol_c kg^{-1}$, [55]).

2.3 Water Storage in Sandy Soils

Annual precipitation in the coastal plain region of South Carolina is high enough for crop production (1,310 mm, [86]). However, erratic rainfall with dry spells of a few days to a few weeks [16, 85] reduces production as seen in (Fig. 6) where less than 5 mm of rainfall was recorded in June 2008 in Darlington SC during the corn growing season (April to July). Low rainfall caused crop moisture stress to occur (Fig. 6, left), resulting in low corn yields (3.8–4.7 Mg ha^{-1}). In contrast, rainfall was sufficient during the 2009 corn growing season (Fig. 6, right) and yield was double the drought year (8.4–9.3 Mg ha^{-1}).

Low water storage [18, 79] and poorly aggregated, hard layers, that restricts root penetration to the top 25–30 cm of the soil profile [36] limit soil water holding capacity to ≈22.5 mm [37, 81]. During the hot summer, evapotranspiration rates of 16.8 mm day^{-1} for soybeans [82] will use this in less than 2 days. Unless water is replenished with rain or irrigation, crops will stress. In contrast, a finer-textured

SOC-enriched Coxville soil series can have between 29 and 51 mm of available H_2O per 300 mm of soil [79]. Under similar conditions, a soybean crop growing in the Coxville soil would have more time (1.7–3 days) before soil water is depleted.

2.4 Management Practices to Increase Soil Water Storage

Tillage management practices disrupt the subsurface hard layer to encourage deeper root growth and increase SOC levels to improve water storage. Physical disruption using deep tillage of the hard layer is expensive and requires specialized equipment [52]. Because hard layers re-cement [13, 19], deep tillage in the coastal plain is usually preformed annually [14]. In today's economy, annual deep tillage is expensive; therefore, less-expensive forms of minimum tillage or no-till are used to build-up SOC contents [8, 12, 50, 69]. Accumulation of SOC is beneficial because the effects have been shown to reduce soil strength [39].

Increases in SOC improve soil aggregation and pore space [8, 34, 93], which favor water infiltration and storage [102]. Minimum tillage systems favor SOC rebuilding, but in sandy coastal plain soils, the increase is depth-dependent [69, 72], and only a small portion (5%) of OC in crop residue is returned to the SOC pool [72]. Other minimal tillage studies reported that SOC increases are not long-lasting, but must be continually resupplied with fresh residue [77, 105].

Considering these problems, an ideal OC supplement should last longer, return more OC to the SOC pool, and increase aggregate formation and pore space. A promising soil amendment that can add recalcitrant OC while concomitantly improving soil chemical and physical issues is biochar [16, 57, 61].

3 Biochar Production and Properties

3.1 Biochar Production

Biochar is a byproduct of the biofuel industry [5, 58, 62]. It is produced by the pyrolysis of organic feedstocks at temperatures between 300 and 700°C in an oxygen-free or low oxygen noncombustible atmosphere. Different feedstocks are used to make biochars, including biomass energy crops, bioenergy residues, crop residues, manures, and kitchen wastes. During the pyrolytic process, these organic feedstocks thermally decompose, releasing volatile compounds, syngas and biochar. The volatile compounds can be recondensed and refined as bio-oil [11]. The biochar residual product has chemical and physical properties that depend on complex reactions during the pyrolysis process and are reported to vary with feedstock selection and pyrolysis conditions [38, 74].

Biochars can be made using various thermochemical processes systems such as slow/fast pyrolysis, flash pyrolysis, and gasification [58, 94]. Slow and fast pyrolysis

Table 1 Biochar percent ash (dry wt. basis), pH, and fertilizer ratios

				Fertilizer (100 kg^{-1} biochar)		
Feedstock	Pyrolysis (°C)	Ash (%)[a]	pH[a]	N	P	K
Peanut hull	400	8.2	7.9	3	0.3	2
	500	9.3	8.6	3	0.3	2
Pecan shell	350	2.4	5.9	0.3	0.03	0.2
	700	7.2	7.2	0.5	0.05	0.5
Poultry litter	350	35.9	8.7	5	3	6
	700	52.4	10.3	3	4	9
Switchgrass	250	2.6	5.4	0.4	0.1	0.5
	500	7.8	8	1	0.2	1
Hardwood	Fast	5.6	6.1	0.3	na	0.6
Pine chips[b]	465	5.6	6.1	0.3	0.08	0.4
Corn stover[b]	500	69.1	7.2	0.6	0.2	1.6

[a] From Novak et al. [74]

[b] Results courtesy of Drs. Don Reicosky and Kurt Spokas (USDA-ARS)

technologies are featured in this review. A more detailed explanation of gasification technologies for syngas production is available [58].

In the slow/fast pyrolysis systems, the feedstock (depending on the delivery feed scheme) can remain in the pyrolysis reactor anywhere from a few seconds to 24 h [94]. Pyrolysis reaction times vary among manufacturers because of differences in reactor temperature ramp settings, choices of dehydration (100–150°C) and carbonization temperatures (300–700°C), and cooling time. Under these conditions, biochar yields can range from 51 to 72% on an oven-dry C basis and between 29 and 57% on an air-dry mass basis [74]. More biochar is recovered at lower pyrolysis temperatures (around 350°C) because less volatile material is driven off as bio-oil. If maximizing bio-oil production is the goal, the manufacturer can adjust the slow pyrolysis process to operate at a higher temperature range (500–700°C). While more bio-oil is recovered, biochar mass yields will decline because of dehydration of hydroxyl groups and thermal degradation of ligno-cellulose structures [4, 5].

Biochars pyrolyzed at higher temperatures (500–700°C) tend to have greater ash contents, and hence, more alkaline pH values (Table 1). High temperature pyrolysis will concentrate the salts because of the loss of C-, O-, and H-containing compounds removed as volatiles [20, 43, 74]. Ash contents for several biochars pyrolyzed at the higher (400–700°C) temperatures regime ranged from 5.62 to 52.9% while at the lower temperature (<350°C) biochar ash contents ranged from 2.4 to 35.9% (Table 1). Biochar pyrolyzed from poultry litter had the highest ash content because of excretion of unassimilated nutrients [92] and from chemical additives to the litter to reduce N volatilization [74]. The high ash content also contributed to the poultry litter biochar having a calcareous pH (Table 1).

The elemental composition in several biochars is heterogeneous (Tables 1 and 2) because of differences in nutrient uptake by the raw feedstock [21] and by chemicals added to manure feedstocks prior to pyrolysis [74]. If the ash contains elements like

Table 2 Elemental composition of four biochars ($\mu g\ g^{-1}$ on a dry-weight basis, unpublished data)[a]

Element	Hardwood	Cotton gin trash	Pine chips[b]	Corn stover[b]
Al	402	208	578	13,915
Ag	0	0	0.1	0.2
As	0.2	0.2	0.2	1.2
Ba	42	12	21	136
Ca	5,164	4,361	3,976	11,831
Cd	0.2	0	0	0
Cr	217	0.7	11	58
Cu	9.1	124	5.3	57
Fe	2,046	163	1,515	8,307
K	6,237	11,451	4,353	52,574
Mg	741	1,086	1,390	4,867
Mn	113	12	172	201
Na	480	384	805	8,525
Ni	8.5	4.3	0.6	18
Pb	2.4	0.4	2.6	31
Se	0.8	0.7	0.7	0.4
V	0.4	0.4	0.6	16
Zn	6.7	6.7	44	41

[a] Biochars digested using EPA method 3052 ($HNO_3 + HF$)

[b] Samples courtesy of Dr. Don Reicosky (USDA-ARS)

N, P, and K, then it could serve as a low grade fertilizer with a corresponding low N-P-K ratio (Table 1). These ratios were calculated based on the total contents of elements in the biochar, and does not necessarily reflect their plant availability status. Poultry litter and peanut hulls have a modest N-P-K fertilizer ratio while biochar made from pine chip and pecan shells had the lowest ratio (Table 1). Results from Table 2 show that the biochars pyrolyzed from different feedstocks can contain sizeable quantities of base cations such as Ca and Mg. While also being essential plant nutrients, the presence of Ca and Mg causes the biochar to act like a liming agent. As Novak et al. [73] reported pecan shell biochar had liming properties since it had an alkaline pH, and contained 3.6 and 0.7 $g\,kg^{-1}$, respectively, of Ca and Mg. Another important property of these four plant-based biochars (Table 2) is the low concentrations of heavy metals (i.e., Cd, Cr, Ni, Pb, and V). If these biochars are used as a soil amendment, low metal concentrations should ease environmental concerns.

In fast pyrolysis, the feedstock is placed in a retort and subjected to a very short burst (1–2 s in duration) of heat (400–600°C) usually under pressure [94]. These conditions also maximize bio-oil production (75%); however, lower biochar mass yields are recovered (≈12%, [94]). For comparative purposes, one biochar made from hardwood using the fast pyrolysis system was included in this review. Its ash content, pH value, and fertilizer ratio were fairly similar to characteristics of the low temperature (350°C) pecan shell biochar (Table 1).

There are considerable time advantages when using fast pyrolysis, including shorter residence, carbonization, and temperature squelching times. The choice of pyrolysis system (slow vs. fast) for biochar manufacturer will ultimately be decided by a balance between biochar, bio-oil, and syngas recovery [94].

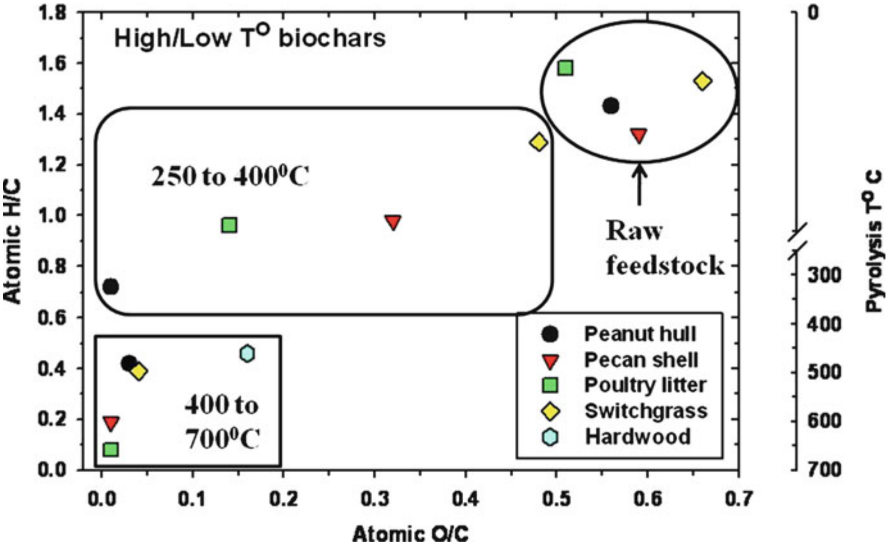


Fig. 7 Atomic ratio distribution shown in the Van Krevelen diagram for raw feedstocks and biochars pyrolyzed using two temperature ranges

3.2 Biochar Characterization

Pyrolysis systems cause many changes to the initial feedstock that inevitability is reflected in the biochars structural and elemental composition. These intensive thermal conditions during pyrolysis cause decomposition of organic structures from the raw feedstock through dehydrogenation, demethylation, and finally decarboxylation resulting in the release of a variety of organic compounds, including volatile C compounds, CH_4, and CO [7]. By assessing the elemental composition of the raw feedstock and the biochar, a determination of these released volatile compounds containing C, H, and O will result in major shifts in their atomic O/C and H/C ratios (Fig. 7).

The Van Krevelen diagram is a convenient way to show that the raw feedstocks are rich in H and O, and as the pyrolysis temperature increases, loss of volatile elements cause biochars to have decreasing O/C and H/C atomic ratios (Fig. 7). Consequently, manufacturers can quickly assess the degree of biochar production by examining for changes in the elemental concentrations of C, H, O, and N, and their associated ratios. For example, low H/C and O/C ratios indicate that the biochar is higher in aromatic structures [7, 48]. Biochars with O/C and H/C ratios in the 0.3–1.2 range indicate that it contains lignin and polysaccharide-like compounds [48]. Krull et al. [56] has listed atomic ratios, including the OC contents, in biochars processed from several feedstocks and pyrolysis temperatures.

Computation of a biochars atomic ratio requires that a sample be digested resulting in its loss for future experiments. Alternative, nondestructive methods for

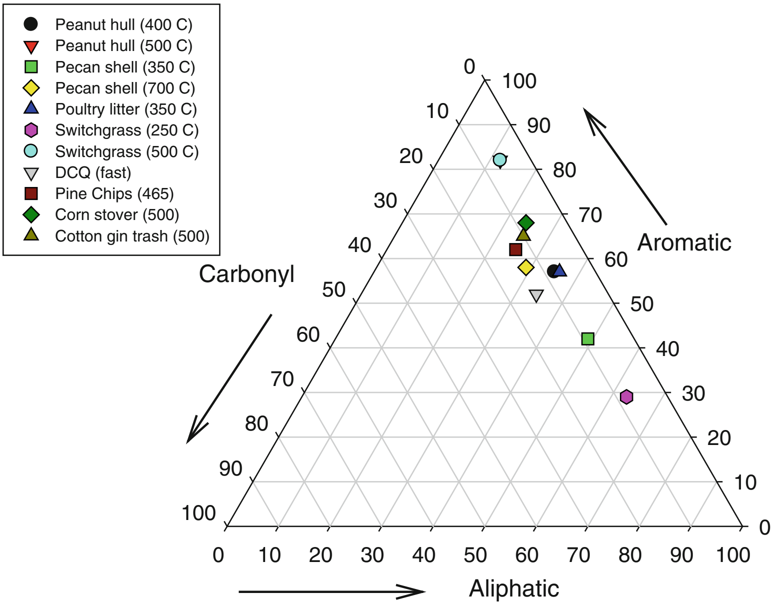
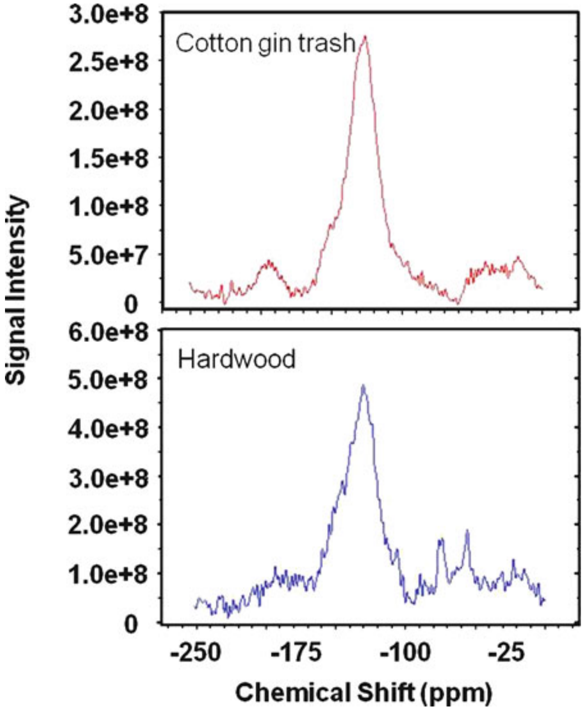


Fig. 8 Carbon distribution in biochars produced from various feedstocks using high (>400°C), low (<400°C) and fast pyrolysis (pine chip and corn stover results courtesy of Dr. Don Reicosky)

biochar characterization are available, such as solid-state ^{13}C nuclear magnetic resonance (NMR, [56]), and Fourier transformed infrared spectroscopy (FT-IR; [80, 84]). If ^{13}C NMR spectroscopy is used, each sample analyses may take several hours to 1 day to acquire the spectral pattern. As presented below, ^{13}C NMR spectroscopy is a more practical tool for examining progressive structural changes in biochars with increasing pyrolysis temperatures. Research has shown that plant-based feedstocks pyrolyzed between 350 and 400°C, cellulose and hemicellulose degradation occurs [7]. In the mid-range temperature of 400–500°C, additional structural modifications can occur through condensation of aromatic molecules in the basal sheets followed by loss of functional groups as a result of decarboxylation and demethylation reactions. At the higher pyrolysis temperature regime (500–700°C), biochars will be dominated by aromatic-C groups, with minor contributions of carbonyl-C, *O*-alkyl-C, and alkyl-C moieties [56, 74]. The dominance of C in aromatic groups in high temperature pyrolyzed biochar is evident when plotting the ^{13}C distribution in each biochars aliphatic, aromatic, and carbonyl region of the NMR spectral patterns (Fig. 8). Biochars pyrolyzed from switchgrass and peanut hull feedstocks at 500°C had the highest aromatic-C character (82%) among the 11 biochars evaluated. Lower temperature pyrolyzed biochars (250–350°C) have more C as aliphatic structures because their polysaccharide-like compounds have not been lost to thermal degradation [5].

As shown in Fig. 9 (top), the ^{13}C NMR spectra of cotton gin trash biochar (500°C) was dominated by a peak at 128 ppm due to resonance of aromatic C structures,

Fig. 9 ^{13}C NMR spectra of (*bottom*) hardwood biochar (fast pyrolysis) and (*top*) cotton gin trash (500°) biochar



while minor spectral peaks were recorded in the aliphatic-C (0–50 ppm), polysaccharide-C (60–110 ppm) and carboxylic-C (194 ppm) region. Integrating the area of the spectral region revealed that the cotton gin trash biochar contained 65% aromatic-C with only 12% occurring as polysaccharides. Most of the polysaccharide-like compounds in the cotton gin trash biochar were lost during pyrolysis at the higher temperature regime (500°C).

Biochar (Fig. 9, bottom), which has been produced from hardwoods using a fast pyrolysis system, had minor peaks at 56 and 75 ppm, respectively, which is indicative of methoxy and C–O groups in polysaccharides. Similar to gin trash biochar, the hardwood biochar was dominated by an aromatic-C peak (126 ppm) which accounted for 52% of the C distribution. A minor amount (20%) of the total C structures occurred in polysaccharide-like compounds.

Fourier transformed infrared spectroscopy can determine the presence of types of organic compounds in biochars [80, 84]. It is a robust system and uses the mid-infrared spectrum (4,000–500 cm^{-1}) to examine for sorption peaks that are diagnostic of rotational and vibrational movements of molecular structures and bonds within those structures [101]. On the one hand, there are issues with FT-IR analyses including broad peaks due to sorbed moisture [101] and sorption overlap that complicates ascribing the organic compound responsible for the sorption peaks [78]. On the other hand, very little sample is needed (few mg), it is nondestructive, and the results are more rapidly obtained when compared to ^{13}C NMR spectroscopy.

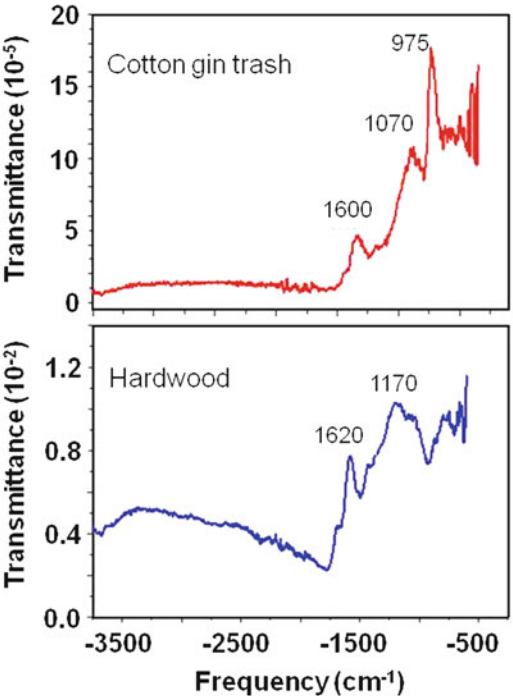


Fig. 10 FT-IR spectra of (*bottom*) hardwood biochar (fast pyrolysis) and (*top*) cotton gin trash biochar (500°C)

These properties make FT-IR an acceptable analytical tool for examination of biochar properties during manufacturer and for biochar mineralization studies. For example, FT-IR spectroscopy has been employed to determine structural and functional group changes during biochar mineralization in soils [23, 24, 75]. The FT-IR spectral analysis of biochar pyrolyzed from cotton gin trash (Fig. 10, top) and hardwood biochar (bottom) show broad peaks between 3,500 and 2,000 cm^{-1}, but also a few sharp peaks between 1,600 and 1,620, and 1,170–975 cm^{-1}. Surface hydroxyls and or sorbed water and C–H stretching are responsible for the broad beak between 3,500 and 2,000 cm^{-1}. Peaks at 1,620 and 1,600 cm^{-1} are ascribed to aromatic C=C and H-bonded C=O and peaks at 1,170, 1,070 and 975 cm^{-1} are indicative of C–O stretching of polysaccharides and OH deformation of COOH groups [101]. The aromatic peak in the FT-IR spectra of the hardwood biochar is more distinct than in the gin trash, which is consistent with ^{13}C NMR results.

4 Biochars Designed to Resolve Specific Soil Issues

Biochar pyrolyzed from organic feedstocks (i.e., woody wastes, crop residues, nutshells, manures, etc.) have the potential to increase long-term soil C sequestration, restore fertility, and promote aggregate formation in soils. Biochar application

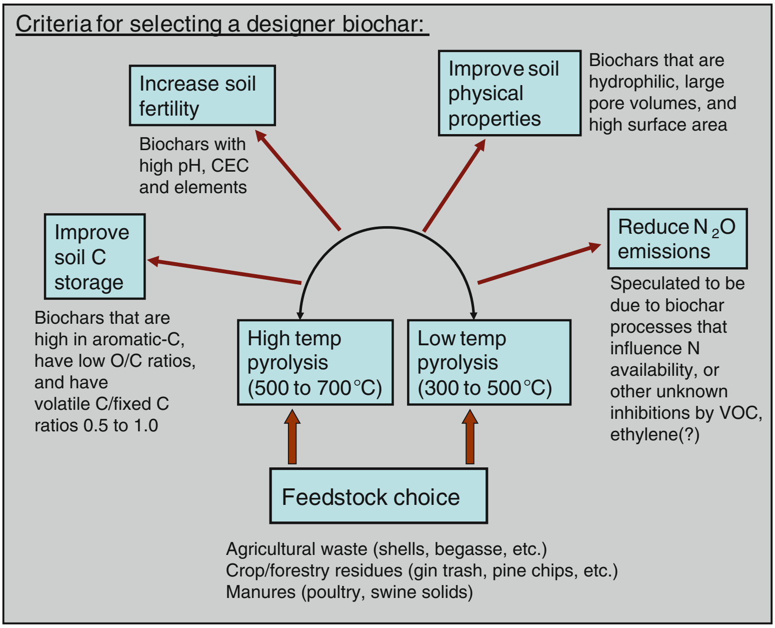


Fig. 11 Criteria for the manufacture of a designer biochar considering relationships between targeted soil properties, feedstock selection, and pyrolysis conditions

to soils unfortunately is not "a one-size fits all" principle, but biochars need to be crafted to target soil chemical and physical deficiencies. This is the creed of designing a biochar.

We can identify a targeted soil chemical and physical characteristics that could be improved, and explain how a designer biochar can be manufactured to possess properties that will ameliorate soil problems. In Fig. 11, we present a diagram that shows four problem areas of coastal plain soils described earlier, and then offers a pick of feedstock and pyrolysis temperature (high vs. low) to produce a biochar designed with specific properties to resolve the select soil problem. The next section discusses relationships between the designer biochar and definite soil problem.

4.1 Increasing Soil C Storage

Because of the coastal plain soils advanced age, the single most important soil quality issue to improve, arguably, is the low soil SOC contents (Fig. 4). While most of the OC from crop residue is lost within a few months [72]; the logical remedy would be to increase long-term SOC by applying a biochar that has recalcitrant properties (Fig. 11). Biochars suited to long-term C storage in soils have highly aromatic composition [45, 87] and black carbon with low O/C ratios (0.2–0.4, [68, 97]).

Table 3 Cumulative CO_2 evolved (mg)[a] from Norfolk E after mixing in 1% (w w^{-1}) crop/wood residue and pecan shell biochar (results submitted for publication)[b]

Norfolk E mixed with	Mean[c]
Control	0.77a
Corn stalk	1.75bc
Cotton hull	1.76b
Soybean	1.39b
Peanut hull	0.81a
Poultry litter	2.37c
Hardwood shavings	0.43a
Pecan shell biochar (700°C)	0.65a

[a] Measured with an Li-Cor 6250 CO_2 analyzer

[b] Sufficient raw crop/wood residues added to E horizon soil to obtain 1% (w w^{-1}) OC and each treatment ($n = 3$) incubated for 67 day at 10% (w w^{-1}) soil moisture content

[c] Tested for significant differences using a 1-way ANOVA with means followed by a different letter being signficantly different

To design biochar with these properties, feedstocks should be pyrolyzed at high temperature (500–700°C) leading to biochar composed of poly-condensed aromatic structures [7, 48] and O/C ratio similar to charcoal (0.2–0.4, [49]). A good example of an appropriate feedstock choice is pecan shells, which after high temperature pyrolysis at 700°C, had 58% C in aromatic structures and an atomic O/C ratio of 0.02 [73]. After 67 days of laboratory incubation in a Norfolk E horizon, pecan shell biochar (700°C) had the lowest CO_2 evolved when compared to the control and several raw crop residues (Table 3). In fact, its CO_2 mass evolved was similar to soil treated with hardwood shavings. These are laboratory results that were obtained only after few months of biochar incubation in the sandy Norfolk soil. But, the relative difference in CO_2 evolution suggests that if pecan shells were pyrolyzed at a high temperature (700°C), they would serve as a suitable designer biochar to increase C sequestration in the sandy Norfolk soil. Other feedstocks (i.e., hardwoods, shells from other nut crops, etc.) may also be suitable, but should also have high aromaticity and atomic O/C ratios of <0.4.

Another characteristic for biochar stability in soils is its volatile matter/fixed carbon (VM/FC) ratio [3]. Biochar with VM/FC of 0.5–1.0 are speculated to be stable in soils [3]. As an acceptable index of biochars longevity in soil, the actual relationship between its VM/FC ratio with CO_2 evolution from soils/culture media needs further evaluation.

4.2 Improving Soil Fertility

Sandy soils in the coastal plain of South Carolina have inherently low soil fertility and a meager capacity to retain nutrients. Increased levels of SOC are regarded as an important determent to improve their fertility. Organic carbon compounds

Table 4 Mean fertility characteristics in a Norfolk Ap after 0 and 120 days laboratory incubation with 2% (w w^{-1}) peanut hull and hardwood biochars ($n=4$, unpublished data)[a]

							Mehlich 1 extractable (mg kg^{-1})			
Treatment	Pyrolysis (°C)	Incubation (day)	pH[b]	CEC ($mol_c kg^{-1}$)	Soil OC (g kg^{-1})	Total N (g kg^{-1})	P	K	Ca	Mg
Control	–	0	5.6	2.2	2.78	0.35	28	37	131	24
		120	5.2a	1.8a	2.81a	0.22a	29a	14a	100a	14a
Peanut hull	400	0	7.3	2.7	18.80	0.77	47	319	173	46
		120	7.1b	2.4b	18.80	0.78b	39b	111b	174b	51b
	500	0	7.4	2.4	21.80	0.75	38	304	151	31
		120	7.4c	2.1ba	19.55	0.71b	33c	145c	159b	37c
Hardwood	Fast	0	6.1	2.6	18.42	0.35	28	85	187	28
		120	6.2d	2.3b	17.18	0.37c	22d	46d	154b	18d

[a] Treatments leached with di. H_2O four times during the 120 day incubation period

[b] Means of soil characteristics measured on day 120 of incubation within a column followed by a different letter are significantly different using a 1-Way ANOVA at a $P=0.05$ level of significance

returned as crop residues to sandy soils are temporal; a longer lasting solution is need. Therefore, it would be sensible to supplement sandy soils with biochar. This is not a new concept, but has been practiced by Amerindian populations for a long period of time [63]. In fact, it is arguably the starkest example of improving impoverished Amazonian soils. In this region, the inhabitants stock piled char-like material on red-colored, infertile soils to convert them into a dark earth colored soil called "terra preta do Indio" [45, 95, 100]. Today, large amounts of C supplied through biochar additions to the Terra Preta soils have lasted for thousands of years after they were deserted [61]. In fact, Glaser et al. [44] reported that as much as 250 Mg C ha^{-1} has been sequestered in the Terra Preta as compared to 100 Mg C ha^{-1} typically measured in surrounding untreated soils. The message is apparent that biochars applied to the Terra Preta soils improved their fertility while also supplying C in recalcitrant forms that have lasted for several thousand years.

Building on the fertility gains by applying biochars to Terra Preta soils, let us establish the Norfolk's Ap low fertility as the target issue to improve (Table 4). The next step would be selection of a feedstock and pyrolysis conditions (Fig. 11) that produces a biochar with properties chosen to compensate for these targeted (pH, SOC, N, P, etc.) problems. Among the biochar properties shown in Table 1, peanut hulls and poultry litter biochar contain greater N, P contents, and would act as a liming agent because of their alkaline pH. Biochars produced from the remainder of the feedstocks contain lesser amounts of nutrients or are not as alkaline. So, a logical choice would be to use peanut hull and poultry litter feedstock and the preference of pyrolysis temperature could be selected based on the desired biochars nutrient concentration or by its alkalinity. If more nutrients and a better liming agent are desired, then the biochars should be produced using a higher pyrolysis temperature (>500°C; Table 1).

The biochar application rates to this example Norfolk Ap, however, should be carefully chosen to avoid causing excessive alkaline or macronutrient imbalances.

Because this Norfolk Ap sample has a low buffer capacity, gross chemical changes occur with high biochar applications. For example, Novak et al. [74] reported that intensive application of poultry litter biochar (40 Mg ha^{-1}) to a Norfolk Ap resulted in high soil pH values (8–9.7) and excessively high Mehlich-1 extractable P concentrations (1,280–1,812 kg ha^{-1}). Under these conditions, the Norfolk Ap contained plant available P concentrations that were grossly in excess of soil plant P sufficiency levels [51]. These disproportionate P concentrations, if moved off-site, poses surface and ground water quality issues [17, 47]. Crops may also experience micronutrient deficiencies; micronutrients have low solubility at elevated soil pH levels [102].

Unwanted soil pH increases may be avoided by employing alternate feedstocks such as peanut hulls, pecan shells, hardwood, or pine chips because they contain modest N-P-K ratios and are not as alkaline (Table 1). It should be understandable that when applying biochar to soil, it is important to not create an additional problem while attempting to solve the target soil problem. The impact of biochars produced from these alternate feedstocks and under different pyrolysis conditions (high vs. low temperature) on the fertility of a Norfolk Ap was shown in Table 4. Both peanut hull (400 and 500°C) and hardwood biochars were added at 2% (w w^{-1}, 40–44 Mg ha^{-1}). The treatments were laboratory incubated for 4 months and were then leached monthly with water to simulate loss of nutrients due to rainfall and/or irrigation. All biochar treatments after 120 days of incubation significantly raised soil pH, SOC, and TN contents, CEC had mixed results, when compared to the control (Table 4). After 120 days of incubation, the CEC increases were not particularly large (<0.6 $cmol_c$ kg^{-1}), but some of the increases were still significant. The Norfolk Ap fertility was increased because Mehlich 1 extractable P, K, Ca, and Mg were all significantly higher than the control (Table 4). Both peanut hull biochars caused the greatest increases in OC, TN, and K relative to the control. Both OC and Ca concentrations were increased after applying hardwood biochar; minimal improvement occurred in pH, TN, P, K, and Mg concentrations. These results imply that hardwood would be an appropriate feedstock for a biochar designed to improve SOC and Ca levels alone, without causing large upward shifts in soil pH. Unfortunately, hardwood did not improve other soil problems such as low N and P contents. If OC and N improvements were the target soil fertility issue, then peanut hull would be an appropriate feedstock and either pyrolysis temperature.

Water leaching of the treatments resulted in loss of K and some P, whereas mixed results were obtained for the other nutrients. Leaching of K is not unexpected in sandy soils; its monovalent charge causes it to be less attracted to cation exchange sites [102]. This Norfolk's Ap fertility status was improved by employing a biochar with appropriately designed characteristics. We avoided using an ill-suited biochar (poultry litter) in this situation because prior laboratory soil incubation showed that would cause a negative soil legacy (e.g., excessive nutrient concentrations, alkaline pH values, etc. [75]) potentially resulting in crop productivity declines. Poultry litter biochar has special chemical properties, such as high P and alkalinity, which may be useful as a fertilizer and lime source if their concentrations are diluted through blending with benign biochar (see Sect. 6).

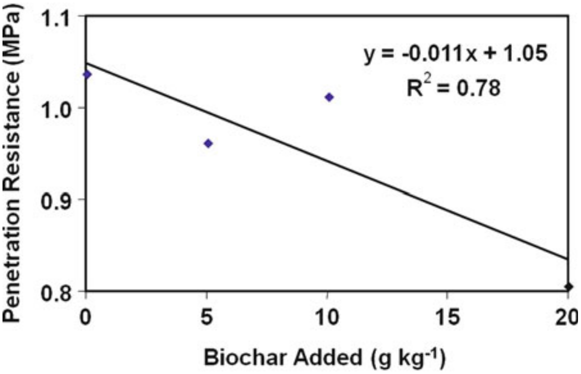


Fig. 12 Penetration resistance of a Norfolk Ap after 44 days of incubation with pecan shell biochar [15]

Biochars applications are not just limited to infertile soils, but the technology can be applied to fertile, mid-western soils as a supplement for increased C sequestration and to replace nutrients lost through plant uptake, erosion and leaching. Laird et al. [59] incubated a hardwood biochar produced by slow pyrolysis in an Iowa Mollisol (Typic Hapludoll) and reported significant increases in total N, OC and Mehlich 3 extractable P, K, Mg, and Ca concentrations. In a similar study, Laird et al. [60] reported that the same biochar reduced total N and dissolved P leaching from swine manure applied to this Mollisol. These results imply that hardwood biochar additions to a mid-western Mollisol can be an effective agricultural and environmental management option by improving fertility and minimizing nutrient leaching. The authors did not choose to investigate if other feedstocks and different pyrolysis temperatures could have resulted in biochars with designed characteristics to improve the biochars performance at modifying fertility and nutrient leaching.

4.3 Improving Soil Physical Issues

The Norfolk soil has several physical problems such as low water retention, and a poorly aggregated subsurface hard layer that challenges agricultural productivity. If these physical problems are targeted for improvement, then their upgrading would also require an assessment of bulk density and aggregate formation since these features significantly influence pore space available to store water and lessen root penetration resistance [102]. Designing a biochar to resolve these soil physical issues once more requires identifying a feedstock and pyrolysis conditions followed by an assessment of their performance. Biochars effects on bulk density, available water storage, and aggregate formation were evaluated in a similar manner as described in Table 4. Pecan shell biochar pyrolyzed at 700°C was further evaluated in the Norfolk Ap to assess its impacts on reducing penetration resistance (Fig. 12; [15]).

Table 5 Mean physical properties in a Norfolk Ap after 0 and 120 days laboratory incubation with 2% (w w^{-1}) peanut hull and DCQ (hardwood) biochars ($n = 4$, data submitted for publication)[a]

Treatment	Pyrolysis (°C)	Incubation (day)	Bulk density (g cm^{-3})[b]	Available H_2O (mm/150 mm)	Aggregate wt.[c] 1.0-mm	Aggregate wt.[c] 0.5-mm
Control	–	0	1.37	–	–	–
		120	1.62a	8.82a	3.08a	18.94a
Peanut hull	400	0	1.49	–	–	–
		120	1.57a	21.64b	3.43b	20.33b
	500	0	1.57	–	–	–
		120	1.59a	17.78c	3.11a	19.92b
Hardwood	Fast	0	1.51	–	–	–
		120	1.57a	20.67b	3.46b	21.47c

[a] Treatments leached with di. H_2O four times during the 120 day incubation period

[b] Means of soil characteristics measured on day 120 of incubation within a column followed by a different letter are significantly different using a 1-Way ANOVA at a $P = 0.05$ level of significance

[c] Percentage of total

The poor physical properties of the Norfolk Ap (control) are evident; it had the lowest available water, small amounts of 1.0 and 0.5 mm sized soil aggregates (Table 5), and the highest penetration resistance (Fig. 12). These physical properties were significantly improved after mixing in the four biochars relative to the control (Table 5 and Fig. 12). Closer examination of the significant differences in these measured properties will reveal the suitable feedstock and pyrolysis temperature for producing the designer biochar. Pecan shell biochar produced at 700°C was found to reduce soil strength in the Norfolk Ap, especially at the 40 Mg ha^{-1} application rate (Fig. 12; [15]). Mixed results, however, were obtained for pecan shell biochar to increase water retention [15]. Pecan shell biochar (700°C) is more suitable under these conditions with resolving soil penetration resistance. On the other hand, peanut hull biochar at the lower pyrolysis temperature (400°C) provided a greater increase in available water and in 1.0-mm aggregate formation. Lower soil water increases were obtained using the higher temperature (500°C) peanut hull biochar.

Biochar produced from hardwood under fast pyrolysis significantly improved two soil physical properties relative to the other treatments. Among these three feedstocks, the hardwood-based biochar appears to be a more appropriate feedstock selection for physical improvement. Hardwoods subject to fast pyrolysis may be the best feedstock for producing a designer biochar. If hardwood biochar is used to resolve soil physical issues, concomitant improvements of SOC and Ca concentrations are obtainable without elevating the Norfolk's pH.

4.4 Biochar and N_2O Dynamics

Greenhouse gas emissions as CO_2, CH_4, and N_2O as a result of fossil fuel usage and agricultural activity within the USA have increased 14% between 1990 and 2008 [40]. The agricultural sector was estimated by the US-EPA to contribute approximately 6%

of the total GHG emissions. Animal and crop production may account for as much as 70% of the annual global anthropogenic N_2O emitted [65]. Globally, N_2O is a significant contributor to the emission total (≈8%, [35]) and has a global warming potential of 298 times greater than CO_2 [41]. The large difference in N_2O radiative force with CO_2 causes it to have a larger destructive potential to the stratospheric ozone layer [26].

N_2O fluxes have been measured in agricultural field, but estimates of their overall contributions to the global GHG budget is difficult to estimate because fluxes have been linked to differences in soil N application, N form, soil pH, soil wetness, and tillage practices [33, 54, 76]. Nevertheless, the sizable hazard that N_2O poses for climate change relative to CO_2, suggests that it is important to have management strategies available to curtail N_2O production from agricultural soils. This will require both field and laboratory evaluations between feedstock, pyrolysis conditions, and biochar chemical properties on N_2O dynamics.

Both field and laboratory studies reported that biochar additions to soil can reduce N_2O emissions [42, 67, 83, 90, 96, 104]. In the field, biochar applications at 20 Mg ha^{-1} to soybean plots were found to cause a 50% curtailment in N_2O emissions [83]. While in the lab, N_2O production was suppressed by a variety of biochars produced from nut shell wastes and hardwoods [96] and from poultry litter and wood [90]. In fact, both studies employed biochars produced at different temperatures and reported difference in N_2O reduction. Neither study reported an over-arching biochar chemical/structural characteristic as responsible for reducing N_2O emissions.

Not all biochars will suppress N_2O emissions when added to soils, in fact, Spokas and Reicosky [96] reported that two out of 16 biochars stimulated N_2O production relative to the control. Similarly, Singh et al. [90] reported that a biochar produced from pyrolyzed poultry manure at 400°C stimulated N_2O production. Based on these reports, it is difficult to make suggestions (Fig. 11) to create a biochar tailored to effectively suppress N_2O production.

What we do know, however, is that biochars may suppress N_2O production if they have properties that influence N availability [90], decrease soil microbial activity [96], and improve soil physical properties that promotes aeration [58]. Whereas, others have reported soil N_2O production can be stimulated with biochar. These conflicting conclusions suggest that additional laboratory and field evaluations involving biochars produced from multi-feedstocks and under different pyrolysis conditions are needed.

5 Biochar Blends Create Hybrid Biochars

This review has shown that each biochar evaluated has a unique set of chemical and physical properties. While one biochar may be effective at resolving one soil problem, it may also have properties that are either benign or promote gross changes to another soil property. It would be beneficial, if a negative characteristic of a biochar could be turned into an advantage through blending. Blending of different biochars to produce a hybrid product with designed characteristics for a specific soil purpose

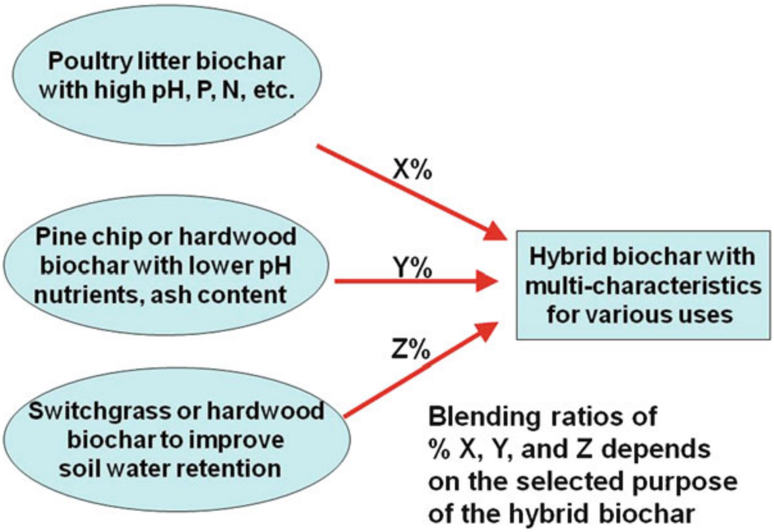


Fig. 13 Blending biochars creates a multifunctional hybrid biochar

is possible (Fig. 13). For instance, in acid environments, such as in mine reclamation, metals such as Al, Cu, Mn, Pb, and Zn are highly soluble [10]. These metals, in sufficient quantities, can pose a hazard to plants. A proper remediation strategy would be to reduce their solubility by raising the pH and/or by complexation with soil organic compounds. This may be achieved by applying a high temperature pyrolyzed biochar (>400°C) produced from peanut hulls, pecan shells, and switchgrass, which have alkaline pH values (Table 1). In fact, peanut hull biochar produced at both pyrolysis temperatures did raise the pH of a sandy soil (Table 2). Biochars made from other feedstocks (i.e., hardwoods, pine chips, poultry litter, etc.) may be unsuitable for application in mine spoil sites because of their inability to act as a liming agent or by potential increases in other nutrients solubility (i.e., P, Fe, etc.). The impact of biochars or blends on remediating mine reclamation sites is largely unknown, but could be a viable assignment for biochars found not to be suitable for agricultural soil improvement.

Poultry litter biochar, although it has some difficult characteristics, can still be used as a low-grade fertilizer (Table 1). It contained the highest N-P-K ratios, is extremely alkaline, and also contained high levels of Na [74]. Problems associated with these properties could be rebalanced or diminished by blending with other biochars (i.e., hardwood, pine chips, etc.) to produce a hybrid biochar (Fig. 13) that has more benign characteristics (Tables 1 and 3; lower N-P-K ratios, ash contents, pH, etc.) or added to improve another soil issue (i.e., low water holding capacity, etc.). The blending ratio of other biochars can be chosen depending upon the purpose of the hybrid biochar (Fig. 13). As an example, a hybrid biochar blend could consist of a mixture of hardwoods, pine chips, and poultry litter biochar; a blend designed to improve soil water storage while also delivering C, N, P and raising the pH as well.

Blending biochars for agricultural production or commercial purposes is beyond the concept stage. Commercial companies have internet sites advertising that their designer biochars made from blended materials that have their own unique properties. These companies have developed a biochar product that could be used in a number of different market sectors (greenhouse, nursery, golf courses, etc.) as a plant media, improvement in golf greens, or in site reclamation.

6 Conclusions

Biochars can be produced from diverse feedstocks and under a variety of pyrolysis conditions. Because resultant biochar properties vary, no one biochar will fit all soil improvement intentions. Each biochar has its own unique chemical and physical signature and when applied to soils may have a positive, negative, or a benign effect. To avoid creating unwanted long-lasting effects in soils, thus the concept of designer biochar was introduced and the utility of producing biochars tailored for specific soil problems was illustrated. If one biochar has unsatisfactory properties, then blends of biochars in unique proportions can be created to produce a hybrid biochar that has tailored characteristics to provide multiple benefits for specific soil problems. In this review, designer biochars were shown to have a positive effect by improving soil fertility and physical properties. In the future, biochars or their hybrid blends may also be formulated to reduce N_2O emissions.

Because of their costs, designer biochars may be regarded as a product for boutique markets; but, they would definitely improve production in agricultural fields if costs were reduced. Given the fact that biochars react in a different way in different soils, more research is needed to understand relationships between feedstock and pyrolysis conditions vs. biochar quality. Therefore, this review has suggested potential protocols and guidelines for the selection of feedstock's and pyrolysis conditions to produced biochars with tailored properties for selected soil problems.

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